

## ABSTRACT

Title of Thesis: KETYL RADICAL RECOMBINATION REACTION IN  
VARIOUS IONIC LIQUIDS

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Ten ionic liquids were made for a series of experiments meant to help characterize the usefulness of room temperature ionic liquids (RTILs) in various settings. This series of experiments used laser flash photolysis to study the effect of ionic liquids on the rate constants of the recombination of ketyl radicals, created from flash photolysis of benzophenone in the presence of benzhydrol. From the RTILs, the data showed that most ionic liquids had a faster rate constant than the diffusion limit predicted by the Einstein-Stokes-Smoluchowski equation. The main exception was that EMIM-NTf<sub>2</sub> where the reaction was slower than its predicted diffusion limit.

KETYL RADICAL RECOMBINATION REACTION IN VARIOUS  
IONIC LIQUIDS

By

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Thesis submitted to the Faculty of the Graduate School of the  
University of Maryland, College Park in partial fulfillment  
Of the requirements for the degree of  
Master of Science  
2009

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Green chemistry is an emerging field of study due to increasing concern about the negative environmental impact caused by large scale production of chemical intermediates. As a result, chemists are searching for ways to decrease or eliminate the production of hazardous and toxic waste. Ionic liquids are a focal point in helping to reduce the use of harmful, volatile chemicals. Due to their low volatility, ionic liquids are being considered as a new medium for industrial applications resulting in a low impact on the environment. To fully understand ionic liquids it is important to review their history and development, how they are prepared, their physical and chemical properties while reviewing previous studies and examples of their use.

In simple terms ionic liquids are what they sound like: liquids that are made of ions only.<sup>10, 11</sup> The most common name found in chemical literature today is room temperature ionic liquid (RTIL). However they can also be referred to as low temperature molten salts, ambient temperature molten salts, room temperature molten salts, ionic fluids, fused salts, organic liquid salts, and neoteric solvents.<sup>11</sup> The basic compositional needs of an ionic liquid are a cation and anion that coordinate weakly to each other. There are many different basic characteristics considered for each ion. Examples of the cationic components include alkylammonium, alkylphosphonium, *N*-alkylpyridinium, and *N, N'*-dialkylimidazolium ions, all with various alkyl side chains.<sup>10</sup> Hexafluorophosphate, tetrafluoroborate, triflimide, and nitrate are typically used as anionic components.<sup>11</sup>

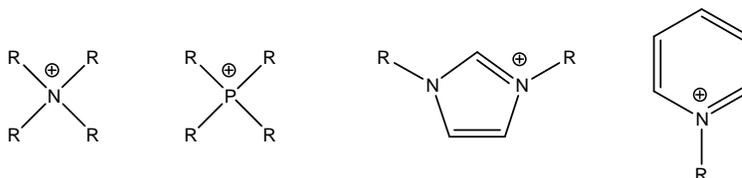


Figure 1: Common cations, left to right: alkylammonium, alkylphosphonium, *N, N'*-dialkylimidazolium, and *N*-alkylpyridinium

The first compound considered to be an ionic liquid was discovered in 1914 by P. Walden during an  $\text{AlCl}_3$ -catalyzed Friedel-Crafts alkylation. This compound, produced as a side reaction, was described as “red oil” and was later identified through NMR spectroscopy as ethylammonium nitrate. It was the first low melting point salt, with a melting point of  $12^\circ \text{C}$ .<sup>11</sup> Later, F. N. Hurley and T. P. Wier used various alkylpyridinium compounds to coordinate to chloroaluminate anions.<sup>10</sup> These early compounds were mainly used for electroplating, as electrolytes in batteries, and other electrochemical applications.<sup>10, 11</sup> The next development in the history of RTIL's was the pairing of various dialkylimidazole cations with chloroaluminate reported in 1982.<sup>32</sup> These compounds were also used for electroplating applications, as they were shown to work better than alkylpyridinium compounds. In the early 1990's the first fluid, air- and water stable ionic liquids were created and characterized based on 1-ethyl-3-methylimidazolium.<sup>31</sup>

Several different cations and anions can be used to make ionic liquids. Some of the more common cations use alkyl-imidazolium as a core component, as shown in Figure 1. 3-methylimidazole, or MIM, is alkylated at N-1 using suitable alkyl halide.<sup>11</sup> Alkoxy chains or ether functional groups have also been used as side chains. It is possible to have the methyl group at other positions than the position 3 nitrogen or to have this group be something other than a methyl group.<sup>13</sup> This produces the desired cation with the halide as its coordinated anion.

Other variations on the cation include pyrazolium, triazolium, thiazolium, and oxazolium.<sup>11</sup> Also, recent research has shown another extremely similar base to

imidazolium called methimazole that can be used to form RTIL's.<sup>21</sup> Ionic liquids can also be divided into two categories: aprotic or protic. Aprotic ionic liquids are formed through alkylation. Brønsted acids and bases can be transformed into protic ionic liquids by a proton transfer between the acid and base.<sup>25</sup> Imidazole cations can also be substituted to form Brønsted-acidic ionic liquids. Brønsted-acidic IL's are formed first through a cationic zwitterion. The main reactants are methylimidazole is added to a sulfone.<sup>21</sup> This process is followed by protonation through an acid, such as trifluoromethane sulfonic acid, for the liquids to have proton-donation potential<sup>11</sup>. These can be used as solvent or catalyst for various reactions.

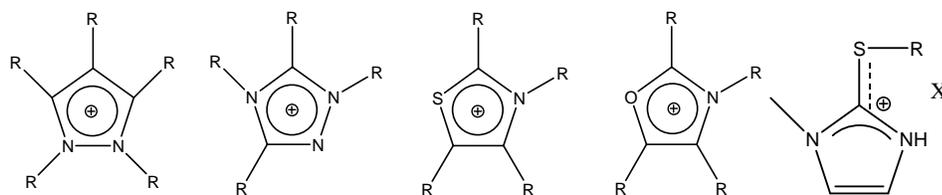


Figure 2: Pyrazolium, triazolium, thiazolium, oxazolium, and methimazole

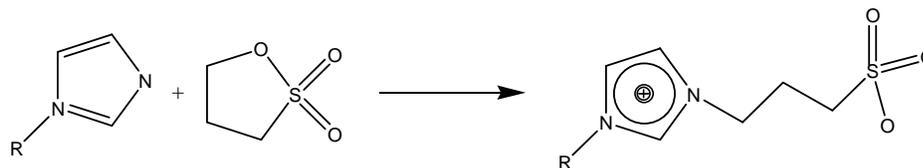


Figure 3: Formation of a Brønsted-acidic cation

Another cation that is often used as a cationic base is pyridinium and its derivatives, as shown in Figure 1. Some of these derivatives are alkylated in the same fashion as imidazolium.<sup>10, 11</sup> A variety of alkylammoniums and an assortment of alkylphosphoniums (Figure 1) are also used as cations, but are not among the common ions employed as cation bases due to side reactions.

Some cations have shown to have prominent aromatic character, more so than compounds like imidazole. This aromaticity has been shown in compounds like benzotriazolium, isoquinolinium, phosphonium, and sulfonium.<sup>11</sup> Also phosphonium and sulfonium have recently been discovered as able to produce ionic liquids. Each of these cations have different uses, for example, benzotriazolium is excellent at dissolving aromatic species.

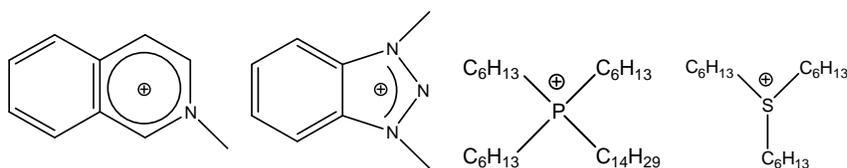


Figure 4: benzotriazolium, isoquinolinium, phosphonium, and sulfonium<sup>11</sup>

One new group of cations brought to light recently is chiral cations. These cations are designed to be very task specific. Many of these chiral cations are naturally occurring amino acids. They can be converted into enantiomerically pure ionic liquids rather simply.<sup>11</sup> These ionic liquids have been shown to have diastereomeric interactions, which can substitute for expensive catalysts or chiral chromatographic separations.<sup>11</sup> One example of an amino acid cation base is glutamic acid. Created by a one-step reaction of protonation by acidification the glutamic acid cation has been coupled with tetrafluoroborate,  $\text{BF}_4^-$ , sulfate,  $\text{SO}_4^-$ , chloride,  $\text{Cl}^-$ , and nitrate,  $\text{NO}_3^-$  to form various ionic liquids.<sup>20</sup>

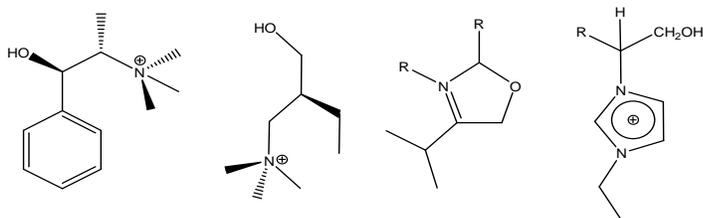


Figure 5: Some Chiral Cations<sup>11</sup>

DNA has also shown itself to be a natural source of cations for ionic liquids. Cytosine, adenine, and guanine have shown that they can be protic organic salts after being mixed with strong acids.<sup>11</sup> In relation, additional research is exploring the possibility of using amino acids as anions. In a recent paper<sup>24</sup>, researchers studied alanine as a candidate for the anionic component for ionic liquids. The study paired alanine with various imidazolium cations and conducted numerous physicochemical experiments to determine values such as density, surface tension, and molar enthalpy of vaporization.

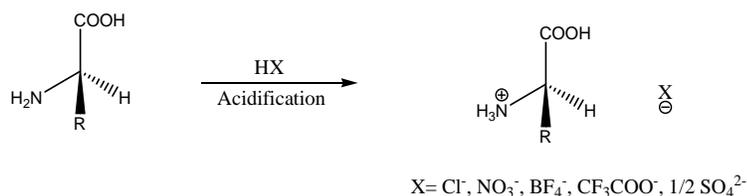


Figure 6: Reaction Scheme of Glutamic Acid Ionic Liquid<sup>20</sup>

The number of cations can seem somewhat limited compared to the number of anions used in ionic liquids. Zhao and Malhorta<sup>10</sup> compiled a list of anions used in ionic liquids and their properties. Others, like Handy<sup>13</sup>, have also compiled similar lists. Among the most commonly used anions are hexafluorophosphate, PF<sub>6</sub><sup>-</sup>, tetrafluoroborate, BF<sub>4</sub><sup>-</sup>, and bis(trifluoromethanesulfonyl)imide, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>. These anions are typically paired with 1-alkyl-3-methylimidazolium and similar cations.

Some of the original coordinating anions in ionic liquids were halides because they were easiest to use due to the fact that they were a by-product after alkylation of the cations. Halides are not used in significant amounts, other than as a stable intermediate ionic liquid to be metathasized. The first ionic liquid that was recognizable by current

standards used tetrachloroaluminate as the anion. The use of this anion was eventually discontinued because it can produce gaseous HCl from the chloride ion produced during alkylation.

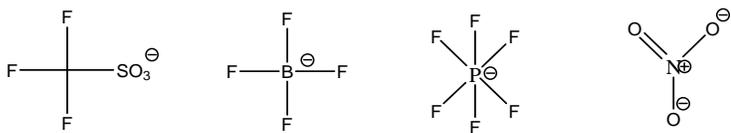


Figure 7: Common anions, left to right: triflate, tetrafluoroborate, hexafluorophosphate, and nitrate

There are many physical and chemical properties that are important in characterizing ionic liquids, such as melting point and viscosity. These properties can be hard to predict. Resolution of properties like miscibility, density, and viscosity depend highly on purity and the structures of the ionic liquids.

One of the most important physical properties for ionic liquids is its melting point. The melting point of any particular ionic liquid helps to determine if the compound is useable. If a melting point is too close to room temperature, it can easily form a solid, making it useless as an RTIL. It is considered that many of these compounds do not have actual melting points. There also can be confusion between whether a value is a melting point value or a glass temperature transition. Some of these RTIL's are thought to be super-cooled liquids or exist at some point as a super-cooled liquid.

The impact of the specific cation-anion pairs is extremely large. Within either group, whether it is anions or cations, there can be a wild swing on the melting point range. For example, the glutamic acid cation based ionic liquids melting points varied from  $-21.98^{\circ}\text{C}$  to  $192.6^{\circ}\text{C}$ , as shown in Table 1.<sup>20</sup> There are several factors that can additionally be attributed to the difference in melting points. The charge distribution on

each ion, the van der Waals interactions, and the hydrogen-bonding ability of the ions can all have an effect on melting points.<sup>12</sup> The charge distribution on the ions is an important factor: the more the charge is distributed over each ion, the less the ions are coordinated to each other. Also, the amount of substituents on the central atom of the anion will lead to the distribution of charge and change the melting point.

Table 1: Melting Points of Glutamic Acid Ionic Liquids

Glu-BF <sub>4</sub>	69° C
Glu-SO <sub>4</sub>	192° C
Glu-Cl	137.2° C

This change can be due to the purity of the compound and the techniques used to determine it. The imidazolium bases' melting points are shown in Tables 2 and 3.<sup>13</sup> It is hard to make any generalizations about how different components affect melting points since there is such variation from cationic base to base and from anion to anion. As shown below, the melting point varies and decreases from ethyl to octyl groups and increases at octodecylimidazole when the anion is PF<sub>6</sub>. Tables 3 and 4 show just how much a melting point can vary when the cation remains unchanged and the anion is changed.

Table 2: Effect of Chain Length on Melting Point (PF<sub>6</sub> Salts)

Chain	Melting Point° C
EMIM	58-60
BMIM	-8
HMIM	-61
OMIM	-82
ODMIM	80

Table 3: Melting Point in Methyl-Imidazole Ionic Liquids

Side Chains	Anions	Melting Point° C
CH <sub>3</sub>	Cl	124.5
C <sub>2</sub> H <sub>5</sub>	Cl	82-87
C <sub>2</sub> H <sub>5</sub>	AuCl <sub>4</sub>	58

Table 4: Impact of Anions on Melting Point

Ionic Liquid	Melting Point° C
EMIM-BF <sub>4</sub>	6
EMIM-AlCl <sub>4</sub>	7
EMIM-CF <sub>3</sub> SO <sub>3</sub>	-9
EMIM-CF <sub>3</sub> CO <sub>2</sub>	-14
EMIM-PF <sub>6</sub>	58-60

Another property that has been studied less extensively is polarity. One way polarity has been measured is through fluorescence probes, specifically AP, DAP, pyrenecarbozaldehyde, pyrene, and bromonaphthalene.<sup>10</sup> These fluorescent probes are used to determine the polarity of several pyridinium and imidazolium based ionic liquids. Other types of probes have been used in resolution of polarity of ionic liquids, including the newly employed 12'-Apo-β-carotenoic-12'-acid.<sup>19</sup> The probe, 12'-Apo-β-carotenoic-12'-acid, was found to be sensitive enough to report the micropolarity of an ionic liquid.

An alternative method to determine polarity is through the use of dyes and calculations based on UV/Vis spectra. One of the most commonly used dyes is Reichardt's dye, a zwitterion complex. The data about charge-transfer absorption bands obtained from this type of experiment, one can then apply the E<sub>T</sub> scale to this data. E<sub>T</sub> is defined as the amount of energy required to go from the ground state to the excited state.

This data can then be normalized,  $E_T^N$ , by measuring the maximum absorption wavelength, shown in Equation 1 below.

$$E_T^N = \frac{E_t(30) - 30.7}{32.4} \quad 1$$

There are also certain parameters that can be determined from the  $E_T^N$  polarity values, Kamlet-Taft parameters  $\alpha$ ,  $\beta$ , and  $\pi^*$ .  $\alpha$  is a quantity calculated to show the ionic liquid's hydrogen-bond-donating acidity (Equation 2).  $\beta$  demonstrates the solvent's ability for hydrogen-bond-accepting basicity by measuring the difference of solvatochromism (Equation 3).<sup>15</sup> Lastly,  $\pi^*$  parameter provides data on the ratio of the solvent's, in this case, the ionic liquid's dipolarity to polarizability (Equation 4).

$$\alpha = \frac{(E_T(30) - 14.6(\pi^* - 0.23) - 30.31)}{16.5} \quad 2$$

$$\beta = \frac{(1.035v(2)max - v(1) + 2.64)}{2.8} \quad 3$$

$$\pi^* = \frac{v_{max} - v_0}{s} \quad 4$$

A recent paper showed how the technique discussed above can be applied to ionic liquids. The study was based on five variously substituted pyridinium cations with bis(trifluoromethylsulfonyl)imide,  $NTf_2$ , as the coordinating anion. The results on polarity and the Kamlet-Taft parameters are shown in Table 5.<sup>15</sup> It is also possible to compare the polarities of the RTIL's to known polarities of commonly used solvents as well as to each other to show trends. For instance, the polarities of BMIM salts are shown to decrease with the increase in size of their coordinated anions. Generally, polarity has been shown to increase as the size of the alkyl side chain increases from

butyl to hexyl, and then decrease as the size of the alkyl side chain continues to increase.<sup>10</sup>

Table 5:  $E_T^N$  and Kamlet-Taft Parameters for Four Ionic Liquids and Common Solvents at 25° C

Ionic Liquid	$E_T^N$	$\alpha$	$\beta$	$\pi^*$
BMIM-Tf <sub>2</sub> N	.644	.617	.243	.984
OMIM-Tf <sub>2</sub> N	.630			
BMIM-PF <sub>6</sub>	.669	.634	.207	1.032
BMIM-TfO	.656	.625	.464	1.006
Hexane	.009	.070	.040	-.120
Water	1.000	1.12	0.14	1.33

There are many influences that can change miscibility, especially the structure of the cation. There are two main influences from the cation structure that affect miscibility: the resemblance of polarity between the solvents and the empty space caused by large side chains on the cations. For example, various imidazolium IL were studied for their miscibility in water. The study concluded that when the alkyl chain length was less than six carbons, they were miscible with water and anything larger formed two layers with water.<sup>10</sup> There is a robust trend for how much water is miscible in ionic liquids, while there is not a clear trend for the amount of ionic liquid miscible in water.

Certain anions, such as NO<sub>3</sub><sup>-</sup>, halides, and AlCl<sub>4</sub><sup>-</sup>, are water-soluble and others, such as PF<sub>6</sub><sup>-</sup> and BR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub><sup>-</sup>, form two layers with water. There are a few that are considered to be both soluble with water and not soluble with water depending on the specific cation that the anion is paired with. For instance, 3-alkoxymethyl-1-alkyl ionic

liquids are not soluble with water but with other organic solvents, such as acetone, THF, and DMF.<sup>10</sup>

Various other experiments have been conducted on specific characteristics of ionic liquids and solvents. The hydrophobicity of an assortment of ionic liquids, such as RMIM-NTf<sub>2</sub>, have been taken by a group at the Universidade de Aveiro. Below are tables showing the solubility of the ionic liquids in water and vice versa.<sup>17</sup> As shown in the tables, there is a great difference between dissolving ionic liquids in water as expressed where chain length decreases water solubility, compared to dissolving water in ionic liquids. The data ranges over assorted temperatures and is used to calculate various constants, such as Henry's constant and the molar solution properties for the biphasic mixture.<sup>18</sup> Lastly, the solubility of substances other than water, like gases, have been explored. A paper from the University of Notre Dame describing how the absorption of CO<sub>2</sub>, carbon dioxide, by HMIM-NTf<sub>2</sub> shows how atomistic simulations predict the gas absorption. The simulations were corroborated by experimental data.

Table 6: Experimental Mole Fraction Solubility of Water in (Tf<sub>2</sub>N)-Based IL's as a Function of Temperature

	C <sub>2</sub> mim-NTf <sub>2</sub>	C <sub>3</sub> mim-NTf <sub>2</sub>	C <sub>4</sub> mim-NTf <sub>2</sub>	C <sub>5</sub> mim-NTf <sub>2</sub>	C <sub>6</sub> mim-NTf <sub>2</sub>	C <sub>7</sub> mim-NTf <sub>2</sub>	C <sub>8</sub> mim-NTf <sub>2</sub>
T/K	(x <sub>w</sub> ±σ <sup>a</sup> )						
288.15	.2755	.2502	.2307	.2052	.1906	.1806	.1715
293.15	.2869	.2581	.2443	.2127	.1978	.1879	.1781
298.15	.2982	.2715	.2568	.2211	.2076	.1971	.1868

Table 7: Experimental Mole Fraction Solubility of (Tf<sub>2</sub>N)-Based IL's in Water as a Function of Temperature

	C <sub>2</sub> mim-	C <sub>3</sub> mim-	C <sub>4</sub> mim-	C <sub>5</sub> mim-	C <sub>6</sub> mim-	C <sub>7</sub> mim-	C <sub>8</sub> mim-
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	NTf <sub>2</sub>						
T/K	$10^4(x_{IL} \pm \sigma^a)$						
288.1 5	7.66	5.15	2.86	1.84	8.90	4.85	3.17
293.1 5	8.03	5.27	2.92	1.88	8.96	4.98	3.23
298.1 5	8.38	5.40	3.07	1.96	9.56	5.09	3.36

Table 8: Gas Solubility Trends in RTIL's

Ionic Liquid	CO <sub>2</sub> /H (atm)	N <sub>2</sub> /H (atm)	CH <sub>4</sub> /H (atm)
EMIM-Tf <sub>2</sub> N	50	1200	560
EMIM-BF <sub>4</sub>	100	3800	2000

Density is a property that has not been explored as well as others. Density data is taken experimentally and is related to other RTIL's according to the length of the side chains on the cation and the anion. Also, the size and type of substituents on the anion will affect the density. The density of an ionic liquid changes with the increase in carbon atoms, like on a 3-alkoxy-1-methylimidazolium cation.<sup>10</sup> As a general rule, the density decreases as the chain length increases in relation to the cation. The temperature of the complex is also taken into account when a density measurement is made. It has yet to be proven whether temperature has a role in the overall density of a liquid. Impurities, like water, halides, or other solvents have little effect on the density measurements.<sup>13</sup>

The ability to pour, transfer, stir, and evaporate solvents from RTIL's is dependent on viscosity. The viscosity of a liquid is thought to be determined by hydrogen bonding and van der Waals forces. For example, the change in chain length

and the amount of fluorines in the cation alters the viscosity due to van der Waals forces. Also, methylation at C-2 of imidazole IL's changes the viscosity disallowing hydrogen bonding. There is no clearly defined trend to address the viscosity of RTILs. Below is a table listing some examples of RTIL viscosity.

Table 9: Dynamic Viscosity of Various BMIM<sup>+</sup> ionic liquids at 20° C

Anion	$\eta$ (cP)
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	90
C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> <sup>-</sup>	373
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	73
<i>n</i> -C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> <sup>-</sup>	182
(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>+</sup>	52

<sup>10</sup>

There are many properties of ionic liquids that have not been explored to determine experimental values. Properties such as surface tension, decomposition, chemical and thermal stability, and vapor pressure have little information printed in chemical literature.

One positive feature of surface tension of ionic liquids is that water does not significant effect on experimentally determined values. Another quality of surface tension is that values decrease as the alkyl chain lengths increase.<sup>11</sup>

There are very few studies on the thermal stability of RTIL's. One known point of decomposition is at the C-N bond in imidazolium salts, specifically the C-N bond between the alkyl chain and the nitrogen.<sup>13</sup> Another possible decomposition point relates to PF<sub>6</sub> salts, where HF is formed when the liquid comes into contact with water.<sup>10</sup>

Stability, both chemical and thermal, is important because of the need to control expenses and the need to recycle the liquids for future use. Without stability, ionic liquids would not be able to be kept for long periods of time.

Lastly, vapor pressure is extremely difficult to determine because of ionic liquid's low volatility. For this very reason ionic liquids have been chosen to replace volatile organic solvents.

There are innumerable examples in chemical literature of how ionic liquids have been used as both reagents and as reactants. Numerous studies have been conducted as a result of this new and promising media, such as pulse radiolysis, electrochemical, thermodynamic, and photochemical experiments. Many groups have chosen to focus on a set of ionic liquids and a specific type of study in hopes to shed new light on previously unexplored areas.

There are numerous examples of how the interaction of ionic liquids can either help or hinder many reactions, many that have been studied in great detail prior to modern RTIL innovations. One such paper published recently showed the effects of several solvents on an intramolecular Diels-Alder reaction.<sup>27</sup> The researchers studied the general effect of ionic liquids on this reaction and what happened when anions were exchanged from tetrafluoroborate,  $\text{BF}_4^-$  to bis(trifluoromethanesulfonyl)imide,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ . The study was on six different  $\text{BF}_4^-$  based ionic liquids and three  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  ionic liquids. The results for the  $\text{BF}_4^-$  ionic liquids indicate that there is a correlation between the rate constants and viscosity. The rate constants of the  $\text{BF}_4^-$  ionic liquids studied decrease as viscosity increase for the  $\text{BF}_4^-$  RTIL's only. There was no

observed correlation for the NTf<sub>2</sub><sup>-</sup> RTIL's however. In the study on the BF<sub>4</sub><sup>-</sup> ionic liquids, there was a uniform variation, independent of the method, the rate constants at the same viscosity are about equal. There is a similar trend for NTf<sub>2</sub><sup>-</sup>, but it is independent of increasing viscosity. The researchers also carried out temperature dependent studies as controls for the viscosity of the RTILs. The overall conclusion from the research was that there is evidence of friction in the form of microviscosity, which is an important factor for controlling rate constants of simple activation-controlled organic reactions.

Another study carried out with BMIM-BF<sub>4</sub> and BMIM-PF<sub>6</sub> deals with direct mediation of converting a lactone and a primary amine into a lactam.<sup>28</sup> These researchers were trying to find a way to make lactams, quickly, easily and without acids. With these ionic liquids, they were able to use a one pot synthesis method that did not include adding any acid. Adding one equivalent of BMIM-BF<sub>4</sub> to the experiment with purified hydroxyamide was found to assist with ring formation while under microwave irradiation at 220° C. The researchers postulated that under the microwave conditions investigated, having the ionic liquids were necessary for acid free ring closure but not for the lactone opening.

Various groups have conducted pulse radiolysis studies with ionic liquids as the focal point. Many of the papers study reaction kinetics in various ionic liquids, ranging from BMIM salts to methylammonium bis(trifluoromethylsulfonyl)imide to *N*-butylpyridinium tetrafluoroborate. The actual reaction kinetic measurements are taken of reactions such as oxidation-reduction<sup>4</sup>, radicals<sup>5</sup>, 4-mercaptobenzoic acid<sup>7</sup>, and hydrogen atoms.<sup>6</sup>

One such example is from a group of researchers who decided to study one ionic liquid, BMIM-PF<sub>6</sub>, and conduct a series of experiments to determine this RTIL's viability as a medium for photochemical experiments and reactions.<sup>3</sup> They conducted experiments on energy transfer, hydrogen abstraction, photoinduced electron transfer, laser flash photolysis, and oxygen quenching. It was found that BMIM-PF<sub>6</sub> should not be considered a highly polar solvent because of the triplet state of a polarity probe, xanthone. For energy transfer, the xanthone triplet state was used as a donor and naphthalene was used as an acceptor. The data showed a rate constant of about two orders of magnitude smaller than other solvents. This was thought to be because the energy transfer became a non-diffusion controlled process or if the process is still a diffusion controlled process then it's considerably slower than conventional organic solvents. Hydrogen transfer between xanthone and diphenylmethane shows the same kind of results as with the energy transfer, a considerably decreased rate constant. The charged quenchers showed a more rapid diffusion in the ionic liquid than a neutral quencher in photoinduced electron transfer. The smaller molecular size of charged iodine and cobalt could account for the differences in diffusion compared to the larger sized neutral biphenyl compound. The laser flash photolysis studies allowed the researchers to measure the triplet excited state of 2,4,6-triphenylthiopyrylium ion, showing an order of magnitude greater than the same state in acetonitrile. The researchers also concluded that BMIM-PF<sub>6</sub> has incredibly low oxygen solubility at atmospheric pressure. Lastly, it was concluded that charge transfer interactions decreased the association constant for the complex of anthracene and methylviologen.

The extensive use and versatility of ionic liquids has been shown through their chemical and physical properties, studies, and examples. There is still a great deal yet to be accomplished in many aspects of this field. The gaps in knowledge of certain chemical and physical properties leave much growing room in this area of chemistry.

## Experimental Procedures:

The experimental procedures for the methylimidazole ionic liquids were adapted from previously published papers<sup>22, 23</sup> and from procedures developed in the Falvey Lab.

Firstly, the methylimidazole needs to be distilled to remove any possible impurities. It is distilled under vacuum in sodium hydroxide and collected in a flask that is placed in an ice bath. To distill enough methylimidazole for any given experiment normally takes several hours. The methylimidazole is normally left overnight to cool to room temperature. It is possible to use the distillate immediately if it is cool enough.

In general, alkylation is performed on methylimidazole and pyridinium with various alkyl halides, which results in alkyl-methylimidazole halide and alkyl-pyridinium halide. This is done with equimolar amounts the alkyl halide and methylimidazole added to a corresponding size round bottom flask. This solution is placed under reflux and can be done under atmosphere or under nitrogen. The experiments were performed under atmosphere and not under nitrogen. This mixture is left to stir in an oil bath at about 70° C for twenty-four hours. It is extremely important not to exceed 70° C because of side reactions. After this step, a two layer solution is formed and allowed to cool to room temperature. Sometimes with small chain alkyl-methylimidazole intermediates, a solid salt forms.

The alkyl-pyridinium halide ionic liquid is formed in a similar way to the alkyl-methylimidazolium halide. There are some important differences, such as the molar ratio of the alkyl halide to pyridine. The molar ratio is 1.1 to 1 of pyridine to an alkyl halide. Also, the length of duration on the heat changes from twenty-four hours to five to seven

days. The solution was usually left the solution to stir for seven days since the yield is comparatively low. All of the other steps are the same as for the methylimidazole-based ionic liquid for alkylation.

Once the alkyl-methylimidazole intermediate ionic liquid is produced, it is washed with ethyl acetate to remove any remaining starting materials. The solution is then set to dry on vacuum, usually over night. The alkyl-pyridinium salt is handled differently than that of the imidazole ionic liquids. A salt is formed and it's collected via vacuum filtration and then recrystallized in a 50/50 solution of ethyl acetate and acetonitrile. The crystals are washed with the same solution of 50/50 solution of ethyl acetate and acetonitrile.

The next step in the creation of ionic liquids is anion metathesis. Anion metathesis is exchanging the halide from the ionic liquid intermediate or ionic salt for the desired anion. The ionic liquids or ionic salts are added to deionized water and dissolved. Hexafluorophosphate and tetrafluoroborate are added via cannula over several hours to minimize the amount of direct interaction with these highly potent acids and to promote ionic liquid formation. Bis(trifluoromethanesulfonyl)imide is bought as a lithium salt and is able to be added easily. This salt is sensitive to water until is it add to the solution, it needs to be handled quickly. This solution is left to stir overnight.

After the ionic liquid is left to stir overnight, it forms two layers with water; the lower layer is extracted with methylene chloride and washed several times with water. The exception to this has been ionic liquids with  $\text{BF}_4^-$  as its coordinating anion. These RTIL's do not form two layers with water and are not washed since they are water

soluble. All ionic liquids are then dried with magnesium sulfate,  $\text{MgSO}_4$ , and vacuum filtered. These cleaned solutions can be put on vacuum directly or it can be placed on a Rotovap to remove most of the methylene chloride. After the Rotovap, the cleaned solution is then placed on vacuum to remove any trace amounts of methylene chloride.

The laser solutions that were used for every ionic liquid, except  $\text{MeBu}_3\text{N-NTf}_2$ , used the same concentrations of benzophenone and benzhydrol. The concentration of benzophenone was  $3 \times 10^{-3}$  M and the benzhydrol concentration was  $6 \times 10^{-2}$  M. The exception,  $\text{MeBu}_3\text{N-NTf}_2$ , the benzophenone concentration was increased by a factor of 5, making it  $1.5 \times 10^{-2}$  M, while the benzhydrol concentration was kept the same. Many of the more viscous liquids were left to stir overnight. Most solutions were made initially made in 10 mL batches, but this was increased to 20 mL for most of the kinetic trials. The ionic liquid was added to a 20 mL vial, 10 mL first to allow equal stirring and to allow the benzophenone and benzhydrol to dissolve more quickly, then 0.0055 g (for 10 mL) or 0.0110g (for 20 mL) of benzophenone was weigh out precisely and added to the RTIL. 0.1105 g (for 10 mL) or 0.2211 g (for 20 mL) of benzhydrol is also weighed out and added to the ionic liquid. The only change for  $\text{MeBu}_3\text{N-NTf}_2$  is that the amount of benzophenone used was 0.0550 g instead of 0.0110 g since this solution needed to have the concentration increased to produce useable data and was only ever made in 20 mL batches. This solution is allowed to stir until the solutes are dissolved and if needed, add the rest of the ionic liquid.

The laser setup was established prior to admittance to the lab and had already been idealized. The crystal used for these experiments generated 355 nm light. The software that was used was from LabView, specifically the “Run to find laser output,”

“Better initialization of info,” and “Total sequence for any multishot.” The settings that used most often were with the Qswitch value of 190 and the value of P at 10. The voltage on the laser was always set to 1.46 volts. For full transient spectras, the monochromator started at 800 nm and was decreased in increments of 10 nm per data set until it reached 360 nm. The laser pulsed 10 times equaling 50 microseconds for the kinetic data, the total time of the laser was 5 milliseconds. The kinetic data was taken at 540 nm only.

## Results and Discussion:

The series of experiments that were conducted used laser flash photolysis to study the effect of ionic liquids on the rate constants of the radical reaction of benzophenone and benzhydrol to see if they were similar in results to previously published data.<sup>22</sup> What was actually being measured was the decay of the ketyl radical formed as a result of laser excitation. Below Figure 11 illustrates how the radical is formed in this series laser flash photolysis experiments and how the radical can react in solution. A laser pulse excites a benzophenone molecule, which then reacts with a benzhydrol molecule to produce two ketyl radicals. The rate being studied is the ketyl radicals that have escaped their solvent cages to recombine to form a pinacol or to disproportionate to the starting materials.

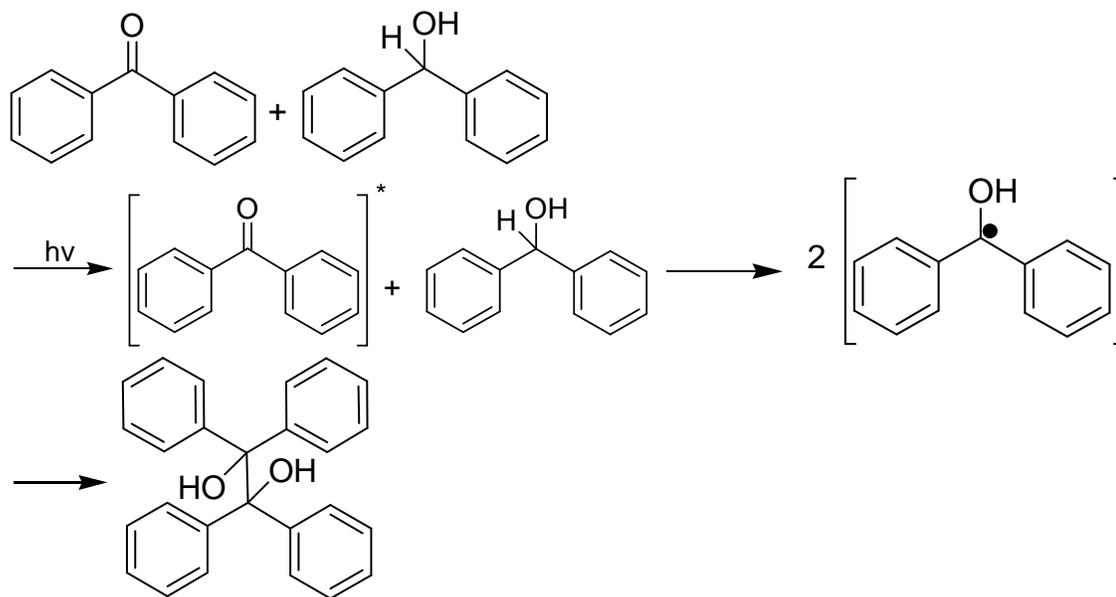


Figure 8: Reaction Scheme of Benzophenone and Benzhydrol<sup>29</sup>

The ionic liquids prepared for this series of experiments, as listed in Table 11, were created according to previously published procedures<sup>22</sup> with only one minor alteration. A general reaction scheme is shown in Figure 8. Newly distilled N-methylimidazole and appropriate alkyl halides were combined in equimolar amounts and heated. The only alteration was made here, instead of performing this step under N<sub>2</sub>, it

was performed under atmosphere. The RTIL intermediate was then added to water with the appropriate anion for anion exchange. The MeBu<sub>3</sub>N-NTf<sub>2</sub> ionic liquid is made by simply mixing two salts together in water for anion exchange, as shown in Figure 9.

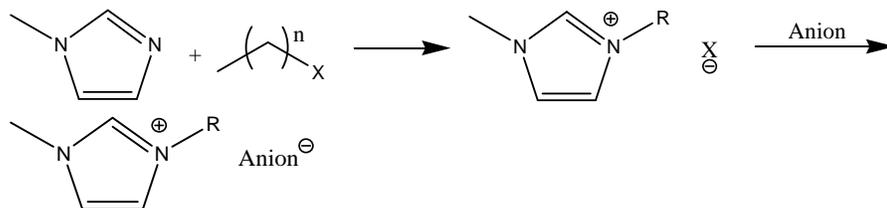


Figure 9: General Reaction Scheme for Imidazole-Based Ionic Liquids. N= 1, 3, 5, or 7; X= Chlorine or Bromine; Anion= triflimide, hexafluorophosphate, or tetrafluoroborate

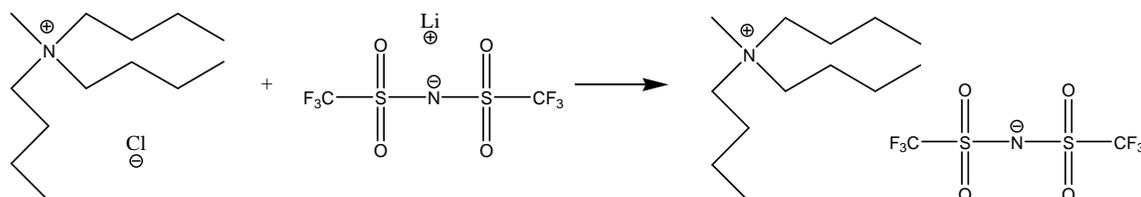


Figure 10: Reaction Scheme of MeBu<sub>3</sub>N-NTf<sub>2</sub>

To ensure purity, each solution was characterized by H<sup>1</sup>-NMR. To ensure transparency of the RTIL's, UV-Vis spectra were taken from 700nm to 200nm to show the absorption at 355nm, as shown in Figure 10 below. From the UV-Vis spectra taken, it was concluded from each that there was no absorbance above 300nm, which is the area of concern.

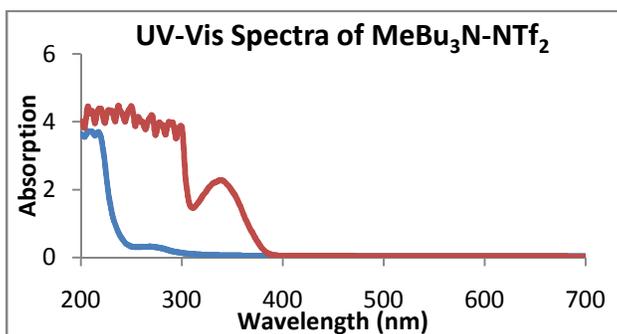
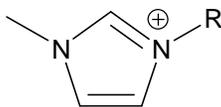


Figure 11: UV-Vis spectra of pure MeBu<sub>3</sub>N-NTf<sub>2</sub> (blue) and MeBu<sub>3</sub>N-NTf<sub>2</sub> with Benzophenone (red)

Table 10: Ionic Liquids Made

EMIM-NTf <sub>2</sub>	HMIM-PF <sub>6</sub>
BMIM-BF <sub>4</sub>	HMIM-NTf <sub>2</sub>

BMIM-PF <sub>6</sub>	OMIM-PF <sub>6</sub>
BMIM-NTf <sub>2</sub>	MeBu <sub>3</sub> N-NTf <sub>2</sub>
HMIM-BF <sub>4</sub>	BuPyr-NTf <sub>2</sub>



When R=1, EMIM; R=3, BMIM; R=5, HMIM; R=7, OMIM

As part of the overall experiment, transient spectra were taken from 800 nm to 360 nm, as shown in Figure 12 below, to ensure that the laser solution, showed a benzophenone radical absorbance at 540 nm. The transient spectra measure the pulse photolysis of benzophenone radicals in each ionic liquid.

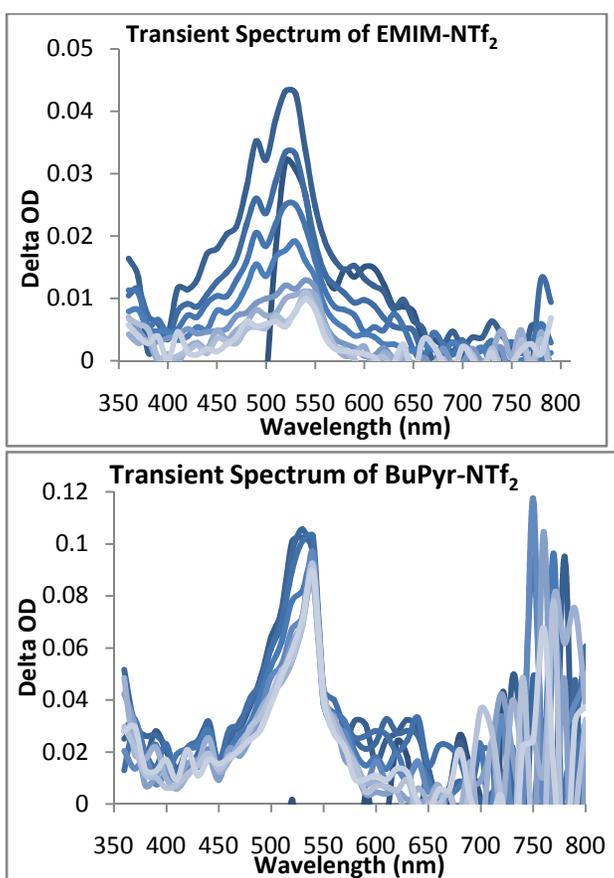


Figure 12: Transient Spectra of EMIM-NTf<sub>2</sub> and BuPyr-NTf<sub>2</sub>

The decay waveform data, as shown in Figure 13, vary greatly in their appearance. The data collected was placed in Microsoft Excel and analyzed. The experimental rate constants were calculated from experimental data. The reciprocal was taken of Absorption (A) versus Time (t) and graphed accordingly to get a straight line.

The slope was then taken of the line and used to calculate the second order rate constant, then converted into a value comparable to rate constants:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad 5$$

$$\frac{1}{c} = \frac{1}{[A]} * \frac{1}{\epsilon} \quad 6$$

where the  $\epsilon$  is the extinction coefficient of  $4340 \text{ M}^{-1} \text{ cm}^{-1}$ <sup>30</sup> and  $[A]$  is the slope. The predicted second order rate constant was derived from the Einstein-Stokes-Smoluchowski equation, shown below.  $R$  is the ideal gas constant ( $\text{J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is temperature (298K), and  $\eta$  is the viscosity taken from various literature sources and converted to Pa·s as needed.

$$k_{diff} = \frac{8000RT}{3\eta} \quad 7$$

The average and standard deviation of each ionic liquid's experimental second order rate constants were taken and compared to the predicted value, given by equation 7. The averages and standard deviations below are obtained from 6 to 11 trials. Also, a Q-test was performed to determine outlying data.

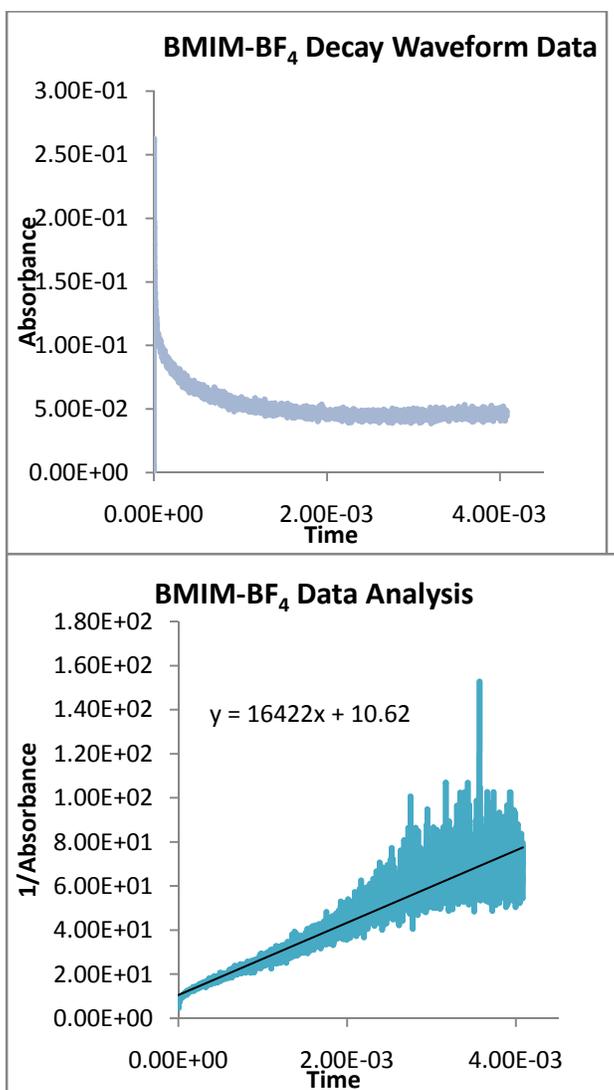


Figure 13: Decay Waveform Data and Data Analysis

As is apparent in Table 11 below, the generalizations able to be made regarding whether the experimental values are faster or slower than the predicted rate constant values for the most part show that they're faster than their predicted values. The experimental rate constants vary indiscriminately, no clear association with viscosity, chain length, or anion can be discerned. EMIM-NTf<sub>2</sub> is the only ionic liquid to have a slower experimental rate constant than its predicted value. BMIM-PF<sub>6</sub> is the closest value to its predicted rate constant, and BMIM-BF<sub>4</sub> is also close to its predicted rate

constant value. Every other experimental rate constant is at least one power of ten higher than its predicted rate constant.

Table 11: Rate Constants for the Ionic Liquids

Name	Viscosity(cP)	Predicted Rate Constant	Experimental Rate Constant
EMIM-NTf <sub>2</sub>	34	1.94E08	3.40E07 ± .86E07
BMIM-BF <sub>4</sub>	233	2.84E07	5.08E07 ± 2.08E07
BMIM-PF <sub>6</sub>	312	2.12E07	2.29E07 ± .88E07
HMIM-PF <sub>6</sub>	680	9.72E06	2.01E07 ± .84E07
HMIM-BF <sub>4</sub>	202	3.27E07	1.07E09 ± 1.24E09
HMIM-NTf <sub>2</sub>	71	9.31E07	3.81E08 ± 2.26E08
OMIM-PF <sub>6</sub>	866	7.63E06	3.88E07 ± 1.96E07
MeBu <sub>3</sub> N-NTf <sub>2</sub>	787	8.40E06	3.27E07 ± 1.75E07

The data collection for most of the RTIL's was simple, straightforward, and easy. However, the transient spectrum of BMIM-NTf<sub>2</sub> showed little absorption at 540nm and was mostly noise. The waveform data also was mainly noise and was not useable. At later inspection of the transient spectrum, the RTIL was shown to have an extremely low delta OD value. It was decided that there are at least three reasons why this occurred: Firstly, that the laser solution did not produce radicals in a significant amount to be detected. Secondly, the radicals escaped their cages and reacted too fast for the detector used in this experiment. Lastly, the benzophenone and benzhydrol had a low solubility in the RTIL.

BuPyr-NTf<sub>2</sub> was also originally tested and the kinetic data taken over several days continued to be noisy and was considered unusable. Upon later inspection of the transient spectrum of BuPyr-NTf<sub>2</sub>, it was shown that the ketyl radical did not decay within the time frame used in this experiment. For future experiments, the length of time for the decay data would have to be increased significantly to observe decay of the ketyl radical.

The last ionic liquid that had any problems was MeBu<sub>3</sub>N-NTf<sub>2</sub>. The full transient spectrum data appeared normal with the original solution however when the kinetic data was taken, it was noisy and approximately one in every ten trials was useable. Eventually a UV-Vis was taken and it showed that the absorption at 540nm was extremely low. This occurred when the benzophenone concentration of the laser solution was increased fivefold. The other problem with MeBu<sub>3</sub>N-NTf<sub>2</sub> was that its melting point is around room temperature. As a result if it became too cold in the lab, the RTIL would solidify.

In relating these results to previous work published in 2007 by Rebecca C. Vieira and Daniel E. Falvey<sup>22</sup>, it was shown that for two RTIL's, BMIM-PF<sub>6</sub> and OMIM-PF<sub>6</sub>, the experimental values for the fluorescence quenching of 9,10-dicyanoanthracene by various electron donors was one to two orders of magnitude higher than predicted. Dr. Vieira was measuring the rate of how fast an electron is donated, while these experiments were looking at how fast ketyl radicals recombined. In this case, the findings do not wholly corroborate that of Dr. Vieira. BMIM-PF<sub>6</sub> has an experimental rate constant about the same as the predicted value; however OMIM-PF<sub>6</sub> is still one order of magnitude higher than its predicted rate constant. EMIM-NTf<sub>2</sub> was not part of this study and perhaps worthy of future study to determine if the data shown here is also applicable to fluorescence quenching.

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