Thermal reversion of Spirooxazine in ionic liquids containing the [NTf$_2$]$^-$ anion

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We have compared the rate of thermal reversion of Spirooxazine (**SO**) from its merocyanine (**MC**) form within ionic liquids and molecular solvents. E$_t$(30) and Kamlet-Taft parameter studies indicate ILs are comparable to polar protic and aprotic solvents. The observed reversion kinetics 15 within the ionic liquids were slower than that of molecular solvents with similar polarity, indicating a greater degree of interactions between the ionic liquid ions and the zwitterionic MC isomer, which led to increased lifetimes for the **MC**-ion complexes. Pre-metathesis cleaning of precursor salts was found to be necessary in order to obtain spectroscopic grade ILs for physiochemical analysis using solvatochromic probe dyes.

Introduction

20 In recent years ionic liquids have become increasingly more attractive as solvents in many synthetic processes. Ionic liquids are, as their name states, compounds that are composed entirely of ions and in liquid state under 100ºC. The 25 subclass of room temperature ionic liquids (RTILs) in particular have the most applicable characteristics for solvent use as they form non-volatile liquids under ambient room conditions (~20ºC). Ionic liquids (ILs) have been found to exhibit low vapour pressures meaning they can be used 30 without the need for containment and so require less controlled working conditions. The high numbers of ions available and the simplicity of the metathesis reaction theoretically implies that over 10^{14} ILs are possibly available[1]. This adds a 'designer' aspect to the liquids and enhances their 35 potential as solvents. In recent years, ILs have been shown to act as recyclable solvents[2] and replaced molecular solvents in catalysis,[3] electrochemistry,[4] synthesis[5] and elemental analysis[6].

40 Current limitations to the introduction of ILs as standard laboratory solvents arise from the lack of physiochemical information relating to the properties of the liquids themselves. If ILs are to be more generally employed, their intra- and inter- molecular solvent interactions must be more 45 fully understood. In this paper we contribute to the growing knowledge of these important materials by reporting the thermal relaxation rates of spiroxazine (**SO**) in a number of bis(trifluoromethanesulfonyl)amide ([NTf$_2$]$^-$) based ILs (fig 1).
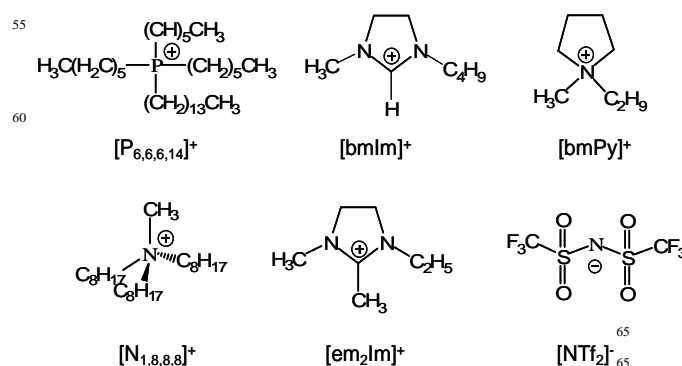
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Fig 1. Cations and anion used in this study. trihexyltetradecylphosphonium [P$_{6,6,6,14}$]$^+$, trioctylmethyl-75 ammonium [N$_{1,8,8,8}$]$^+$, 1-butyl-1-methylpyrrolidinium [bmPy]$^+$, 1-butyl-3-methylimidazolium [bmIm]$^+$, 1-ethyl-2,3 dimethyl-imidazolium [em$_2$Im]$^+$ and bis(trifluoromethanesulfonyl)amide [NTf$_2$]$^-$.

80 The physiochemical properties of ionic liquids have been previously examined by direct molecular analysis using picosecond time-resolved fluorescence[7] and solvatochromic probe dye studies. Probe based analysis have included both single parameter studies based on, for example, pyridinium *N*-85 phenolate betaine dye,[8, 9] nile red[10, 11] and 2-nitrocycloexanone[12] and multiparameter studies using the Kamlet-Taft parameters[5, 13-15]. Solvatochromic methods are based on the fact that these dyes interact with the solvent into which they are added and the extent of these interactions is

related to the chemical shifts observed for the dye in that chemical environment. Hence the optical properties enable the specific and non-specific interations between the solvent and the dye molecules to be probed. The varying strength of these interactions, dependant on the solvent chosen, results in a shift in the energy levels associated with the dye electronic transitions in the visible region and a corresponding shift in the absorbance of the dye[9]. We have carried out single parameter studies to determine solvent polarity using Reichardts dye 30. Multipaparameter studies were carried out in parallel to give a more detailed insight into the processes within the solvent which contribute to the overall polarity characteristics of the solvent. Reichardts dye was used to produce the $E_t(30)$ scale of polarity. Kamlet-taft analysis of molecular interactions divides them within the solvent into three parameters: α, β and π*, which had the following meanings;

α scale

The alpha scale is an empirical measure of the hydrogen bond acidity of the solvent system. This is associated with the ability of solvent molecules to form hydrogen bonds with other species, for example, via hydrogen atoms, which exhibit particularly strong interactions with small, strongly electronegative anions like oxygen, nitrogen or fluorine. Hydrogen bonding is a dominant force in molecular solvents and thus related directly to the polarity of the solvent. In the case of ILs it is found that the hydrogen bond ability is attributed to the particular cation species.[16]

β scale

The beta scale is the measurement of the hydrogen bond basicity or the solvents ability to accept a hydrogen bond. This force is commonly observed for protic solvents or solvents where appreciable dipole moments occur within the solvent. Molecules containing electron withdrawing atoms such as oxygen typically exhibit this characteristic and this serves to enhance solvent solute interactions. In the case of ILs, basic hydrogen bond capability is usually related to both the cation and anion species with the anion having particular influence.[16]

π* scale

The π* scale measures the polarisability of the solvent molecule by examining π-π* transitions. Polarisability is concerned with the distribution of the charge across the solvent molecule. This force is typically unimportant in small molecule systems such as the molecular solvents chosen for this study. However, in more complex systems and solvents containing delocalised charges or ring structures this feature becomes more important. In the case of ILs this factor is commonly observed to be enhanced compared to molecular solvents due to the inclusion aromatic structures and the charged nature of the binary (anion/cation) system.

Using the following equations it was possible to determine the parameters based on the peak shifts observed for the probe dyes[16]:

$$\alpha = -0.186 \times [10.91 - \upsilon_{RD30}] - 0.72\pi^* \qquad (1)$$
$$\beta = [1.035\, \upsilon_{(max)\,nn} - \upsilon_{(max)\,na} + 2.64\, kK] / 2.80 \qquad (2)$$
$$\pi^* = [27.52 - \upsilon_{(max)\,nn}]/3.182 \qquad (3)$$

Where $\upsilon = 10000/\lambda_{max}$ kK

Recently, we reported the interactions of benzospiropyran (**SP**) with ILs containing the anion NTf_2[17]. These studies found that the kinetics and thermodynamics of the **SP↔MC** equilibrium was sensitive to the nature of the cation. It was also found that the imidazolium cation formed a through space orbital interaction rather than just electrostatic interactions with the MC isomer, thus preventing the MC conversion back to the $BSP-NO_2$ isomer. We now extend the investigation to Spirooxazines. The photochromic spirocyclic compound, spirooxazine (**SO**) has been the subject to much interest due to its ability to be switched reversibly between two molecular states that exhibit dramatically different properties. Such multi-functionality has led to it being assessed for practical applications such as photosensitive lenses in eyewear (Transitions Opticals Inc) and their proposed use in molecular switches[18] and information storage[19]. This is primarily due to the highly dynamic nature of this class of molecule and precise control of this switching based on irradiation of the molecule with ultraviolet and visible light (scheme 1).

Spirooxazine (**SO**)
Colour: pale yellow/green

Merocyanine (**MC**)
Colour: Blue
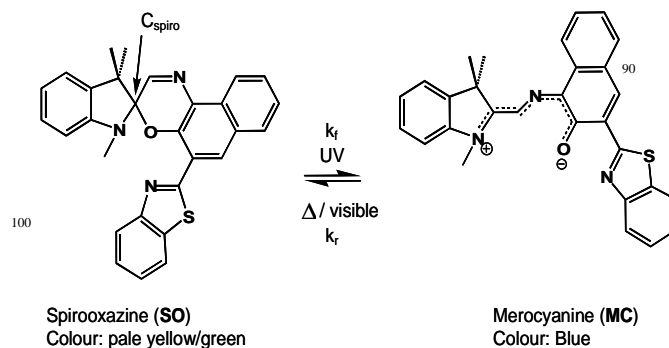
Scheme 1. Spirooxazine and its photoswitching

The process of ring opening and closing in **SO** molecules occurs due to the cleavage of the spiro carbon and delocalisation of charge across the molecule. When the closed form of **SO** is irradiated with ultraviolet light a cleavage occurs at the C-O bond of the C_{spiro} (sp^3) carbon (scheme 1). The result is a reorientation of the molecule to a planar configuration which absorbs strongly in the visible region of the spectrum at around 650nm[20, 21]. Previous studies have found that spirooxazines are more resistant to photobleaching than spiropyrans.[22, 23] This property is believed to be attributed to the oxazine ring nitrogen group and the proposed enhanced freedom of rotation of the C=N bond.[24]

It has been previously found that the rate at which the closing of the ring occurs after UV irradiation is directly

affected by solvent polarity[21]. The rate of **MC**→**SO** switching has been observed to increase with decreasing solvent polarity within molecular solvents. This is due to solvent-solute interactions such as hydrogen bonding, dipole-dipole forces, polarizability of the molecule and dipole moments which all contribute to the stabilisation of the merocyanine form.[21, 25] The binding of certain metal ions by **MC** has also been found to stabilise the open **MC** form through charge-based interactions that also generate changes in the visible absorbance spectrum of the **MC** form, indicating that a strong molecular interaction is taking place[26] These changes in colour and visible absorbance means that the **SP**/**MC** system is essentially self-indicating, in terms of which form (**SP**, **MC**) is present, and whether ions have been bound by the **MC** form. These intermolecular interactions play an important role in the kinetics of **SO**↔**MC** switching based on their ability to stabilise the **MC** form of the molecule. Upon irradiation with ultraviolet light, the non-binding form of the (**SO**) becomes zwitterionic in nature[20]. This produces two areas of distinct charge and so creates two regions for charge based interactions to occur. These occur primarily through hydrogen bonding and electrostatic forces although other forces such as lone pair donation/acceptance and dipole interactions can also play a role. With several phenyl rings and double bonding within the structure, it is possible that the π electrons play a role in the interactions within the solvent[25] and the distribution of the charges across the molecule. The influence of polarity has been observed optically in solutions containing **SO** at thermodynamic equilibrium. **SO** dissolved in non polar solvents are found to be colourless due to the predominance of the closed form. In polar solvents, the equilibrium shifts towards a mixture of the **MC** and **SO** forms which results in faintly coloured (yellow-green) solutions. Therefore, studying **SO**↔**MC** equilibrium in ILs will provide information regarding the various modes of solute-solvent interactions taking place in the molecular environment in which the **SO** molecule resides.

Ionic liquids consist solely of ions and because of this they present a highly charged environment in which the dynamics of the **SO**↔**MC** switching can be explored. Intuitively, one would expect these charges provide a basis for relatively strong interactions with the **MC** form and enhance its stability relative to the **SO** form. Ionic liquids are therefore of particular interest for spirocyclic compounds as they could provide more defined control of the photoswitching behaviour through careful tailoring of the IL constituents.

Experimental

ILs were synthesised and purified in-house using salts obtained from Sigma-Aldrich using previously reported techniques[27].. ILs produced were stored under nitrogen to exclude absorption of atmospheric water. Spectrometric studies were carried out using a Perkin Elmer Lambda 900 spectrometer (Foss Ireland) with Perkin Elmer PTP-1 themperature controller . Samples were irradiated with UV light at 365nm using a Bondwand (Electro-lite Corporation, Bethel, Ct). Reichardts dye 30 (Sigma-Aldrich chemicals), 4-

nitroaniline (Sigma-Aldrich) and n,n diethyl-4-nitroaniline (Fluorochem) were used as purchased with no further purification. 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spiroindoline-2,3'-naphtho(2,1-b)(1,4) oxazine was previously synthesized and used as supplied. Pre-metathesis cleaning was required to remove impurities which absorbed strongly below 400nm Pre-metathesis cleaning was required to remove impurities which absorbed strongly below 400nm. Removal allowed for successful detection of probe dye peaks.

Results and Discussion

Physiochemical analysis

Single Parameter study: Solvent polarity

1x 10^{-3}M solutions of Reichards dye 30 were prepared to analyse selected molecular solvents and ionic liquids. Immediate differences in polarities were apparent by distinct colouring of each solution. For the comparison, solvents were labelled below **1 – 9**: **1-** methanol, **2-** ethanol, **3-** acetonitrile, **4-** acetone, **5-** [bmIm][NTf$_2$], **6-** [em$_2$Im][NTf], **7-** [bmPy][NTf$_2$], **8-** [P$_{6,6,6,14}$][NTf$_2$], **9-** [N$_{1,8,8,8}$][NTf$_2$]
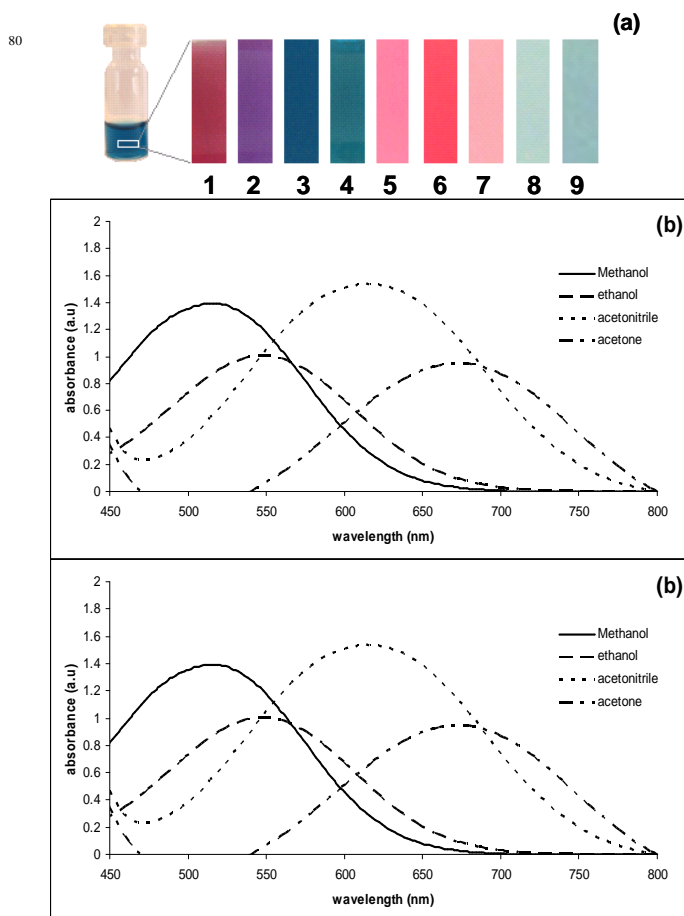

Fig 2. (a) Photograph of segments of Reichardts dye 30 in ILs and molecular solvents. Colours were enlarged from vials as shown. (b) UV-vis spectra of Reichardts dye 30 in molecular solvents. (c) UV-vis spectra of Reichardts dye 30 in ionic liquids.

According to convention, the polarity effect can be quantified using $E_t(30)$ values obtained from the empirical relationship;

$$E_t(30) = 28591/\lambda_{max} \qquad (4)$$

where, λ_{max} is peak absorbance of dye solvatochromic shift

$E_t(30)$ values for selected solvents are summarised in table 1. $E_t(30)$ values were found to decrease with decreasing solvent polarity. Protic solvents, methanol (55.4 kcal/mol) and ethanol (52.1 kcal/mol), exhibited high values with a marked decrease in values upon removal of the hydroxy functional group as observed in acetonitrile (46.4 kcal/mol) and acetone (42.5 kcal/mol). This distinct change in polarity confirms that the Reichardts polarity scale was directly related to the dipole moments inherent within the solvent molecules and their subsequent interaction with the solute dye[9]. Previous studies in ILs have shown that polarity is related to the cation and its functional group.[17] Dzyuba et al[10] examined ILs based on the imidazolium cation and $[NTf_2]^-$ anion and found that increasing chain lengths of functional groups decreased the polarity observed for the IL. $E_t(30)$ values of molecular solvents and ionic liquids were compared and it was found that ionic liquids had similar values suggesting that similar effects may be at play. Imidazolium and pyrrolidinium based ILs were comparable to that of short chain alcohols while phosphonium and alkylammonium ILs had similar polarites to acetonitrile. Solvents were ordered based on $E_t(30)$ values from most polar to least polar (table 1). Grouping of values between ring based and alkylated cation provided a similar trend to that observed with aprotic and protic solvents. The imidazolium based cation, $[bmIm]^+$, has a site of strong hydrogen bonding at the C2 proton while $[em_2Im]^+$ and $[bmPy]^+$ cations had moderate hydrogen bonding sites at the C4 and C5 protons. As seen in previous work[17], imidazolium based ILs interact strongly with the **MC** isomer, similar to that of short chain alcohols and so as expected have similar $E_t(30)$ values. This hydrogen bond ability placed a 'protic' characteristic upon this group of cations which may go some way to explaining the relationship between results obtained with alcohols and ILs.

Multiparameter Study: Intra- and inter-molecular properties

Due to the limitations of single parameter studies[28], Kamlet-Taft multiparameter studies were carried out to better understand dominant molecular interactions of hydrogen bonding and charge distribution in solvent systems. To investigate this, three solvatochromic dyes, 1×10^{-3}M reichardts dye and 5×10^{-5}M 4-nitroaniline and n,n diethyl-4-nitroaniline, were added to each of the ionic liquids and the resulting peak shifts were recorded using UV-Vis spectrometry. These shifts were converted empirically to quantify each parameter using equations (**1**), (**2**) and (**3**) which are summarised in table 1.

Kinetics studies

In conjunction with multiparameter studies, the kinetics of thermal relaxation of **MC→SO** was investigated at the corresponding λ_{max} of **MC** found in the selected solvents in the dark. This rate followed an exponential decay curve from which the first order decay in each solvent was found by plotting $\ln(A/A_0)$ vs time and the rate was determined from the slope of the curve (table 1).
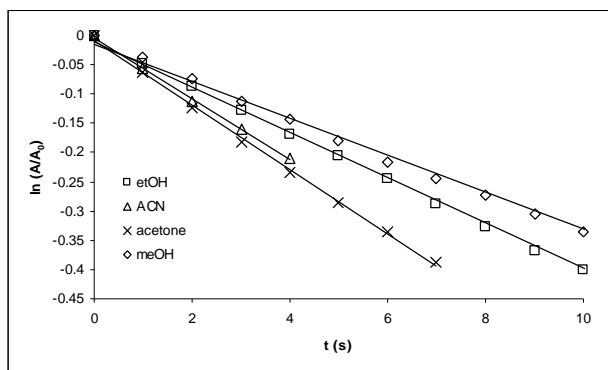

Fig 3. Thermal relaxation of **SO** in molecular solvents.

From fig. 3 it is apparent that the rate of thermal relaxation was dependent on the polarity of the molecular solvent. It was observed that there was a linear relationship between $E_t(30)$, α and β values and rates of relaxation. It was found that α valves in molecular solvents were relatively high (1.05 in methanol) which reinforces the fact that hydrogen bonding is a dominant force in the solvent-solvent (intermolecular) and solvent-solute (intramolecular) interactions in molecular solvents. Similar trends were observed for β values. For polar protic solvents both hydrogen bond donation and acceptance were high which implied that the solvents could interact with the charge sites of the **MC** and thus increase the lifetime of this form. Rates found for these solvents were 3.2×10^{-2} s^{-1} (methanol) and 3.9×10^{-2} s^{-1} (ethanol). This was in contrast to polar aprotic solvents which had an approximate 1.5 fold increase in relaxation rates with 5.2×10^{-2} s^{-1} (acetonitrile) and 5.5×10^{-2} s^{-1} (acetone) due to the lack of the hydrogen bonding in these aprotic solvents, which enhances the relative stability of **SO**.

Photoswitching of **SO** in ILs (fig 4) appeared to increase the **MC** lifetime with rates corresponding to that of highly polar molecular solvents. When the thermal relaxation rates were compared to the Kamlet-Taft parameters it was found that ILs did not show the same correlation as observed in molecular solvents. α values appeared reduced for $[N_{1,8,8,8}]^+$ and $[P_{6,6,6,14}]^+$ two fold relative to the rest of the ILs studied. Comparison of these values to rates of relaxation did not explain the kinetics observed since the reverse trend was expected as found in molecular solvents. Furthermore, β values were all relatively constant across the ILs and
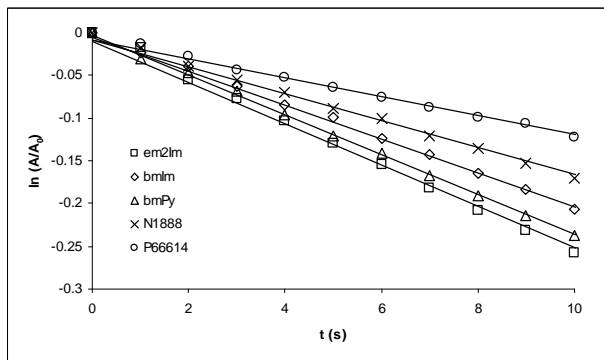
Fig 4. Thermal relaxation of **SO** in selected ionic liquids.

Fig 5. Normalised kinetics curves of thermal relaxation of **SO-1** in solvents of similar $E_t(30)$:
ethanol (52.1 kcal/mol)/ [bmIm][NTf$_2$] (52.4 kcal/mol)
acetonitrile (46.4 kcal/mol)/ [P$_{6,6,6,14}$][NTf$_2$] (46.1 kcal/mol)

generally smaller than those found in molecular solvents. Since β values corresponded to the influence of the anion, this implied that the [NTf$_2$]$^-$ anion was benign and had minimal interactions with the **MC** which correspond well to previous studies[17]. This meant that any variations in the relaxation kinetics primarily arise through interactions involving the IL cation. However, since the rate constants observed were all relatively constant, this suggested that variations in H-bonding behaviour had limited influence on the mechanism. The relatively high π* values suggested that coloumbic interactions are dominant in ILs and would be intuitively expected. Furthermore, the relatively constant π* values map well against the equivalent rate constants. Since ion based electrostatic interactions tend to be much stronger than that of hydrogen bonds they appear to dominate the relaxation kinetics and consequently polarity scales like $E_t(30)$ values are of limited use for interpreting kinetics of thermal relaxation of **SO** in ILs.

Comparison of **MC**→**SO** thermal relaxation in molecular solvents and ILs highlighted these deviations in solvent properties observed for ILs. Fig 5 shows that the relaxation of **MC**→**SO** in ILs is enhanced compared to molecular solvents. The kinetic curves of [bmIm][NTf$_2$] and ethanol and [P$_{6,6,6,14}$][NTf$_2$]and acetonitrile show clearly that ILs were different to that of molecular solvents with extended lifetimes of **MC**. This was not expected from comparison of $E_t(30)$ values. Similar Et(30) values of ILs and molecular solvents would suggest that **MC**→**SO** kinetics should be similar. However, the kinetics are very different and therefore the $E_t(30)$ scale was deemed misleading in terms of predicting the behaviour of **SO** in ILs.
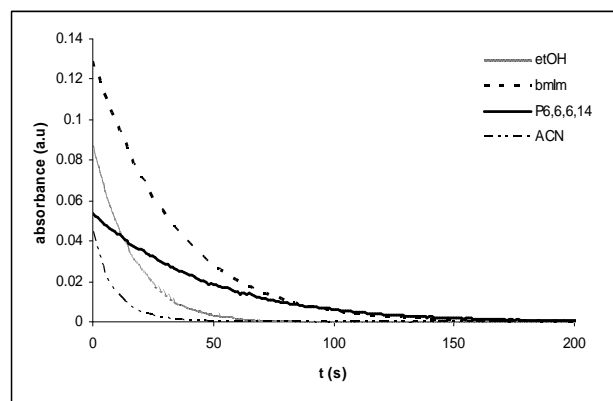
Thermodynamic parameters - Arrhenius and Eyring plots

The linear dependence of temperature to the rate of thermal relaxation was plotted using equations **(5)** and **(6)** to find the activation energy (E$_a$), entropy of activation (ΔS‡), enthalpy of activation (ΔH‡) and Gibbs energy of activation (ΔG‡). An alternative form of the eyring equation **(7)** was also employed to derive the equilibrium of the activated complex of the transition state theory.[29] The thermodynamic parameters found were summarised in table 2.

$$\ln k = E_a/RT + \ln A \qquad (5)$$
$$\ln (k/T) = -\Delta H^{\ddagger}/RT + \ln (k_B/h) + \Delta S^{\ddagger}/R \qquad (6)$$
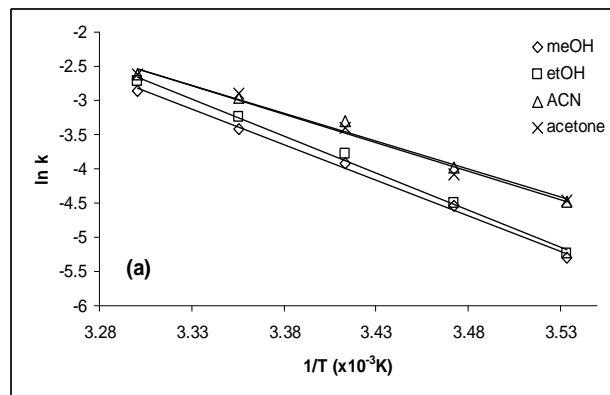$$k = (k_B T/h)K^{\ddagger} \qquad (7)$$

where,
R = gas constant
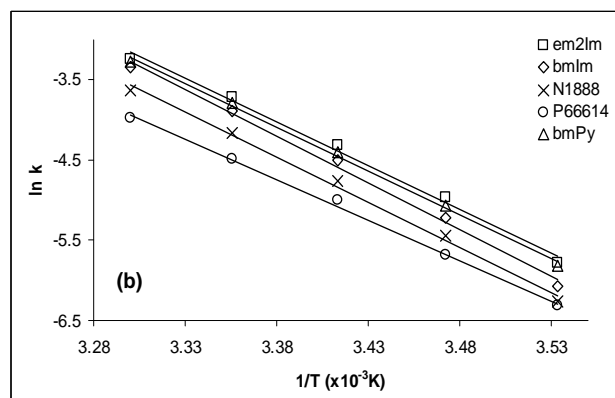h = plancks constant
k$_b$ = Boltzmann constant

Fig 6: Arrhenius plots of (a) molecular solvents and (b) ionic liquids.

Fig 7: Eyring plots of (a) molecular solvents and (b) ionic liquids.

E_a values varied between 67.83 and 89.89 kJ.mol^{-1} in molecular solvents and 83.97 and 97.06 kJmol^{-1} in ILs. Theses values reflected that the energy barrier was required to be overcome in the reorientation of the **MC** molecule during its thermal relaxation to the **SO** form once again. The values found for **SO** in ILs was similar to that the polar moleclar solvents further justifying the similiarities of the environments in both classes of solvents. Rates of closure were still slower than polar solvents which was believed to be due to the electrostatic interactions of the ion constituents which enhanced **MC** stability.
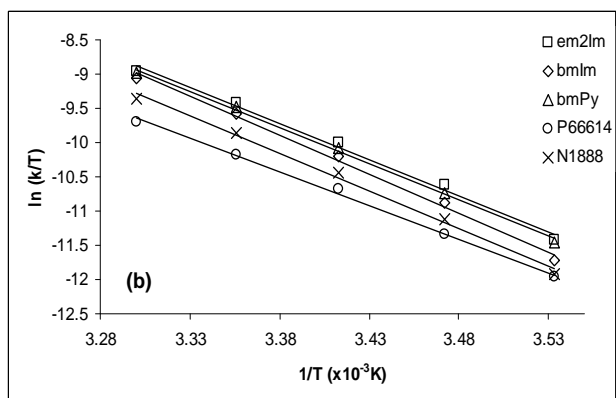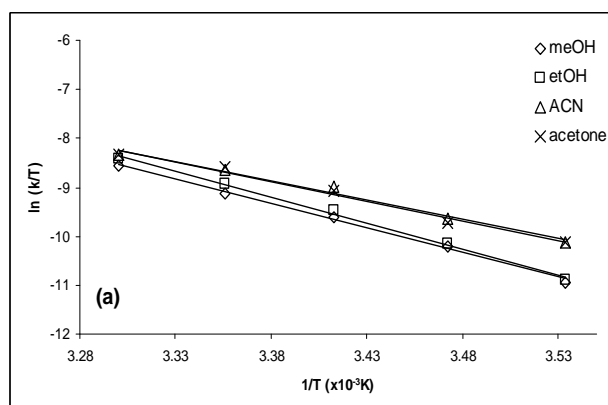

$\Delta S^{\ddagger}$ observed for **SO** ranged from -50.29 to 21.48 in molecular solvents and -8.67 to 40.07 J.K^{-1}.mol^{-1} in ILs. Positive values would indicate that the transition state intermediate between **MC** and **SO** is more disordered compared to the ground state form. Since solvent-solute interactions are common between the polar **MC** and solvent molecules it is proposed that the resulting disorder of the system would result in such interactions occuring and resulting in an overall stabilisation of the system and slower reversion to **SO**. Negative values would therefore indicate that a more rigid system was presented in the solution. Non-polar solvents such as toluene are known to have minimal interaction with spirocyclic compounds.(REF) Previous studies of spirocyclic compounds have shown this kinetic relationship.[30, 31] The resulting order in the solvent (association of solvent molecules with one another) should result in less stabilisation of the **MC** form and thus faster kinetics. Values found for **SO** in ILs were similar to that of polar protic solvents and the similiarity was further indicated in the slow rates of closure. $\Delta S^{\ddagger}$ values were found to be more positive in ILs which resulted in further enhancement of **MC** lifetimes. $\Delta G^{\ddagger}$ for the **MC→SO** process was found to be positive and approximately 82 kJ.mol^{-1} in all solvents chosen. This was expected as the reaction was not spontaneous, requiring heat from surroundings, to aid in the reorientation and relaxation to the closed **SO** form. $\Delta H^{\ddagger}$ values agreed with these findings with its positive values (67.08 to 97.06 kJ.mol^{-1}) also indicating that an activated process at play during thermal relaxation.

The thermodynamic parameters found further enforced the conclusion that it was difficult to correlate physicochemical parameters to the observed rates of relaxation. Previous attempts to ratioanalise properties of spirooxazines has also yielded similar conclusions.[32] Chibsov and Gorner stated that variations in activation energy was found for spirooxazines they studied in different solvents and substitutions but that trends in polarity may be ruled out For **SO** in molecular solvents it is possible to see general relationship between rates

of thermal relaxation and activation energies between protic an aprotic solvents. It was found that upon going from protic to aprotic solvents that E_a reduced by around 20 kJ.mol^{-1} with a 1.5 time increase in kinetics. This was expected since lower activation energy barriers would result in faster relaxation processes. However, specific correlation of exact rates to corresponding E_a does not yield a linear relationship and may be due to solvent stabilisation of the charged **MC** form. The relationship between $\Delta H^\ddagger$ and E_a resulted in similar responses while $\Delta G^\ddagger$ showed subtle but linear reponse to kinetics. Since decreasing gibbs energy would indicate the system becoming more spontaneous this could account for the increasing rates of relaxation.

Interestingly, no trends whatsoever we visible between E_a and $\Delta H^\ddagger$ and the rates for **SO** in ILs. However, The relationship of $\Delta G^\ddagger$ and thermal reversion is maintained following the same convention as that of molecular solvents. $\Delta G^\ddagger$ was observed to be higher in ILs compared to molecular solvents. This correlates well with observed kinetics since the rates observed in ILs were noticably slower than that of molecular solvents. The complexity of the ILs may have resulted in an environment that was far too complex for current equations to rationalise.

Conclusions

It has been found that ILs exhibit typically polar environments when employed as solvent media for photochromic switching. $E_t(30)$ calculations found ILs to be similar to polar and mildly non polar molecular solvents. However, it was found that polarity scales were not sufficient to account for **MC→SO** thermal relaxation kinetics in ILs. It is believed that this is due to the charged nature of the solvent components which resulted in ion-charge interactions between the individual solvent ions and opposing charges of the **MC**. Current studies have indicated that without significant changes to the ion structures, subtle changes in ion constituents such as alkyl chain length are not sufficient to allow for a range of relaxation rates and thus control over the photoswitching of **SO** in ILs. In conclusion, no relationship was found between the $E_t(30)$, α and β values and the thermal relaxation kinetics of **MC→SO** in the ILs studied. However, the slower and relatively equal kinetic values corresponded well to the high π^* values observed in ILs which suggested that the solvent charge was the dominant factor in controling the kinetics of **MC→SO**. This differed from previous investigations of **SP** in ILs which indicated different processes may be at play in the solvent-solute interactions of **SO** in ILs. Thermodynamic parameters such as $\Delta S^\ddagger$ $\Delta H^\ddagger$ and $\Delta G^\ddagger$ failed to give a clear relationship to the rate of thermal relaxation which may indicate that the complexity of the IL itself results in aditional interactions not accounted for by these values.

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Table 1

Physicochemical properties (298K) of **SO** in molecular solvents and ionic liquids. Reference values in parenthesis

Solvent	Et(30) (kcal/mol)	α	β	π*	SO MC λ$_{max}$	k (10^{-2} s^{-1})
methanol	55.4 (55.4)[7]	1.06 (1.05)[22]	0.62 (0.61)[22]	0.71 (0.73)[22]	640	3.2
ethanol	52.1 (51.9)[7]	0.90 (0.83)[26]	0.72 (0.77)[26]	0.63 (0.54)[26]	642	4.2 (2.0)[21]
acetonitrile	46.4 (45.6)[7]	0.42 (0.35)[22]	0.37 (0.37)[22]	0.79 (0.79)[22]	642	5.2 (5.2)[21]
acetone	42.5 (42.2)[7]	0.25 (0.20)[22]	0.57 (0.54)[22]	0.67 (0.70)[22]	642	5.5 (5.4)[21]
[bmIm][NTf$_2$]	52.4 (51.5)[27]	0.72(0.69)[22]	0.24 (0.25)[22]	0.90 (0.97)[22]	642	2.0
[em$_2$Im][NTf$_2$]	50	0.42	0.1	1.02	640	2.4
[bmPy][NTf$_2$]	49.6 (50.2)[9]	0.57 (0.43)[8]	0.23 (0.25)[8]	0.87 (0.95)[8]	642	2.3
[P$_{6,6,6,14}$][NTf$_2$]	46.1	0.37	0.27	0.83	648	1.1
[N$_{1,8,8,8}$][NTf$_2$]	45.9	0.33	0.23	0.87	646	1.6

Table 2

Thermodynamic Parameters of activation. a parameters found at 298K

Solvent	k ^{a} (10^{-2} s^{-1})	Activation energy(E_a) kJ.mol^{-1}	ΔH‡ kJ.mol^{-1}	ΔG$^{‡ a}$ kJ.mol^{-1}	ΔS‡ J.K^{-1}.mol^{-1}	K$^{‡ a}$ (x10^{-15})
methanol	3.2	85.74	83.31	81.40	6.4	5.23
ethanol	3.9	89.89	87.45	81.05	21.48	6.28
acetonitrile	5.2	67.83	65.39	80.38	-50.29	8.42
acetone	5.5	69.51	67.08	80.41	-44.73	8.83
[P$_{6,6,6,14}$][NTf2]	1.1	83.97	81.54	84.12	-8.67	1.82
[N$_{1,8,8,8}$][NTf2]	1.6	93.45	91.03	83.37	25.71	2.51
[bmIm][NTf2]	2.0	97.06	94.63	82.69	40.07	3.29
[bmPy][NTf2]	2.3	90.72	88.28	82.45	19.56	3.64
[em2Im][NTf2]	2.4	90.32	87.88	82.30	18.74	3.93