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Room Temperature Ionic Liquids Structure and its Effect on the Mononuclear Rearrangement of Heterocycles: An Approach Using Thermodynamic Parameters

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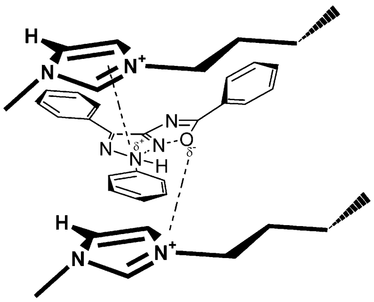

The kinetics of the rearrangement of the *Z*-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (**1**) into the relevant 4-benzoylamino-2,5-diphenyl-1,2,3-triazole (**2**) induced by amines have been studied in five room-temperature ionic liquids (RTILs) at different temperatures. The kinetic data collected show that both cationic and anionic parts of RTILs significantly influence the reactivity of the title reaction. The calculated activation parameters allow us to advance hypotheses about the weak interactions operating in RTIL solutions.

Introduction

Room-temperature ionic liquids (RTILs) have become very popular solvents over the past decade.[1] Much of this popularity is centered on their controversial "green" character. However, they are also of great interest for the unusual solvent environment that they provide for solute species. This might affect reactivity in several different ways. For example, they have been considered as oriented solvents that could affect selectivity by ordering the reactants.[2]

Both quantitative[3] and qualitative[4] effects of the RTILs on the course of reactions are well documented. However, it is quite difficult to explain the effect of RTILs on a reaction by means of a single solvent property such as their polarity. Indeed,

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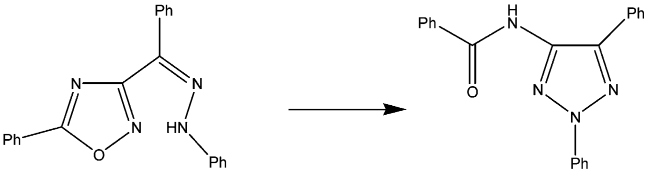
CHART 1



1 2

hydrogen bond acidity (α) and basicity (β) as well as polarizability effects (π*) can often be considered in describing the different influence of the RTILs. Of course, each of the above solvent parameters is a function of both cation and anion components of the RTILs. Then, considering that each RTIL represents a particular combination of α, β, and π* parameters and that several RTILs are possible, tailor-made RTILs can be thought of in order to have a lot of different effects at one's disposal.

In contrast, an alternative view of the solvent effect of RTILs is based on their partially pre-organized structure.[5] This structure, also dependent on the reagents' structural requirements, may be able to give them an ordered disposition suitable for reaction. In this manner, RTILs may function as "entropic drivers".[6] For the above reasons, the study of chemical and physical properties of the RTILs is an active and attractive area of research.[7]

Recently, we have investigated the effect of [bmim][X] (bmim = 1-butyl-3-methylimidazolium and X = BF_4^- and PF_6^-) on the amino-catalyzed mononuclear rearrangement of heterocycles (MRH) of the *Z*-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (**1**) into the relevant 4-benzoylamino-2,5-diphenyl-1,2,3-triazole (**2**) at 298 K (Chart 1).[8]

The title reaction is a peculiar intramolecular nucleophilic substitution occurring through a bicyclic quasi-aromatic (10π) transition state.[9] It has been largely investigated in conventional organic solvents,[10] as well as in organized or in preorganized systems such as micelles[11] and cyclodextrins.[12]

Data collected[8] in RTILs seem to indicate that, in spite of the significant increase in reaction rate, such interactions as substrate−solvent, amine−solvent, and amine−amine, compared with those present in conventional solvents, have scarce relevance. However, they determine the peculiar effects that the different RTILs have on the outcome of the reaction.

In order to gain new insights into the above investigation, other ionic liquids such as [bmim][NTf_2], [bm_2im][NTf_2], and [bmpyrr][NTf_2] [bm_2im = 1-butyl-2,3-dimethylimidazolium, bmpyrr = 1-butyl-1-methylpyrrolidinium, and NTf_2 = bis(trifluoromethylsulfonylimide)] have been considered. Among these, bm_2im^+ and $bmpyrr^+$ have a lesser hydrogen bond donor ability than $bmim^+$; furthermore, the $bmpyrr^+$ is not able to give $\pi-\pi$ interactions that in some cases determine a strong effect on the reactivity. At last, the substitution of the anion part of [bmim][X] going from previously studied RTILs to [bmim][NTf_2] should cause a different packing and possibly a different catalytic effect.

Because also a modest variation in temperature can cause significant differences in the packing of ionic liquids, it seems interesting to study the title reaction at various temperatures (293−313 K).

The present study has been carried out at six molar concentrations ($2.0 \times 10^{-3}-1.33 \times 10^{-2}$ M; see Table 4 in the Supporting Information) of the following bases: butylamine (BuA, a primary amine), piperidine (Pip, a secondary amine), and triethylamine (TEA, a tertiary amine), showing different structure, basicity, and steric requirements. The reaction rates were measured spectrophotometrically by monitoring the disappearance of **1** at its λ_{max}.

Results and Discussion

According to our previous report,[8] for all of the RTILs studied and for each of the amines, an excellent linear dependence of the apparent first-order rate constant ($k_{A,R}$) on amine concentration has been found.

The relevant k_{II} values are reported in Table 1.

$$k_{A,R} = k_{II}[\text{amine}] + i \qquad (1)$$

The above result is different from that previously obtained in conventional organic solvents where different kinetic laws with first- or second-order dependence on amine concentration were found as a consequence of solvent polarity, amine structure, and basicity (see some examples for Pip in Table 2), according to the different interactions operative in conventional solvents.

In all cases considered, significant "negative" intercept values were also calculated. They were related to an acid−base interaction between the cation component of the RTIL and the amine.[8] A careful analysis of data collected in Table 1 seems to indicate that, for the same anion [NTf_2^-], the intercept values decrease, as absolute values, going from $bmim^+$ and bm_2im^+ up to $bmpyrr^+$, according to the decrease of cation part acidity. The acidity properties of the three analyzed cations are attribut-

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TABLE 1. Calculated Second-Order (k_{II}) Rate Constants[a] for the MRH of 1 in Ionic Liquid Solution at 298 K

IL	amine	k_{II} (M^{-1} s^{-1})	*i*
[bmim][BF$_4$]	BuA	0.125 ± 0.004	$(-3.07 \pm 0.41) \times 10^{-4}$
	Pip	0.517 ± 0.028	$(-1.35 \pm 0.32) \times 10^{-3}$
	TEA	0.156 ± 0.008	$(-3.44 \pm 0.96) \times 10^{-4}$
[bmim][PF$_6$]	BuA	0.0035 ± 0.0002	$(-1.71 \pm 0.32) \times 10^{-5}$
	Pip	0.0261 ± 0.0010	$(-2.09 \pm 0.15) \times 10^{-4}$
	TEA	0.0219 ± 0.0015	$(-1.69 \pm 0.25) \times 10^{-4}$
[bmim][NTf$_2$]	BuA	0.0229 ± 0.0008	$(-2.64 \pm 0.92) \times 10^{-5}$
	Pip	0.192 ± 0.009	$(-3.57 \pm 1.09) \times 10^{-4}$
	TEA	0.0765 ± 0.0006	$(-1.85 \pm 0.67) \times 10^{-5}$
[bm$_2$im][NTf$_2$]	BuA	0.0130 ± 0.0008	$(-2.30 \pm 0.89) \times 10^{-5}$
	Pip	0.095 ± 0.005	$(-1.82 \pm 0.53) \times 10^{-4}$
	TEA	0.0277 ± 0.0010	0[b]
[bmpyrr][NTf$_2$]	BuA	0.00162 ± 0.00008	$(-2.73 \pm 1.03) \times 10^{-6}$
	Pip	0.00432 ± 0.00030	$(-1.08 \pm 0.39) \times 10^{-5}$
	TEA	0.00347 ± 0.00020	$(-7.03 \pm 2.15) \times 10^{-6}$

[a] The rate constant values were reproducible to within ±3%. [b] The calculated intercept value was $(-0.53 \pm 1.56) \times 10^{-5}$.

able to the hydrogen atom on C2 for bmim$^+$,[13] to the methyl group at the C2 position for bm$_2$im$^+$,[14] and to the hydrogen atom on a carbon α to the quaternary nitrogen for bmpyrr$^+$.[15] The cation acidity is also affected by the anion part of RTIL (see later). Thus, the intercept values for bmim-based RTILs decrease regularly, with the exception of TEA, going from [BF$_4^-$] to [NTf$_2^-$] up to [PF$_6^-$]. The different behavior of TEA, with respect to Pip and BuA, should be a consequence of its structure (tertiary amine), which causes a lack of interaction between this amine and the anion counterpart of RTIL.

Looking at the solvent effect on the reactivity, we observed a very large increase in reactivity on going from conventional solvents to RTILs. For a correct comparison, one needs to consider the reactivity at a fixed amine concentration (for example, $[\mathrm{Pip}] = 1.30 \times 10^{-2}$ M; see Table 2) because different kinetic laws can describe the course of the reaction in conventional solvents and in RTILs.

Actually, the reactivity in acetonitrile is comparable or higher than that measured in RTILs, but the peculiar behavior of acetonitrile can be related to its ability in providing assistance to the nucleophilic substitution reaction intermolecularly[18] or intramolecularly[10f] as well as to its solvent properties. In contrast, in some cases, the comparable or even higher reactivity in methanol could be a consequence of the catalytic effect of the methoxide ion, significantly present in the basic solution.

A careful analysis of data reported in Table 2 shows that the higher reactivity in RTILs, with respect to conventional organic solvents, cannot be ascribed only to a polarity effect.

Indeed, although the E_T^N values for the RTILs considered are lower than that reported for methanol, in three of the five cases considered ([bmim][BF$_4$], [bmim][NTf$_2$], [bm$_2$im][NTf$_2$]), the reaction proceeds faster.

In contrast, the inadequacy of polarity parameters in explaining reactivity data is evident considering the RTIL solvents. Thus, the E_T^N values do not account for the different reactivity in [bmim][BF$_4$] and [bmim][PF$_6$] or in [bm$_2$im][NTf$_2$] and [bmpyrr][NTf$_2$].

Similar considerations can be carried out by looking at the π^* values as quantitative measurements of polarity. As a matter of fact, the reaction proceeds faster in [bmim][NTf$_2$] than in [bm$_2$im][NTf$_2$], despite the higher π^* value for the latter IL.

These results agree with the observations previously reported about the lack of universality of polarity parameters of RTILs and their dependence on studied reactions or tested compounds.[19]

In some cases, the viscosity entity of RTILs has been considered to explain the reactivity order. For the studied reaction, the viscosity effect can be quite complex. Indeed, in the transition state, bond making and bond breaking occur simultaneously and, as they are differently influenced by the viscosity increase (it favors the former but disfavors the latter),[20] the overall result should depend on the position of the transition state along the reaction coordinate. In general, the viscosity value[21] increases in the order: [bmim][NTf$_2$] ($\nu = 52$ cP) < [bmpyrr][NTf$_2$] ($\nu = 85$ cP) < [bmim][BF$_4$] ($\nu = 233$ cP) < [bmim][PF$_6$] ($\nu = 450$ cP), and the reactivity increases in the order: [bmpyrr][NTf$_2$] < [bmim][PF$_6$] < [bmim][NTf$_2$] < [bmim][BF$_4$]. Thus, experimental data do not show complete agreement between viscosity and reactivity, and also, when the RTILs were separated into two series (the bmim- and the NTf$_2$-based salts), a homogeneous trend was not found. Thus, the viscosity parameter alone also seems to be inadequate.

Probably, some other factors such as the organizing ability (deriving, for example, from $\pi-\pi$ interactions; see later) of RTILs should contribute to the determination of the higher reactivity.

As can be seen from data reported in Table 1, in all cases, the reactivity increases going from BuA to TEA up to Pip. As far as base effects are concerned in each RTIL, only a small reactivity variation has been observed. The ratios of reactivity (BuA/TEA/Pip) go from 1:2.1:2.7 for [bmpyrr][NTf$_2$] up to 1:3.3:8.4 for [bmim][NTf$_2$]. In contrast, generally much larger (1:66:188 for PhH at 313 K) reactivity ranges were observed in conventional organic solvents.[10e] Probably in conventional solvents, amine−solvent and amine−amine interactions could strongly differentiate the amines on the basis of their nature and steric requirements, unlike that which occurs in RTILs, which at least in comparison with benzene would exert a significant leveling effect.

As a consequence of the fact that the properties of RTILs are largely controlled by the nature of both the cation and anion, data reported in Table 1 allow us to outline, for each amine, the following reactivity order: [bmim][BF$_4$] > [bmim][NTf$_2$]

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TABLE 2. Kinetic Laws and Apparent Pseudo-First-Order Rate Constants for the Piperidine-Catalyzed MRH of 1 in Organic Solvents and in Ionic Liquid Solution at 313 K and at [Pip] = 1.30 × 10^{-2} M

solvent	kinetic law ($k_{A,R}$ =)	$k_{A,R}$ (s^{-1})	β	π^*	E_T^N
benzene[a]	$k_{II}[Pip] + k_{III}[Pip]^2$	5.47×10^{-8}			0.111[b]
1,4-dioxane[a]	$k_{II}[Pip] + k_{III}[Pip]^2$	4.29×10^{-7}			0.164[b]
ethyl acetate[a]	$k_{II}[Pip] + k_{III}[Pip]^2$	7.77×10^{-7}			0.228[b]
methanol[a]	$k_u + k_{II}[Pip] + k_{MeO^-}[MeO^-]$	4.49×10^{-4}			0.762[b]
acetonitrile[a]	$k_u + k_{II}[Pip]$	6.18×10^{-3}			0.460[b]
[bmim][BF_4]	$k_{II}[amine] + i$	1.42×10^{-2}	0.376[c]	1.047[c]	0.670[c]
[bmim][PF_6]	$k_{II}[amine] + i$	3.99×10^{-4}	0.207[c]	1.032[c]	0.669[c]
[bmim][NTf_2]	$k_{II}[amine] + i$	5.99×10^{-3}	0.243[c]	0.984[c]	0.644[c]
[bm_2im][NTf_2]	$k_{II}[amine] + i$	2.45×10^{-3}	0.239[c]	1.083[c]	0.541[c]
[bmpyrr][NTf_2]	$k_{II}[amine] + i$	1.62×10^{-4}	0.252[c]	0.954[c]	0.544[c]

[a] See ref 10f. [b] See ref 16. [c] See ref 17.

> [bm_2im][NTf_2] > [bmim][PF_6] > [bmpyrr][NTf_2]. In order to search for an explanation of the above trend, it could be convenient to divide the RTILs into two homogeneous series, one including the bmim-based salts and the other including the NTf_2-based salts.

Regarding the reactivity in the bmim-based salts, the order [BF_4^-] > [NTf_2^-] > [PF_6^-] can be explained on the basis of β values ascribable to the anionic component of the RTILs. Indeed, when the amine attacks the hydrogen atom of the NH moiety of the phenylhydrazonic chain, the amine begins to develop a positive charge. This will cause an increase in the hydrogen bond donor properties of any proton bound to a nitrogen atom. As a consequence, a stronger (higher β value) hydrogen-accepting anion will preferentially stabilize the transition state with respect to the reagents and, for a domino effect, increase the nucleophilicity of the NH phenylhydrazonic by interacting with this proton. This effect should be greater when more protons are bound to the nitrogen. In confirmation of the above hypothesis, the reactivity ratio increases in the order TEA < Pip < BuA. The above effect could also explain the trend for the intercept values previously seen.

Taking into account the reactivity in the NTf_2-based salts, the order $bmim^+ > bm_2im^+ > bmpyrr^+$ can be explained on the grounds of the cation ability to give $\pi-\pi$ interactions. The relevance of $\pi-\pi$ interactions in RTILs has been frequently outlined, and it has allowed us to explain the high solubility of aromatic compounds, such as benzene and thiophene,[22] in these solvent media. An r parameter has been proposed in order to evaluate the ability of RTILs to give $\pi-\pi$ interactions.[23] The higher reactivity of the two imidazolium RTILs compared with $bmpyrr^+$ may be ascribed to a stabilizing $\pi-\pi$ effect of the heteroaromatic cations, lacking in the last one. Indeed, these cations result in more efficiency than $bmpyrr^+$ in the stabilization of the transition state. Between $bmim^+$ and bm_2im^+, one should expect that the latter might be more efficient in the stabilization of the TS according to its higher r value ($r = 0$ for [bmim][NTf_2] and $r = 0.073$ for [bm_2im][NTf_2]), due to the electron repulsive effect of the methyl group at the C2 position. Instead, in our case, the reaction proceeds faster in $bmim^+$ than in bm_2im^+. Probably, two opposite effects could determine the observed reactivity order. The former, relative to the entity of $\pi-\pi$ interactions, favors the reactivity in bm_2im^+; the latter, relative to the different order around the transition state, favors the reaction in $bmim^+$ (see later).

TABLE 3. Activation Parameters for the MRH of 1 in Ionic Liquid Solution

IL	amine	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ [J/(K mol)]	$\Delta G_{298.1}$ (kJ/mol)
[bmim][BF_4]	BuA	49.9 ± 4.0	−133 ± 13	89.5
	Pip	50.5 ± 0.6	−120 ± 2	86.3
	TEA	57.3 ± 2.2	−107 ± 7	89.2
[bmim][PF_6]	BuA	59.9 ± 2.4	−133 ± 8	99.5
	Pip	54.6 ± 0.7	−136 ± 2	95.1
	TEA	67.6 ± 3.0	−91 ± 10	94.7
[bmim][NTf_2]	BuA	53.1 ± 1.4	−136 ± 5	93.6
	Pip	48.3 ± 1.6	−135 ± 5	88.5
	TEA	56.1 ± 0.5	−115 ± 5	90.4
[bm_2im][NTf_2]	BuA	45.6 ± 1.4	−166 ± 5	95.1
	Pip	45.5 ± 1.2	−150 ± 4	90.2
	TEA	54.1 ± 1.8	−130 ± 6	92.9
[bmpyrr][NTf_2]	BuA	62.6 ± 3.3	−126 ± 11	100.2
	Pip	67.9 ± 1.5	−101 ± 5	98.0
	TEA	61.2 ± 2.2	−124 ± 7	98.2

Activation Parameters. It has been reported that, for kinetics carried out in RTILs, a significant curvature in Arrhenius or Eyring plots could be observed as a consequence of structural changes in the solvent.[24] So for a careful analysis of the temperature effect, the reaction was carried out at five temperatures from 293 to 313 K.

For each amine and RTIL, an excellent linear correlation of $\log(k_{obs}/T)$ versus $1/T$ was obtained, indicating that, in the analyzed range, the above upsetting effect is not operative and the calculated activation parameters are only dependent on the MRH process. The activation parameter values are reported in Table 3. (Data at different temperatures are available in Table 5 of the Supporting Information.)

The enthalpy values range from 45.5 to 67.9 kJ/mol, whereas the entropy values range from −166 to −91 J/(K mol). The present data are significantly different from those collected in dioxane−water both in the uncatalyzed (in the 3.8−6.0 pS^+ interval: $\Delta H^{\ddagger} = 84 \pm 2$ kJ/mol and $\Delta S^{\ddagger} = -92$ J/(K mol)) and in the base-catalyzed range (in the 8.5−12.5 pS^+ interval: $\Delta H^{\ddagger} = 92 \pm 2$ kJ/mol and $\Delta S^{\ddagger}$ ranges from −44.3 to 2.1 J/(K mol)).[10c,25] They show that the analyzed reaction in RTILs is largely enthalpy-favored with respect to the dioxane−water mixture.

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(25) Because in the base-catalyzed range the rate constants are composite values [k_{OH} and k_B represent the kinetic contribution from the OH^- and the base (buffer)-dependent pathways], only rough information from the activation parameters could be obtained.[10d]

Regarding the entropic contribution, the reaction is surely disfavored with respect to the base-catalyzed range; in the uncatalyzed range, less dramatic differences were observed. We think that the differences depend on the fact that in dioxane−water the activation parameters were largely affected by the difference in solvation between the initial and the transition state. Indeed, stronger interactions or more extensive solvation of the reagents causes an unfavorable enthalpic contribution that is significantly larger in dioxane−water than that in RTILs. In contrast, the entropic contribution is largely unfavorable in RTILs because the passage from the initial to transition state causes a decrease of molecular freedom as well as an increase in the structural order, in agreement with the proposed structure of the zwitterionic transition state, stabilized by dipole−dipole interactions with the ionic liquid.

However, this increase in structural order is not counterbalanced by the desolvation process that normally assists the course of a reaction going toward the transition state. This is a consequence of scarce relevance of substrate−solvent, amine−solvent, and amine−amine interactions in RTILs. In order to gain insight into the effect of the RTILs, we shall try to analyze separately the activation parameters as a function of the (i) cation component, (ii) anion component, and (iii) amine structure.

Cation Component. Looking at activation parameters as a function of the RTILs cation part, for each amine, the favorable effect on enthalpy values decreases in the order $\mathrm{bm_2im^+} > \mathrm{bmim^+} > \mathrm{bmpyrr^+}$; the opposite effect has been observed for the entropy counterparts. As pointed out above, the three cations considered differ on the basis of their abilities to H-bond and have $\pi-\pi$ interactions. Both of these factors can significantly affect activation parameter values. In general, an increase in H-bonding ability could give an unfavorable enthalpic contribution, due to the energy that is needed to break the N···H interaction between the cation and amine (see above), but a favorable entropic contribution from this breaking, going from initial to transition state, could increase the disorder degree of the system.

In contrast with expectation, experimental data show that the highest activation enthalpy was measured in the presence of [bmpyrr][$\mathrm{NTf_2}$], that is, the RTIL with the cation less able to act as the H-bond donor. Likewise, entropy values in [bmim][$\mathrm{NTf_2}$] or in [$\mathrm{bm_2im}$][$\mathrm{NTf_2}$], lower than those calculated in [bmpyrr][$\mathrm{NTf_2}$], do not account for the disorder increase that should characterize the system in the transition state. The activation parameters trend could be better explained on the basis of the cation ability (see above) to give $\pi-\pi$ interactions. Thus, the aromatic cations perform a stabilizing effect on the transition state, which will be more ordered than that resulting in the presence of a $\mathrm{bmpyrr^+}$ cation.

Anion Component. The data reported in Table 3, analyzed with respect to the anion of the RTILs, show that this seems to be less effective in influencing the activation parameters. However, some comments can be made. Regarding the entropy values, those collected for TEA are less negative than those for BuA and Pip, and this could be a consequence of the absence of a hydrogen atom on the nitrogen, which could induce different types of amine−anion interaction.

A different behavior can be observed for the enthalpy values. In particular, values relative to [$\mathrm{PF_6^-}$] are less favorable. The greater $\Delta H^{\ddagger}$ values in the [$\mathrm{PF_6^-}$] salt may reflect the greater extent of ionic cross-linking possible in RTILs with this anion compared, for example, to [$\mathrm{NTf_2^-}$].[26] Neither significant differences or a definite order were observed between [bmim][$\mathrm{BF_4}$] and [bmim][$\mathrm{NTf_2}$].

Amine Structure. The analysis of activation parameters as a function of amine structure shows that, considering the bmim-based RTILs, the values of $\Delta H^{\ddagger}$ for the tertiary amine are significantly higher than those for the primary and secondary amine. In contrast, the latter are similar between themselves in [bmim][$\mathrm{BF_4}$]; in [bmim][$\mathrm{PF_6}$] and [bmim][$\mathrm{NTf_2}$], the $\Delta H^{\ddagger}$ value for BuA is 5.3 and 4.8 kJ/mol higher than that for Pip.

Similarly, the entropy values for BuA and Pip are quite similar in [bmim][$\mathrm{PF_6}$] and [bmim][$\mathrm{NTf_2}$], the values for the tertiary amine being, in contrast, usually lower.

The above results agree with reactivity data: indeed, they account for the ability of BuA and Pip to give, as the main interaction, that with the anion component of RTILs by means of their hydrogen atoms (see above). This anion−amine interaction involves an associative contribution to the process and leads to a significant decrease in entropy values. In contrast, TEA should act only as a hydrogen bond acceptor versus the cation part. As a consequence of this, the higher enthalpy values account for the need to break this interaction, allowing the action of TEA as a base, giving a dissociative contribution to the process and resulting in a significant increase in entropy values.

In general, the above trend is confirmed going from [bmim][$\mathrm{NTf_2}$] to [$\mathrm{bm_2im}$][$\mathrm{NTf_2}$], but a different and more complex behavior was detected in the [bmpyrr][$\mathrm{NTf_2}$] solution. In fact, in this case, the entropy value calculated for TEA is quite similar to that for BuA but different from that for Pip.

Conclusions

Data collected show that RTILs are very intriguing reaction media. They are able to affect the outcome of a reaction in a way completely different from that normally observed in conventional organic solvents. In particular, in this case, the higher reactivity cannot be ascribed only to the higher polarity of the solvent medium but is rather due to the scarce relevance of solvation effects, as confirmed by comparison among activation parameters collected in these media and in conventional organic solvents. Furthermore, the peculiar structure of the transition state of the studied reaction (cyclic and quasi-aromatic) has allowed us to outline the importance of organized structure and organizing ability of these organic liquid salts in determining the reactivity. For all of the above reasons, RTILs cannot be considered “simple solvents” but should rather be considered as polymeric supramolecular fluids with regions characterized by “different polar character”.[27]

Experimental Section

Materials. Commercial 1,4-dioxane was used without any further purification. Commercial [bmim][$\mathrm{BF_4}$] and [bmim][$\mathrm{PF_6}$] were dried on a vacuum line at 60 °C for at least 2 h and stored in a dryer under argon and over calcium chloride. [bmim][$\mathrm{NTf_2}$],[28] [$\mathrm{bm_2im}$][$\mathrm{NTf_2}$],[28] and [bmpyrr][$\mathrm{NTf_2}$][29] were prepared according to a

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procedure previously reported. Amines were freshly distilled before use. Compound **1** was prepared according to the method reported.[30]

Kinetic Measurements and Calculations. UV−vis spectra and kinetic measurements were carried out by using a spectrophotometer equipped with a Peltier temperature controller, able to keep the temperature constant within 0.1 K.

Kinetic runs were carried out over the temperature range 293−313 K. The sample for a typical kinetic run was prepared by injecting into a quartz cuvette (optical path 0.2 cm) 500 μL of IL, 50 μL of a solution of substrate in 1,4-dioxane, and then 25 μL of a concentrated solution of amine in 1,4-dioxane, previously thermostated. The concentration of substrate was constant and equal to 1.9×10^{-4} M, and the amine concentration ranged from 2.0×10^{-3} to 1.33×10^{-2} M. The reactions were all studied over three half-lives or more. In every case, the correlation coefficient was higher than 0.9998.

To evaluate the possibility of reusing RTILs, we tried a fast and simple treatment of the solvent used. Thus, 5 mL of the used [bmim]-[BF_4] was extracted four times with 3 mL of Et_2O. The RTIL layer was kept under vacuum at 60 °C for 2 h and reused. The apparent first-order rate constants then obtained were reproducible within ±15% with respect to values determined in fresh RTIL. All kinetic data were analyzed by means of the KALEIDAGRAPH 3.0.1 software.

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Supporting Information Available: Rate constants collected at different amine concentrations and at different temperature values. This material is available free of charge via the Internet at http://pubs.acs.org.

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