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Effect of ionic liquid organizing ability and amine structure on the rate and mechanism of base induced elimination of 1,1,1-tribromo-2,2-bis(phenyl-substituted)ethanes

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Abstract—The kinetics of the elimination reaction of 1,1,1-tribromo-2,2-bis(phenyl-substituted)ethanes into the corresponding 1,1-dibromo-2,2-bis(phenyl-substituted)ethenes induced by amines were studied in three room temperature ionic liquids ([BMIM][BF_4], [BMIM][PF_6], [BdMIM][BF_4]). In order to have information about reagent–ionic liquid interactions, the reaction was carried out over the temperature range (293.1–313.1 K). To study the effect of the amine on the rate and occurrence of the elimination reaction, several primary, secondary and tertiary amines with different structure (cyclic and acyclic), basicity and steric requirements were used. The data collected show that the reaction occurs faster in ionic liquids than in other conventional solvents. Furthermore, ionic liquids seem to be able to induce, for the studied reaction, a shift of mechanism from $E1_{cb}$ (in MeOH) versus E2 (in ionic liquid).

1. Introduction

There is growing interest in the utility and application of the room temperature ionic liquids (RTILs). Ionic liquids have been proposed as environmentally benign solvents for their non-detectable vapor pressure, their non-flammability and for easy recyclability.[1] ILs promise several advantages in organic synthesis both making the process more efficient and reducing use of raw materials.[2] Several organic reactions have been performed with success and for some of these the quantitative aspects in ILs have also been much investigated.[3] The ILs, with respect to conventional organic solvents, can provide a very different microenvironment and this can significantly influence the outcome of a reaction. At least two factors must be considered in determining how IL and solute influence one another. The former concerns the fact that ILs are systems having some degree of organization and this could be strongly affected by guest molecules. The latter is related to organizing ability of ILs, these, owing to π–π interactions, can help the substrate to maximize the stabilizing interactions. Therefore, we believed it interesting to investigate kinetically the effect that ILs have on classical organic reactions such as β-elimination. This is one of the most studied reactions in organic chemistry. It is well known that both the electronic and steric properties of β-substituent (generally an aryl-substituted ring) are able to affect the reactivity and, in some cases, the mechanism of base promoted elimination. We chose as substrates the 1,1,1-tribromo-2,2-bis(phenyl-substituted)ethanes (**1**) as the alkoxide-induced β-elimination has been studied by some of us (Fig. 1).[4]

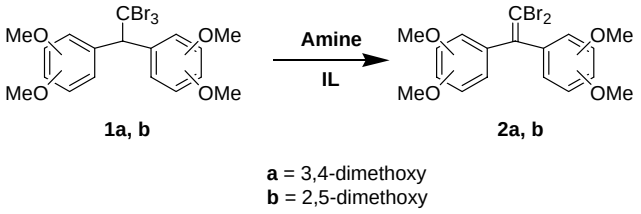

Figure 1.

The data collected allowed us to hypothesize that the reaction of **1** to the corresponding 1,1-dibromo-2,2-bis(phenyl-substituted)ethenes (**2**) occurs through an irreversible $E1_{cb}$ mechanism. The E2 mechanism seemed unlikely. The analyzed substrates differ for steric requirements (**1a**,**b**) of aryl groups. Their reactivity changes drastically with the conformation. This seemed stimulating for quantitative studies because the IL, owing to π–π interactions, could constrain **1** to assume a planar conformation, that should maximize the electronic effects exerted by aromatic rings on the route of reaction. To avoid strong interactions between charged bases, as alkoxide ions,

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and imidazolium cation, we chose to use neutral amine bases. These are, in conventional organic solvents, largely used while, in ILs, they have been less investigated both as nucleophiles and bases. Several primary, secondary and tertiary amines with different structure (cyclic or acyclic), basicity and steric requirements were chosen as base for inducing elimination of **1a**. The pseudo first-order kinetics of amine-promoted elimination reaction were studied following the appearance of **2** spectrophotometrically. The reaction was performed in solution of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) at various concentrations (from 0.008 up to 0.0304 M) of amine over the temperature range (293.1–313.1 K). Several recent studies demonstrated that changes in the nature of cation part or the counterion could bring about notable variations in the reaction mechanism;[5] for this reason the piperidine-promoted elimination reaction was also studied in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and in 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BdMIM][BF_4]). The [BMIM][PF_6] was chosen to investigate the effect of the anion. As a matter of fact, the presumably unlike cation–anion of different size interactions between BMIM and two anions (a larger PF_6^- and a smaller BF_4^-) could in turn affect the interaction between the activated complex and solvent. The [BdMIM][BF_4] was chosen to evaluate the effect of hydrogen bond donor ability of imidazolium cation.

2. Results and discussion

First, we verified that **1a** did not spontaneously give the elimination product **2a** in IL within 10 days (i.e., if a reaction occurs $k_{obs} \approx 10^{-8}\ s^{-1}$). Then, we analyzed the behavior of **1a**, in [BMIM][BF_4], in the presence of amines. The results are reported in Table 1.

Table 1

Amine	pK_{BH^+} in H_2O[a]	nr/er[b]
Primary amines		
Butylamine	10.68	nr
Cyclohexylamine	10.66	nr
Secondary amines		
N-Butyl-*N*-methylamine	[c]	nr
Pyrrolidine	11.27	er
Piperidine	11.12	er
Hexamethyleneimine	10.89	er
Heptamethyleneimine	10.78	er
Morpholine	8.33	nr
2,2,6,6-Tetramethylpiperidine	11.07	nr
Tertiary amines		
Triethylamine	10.75	nr
N-Methylpyrrolidine	10.46	nr
N-Methylpiperidine	10.08	nr

[a] See Ref. 6.
[b] nr=no elimination reaction was detected; er=elimination reaction was detected.
[c] The pK_{BH^+} value should be in the range 10.64 (*N*,*N*-dimethylamine)–11.25 (*N*,*N*-dibutylamine).

As can be seen from Table 1, the primary and tertiary amines, independent of their basicity and alkyl groups structure, were unable to induce the elimination reaction. The secondary amines were more variable. The acyclic *N*-butyl-*N*-methylamine was unreactive as was the highly hindered 2,2,6,6-tetramethylpiperidine and the scarcely basic morpholine (pK_{BH^+}=8.33). We are aware of the fact that the amines basicity, measured in water, could not be adequate to describe the effective strength in IL. Indeed, the occurrence of peculiar interactions IL–amine should determine a different basicity order in IL and water. In this light, dramatically different behaviors can be surely related to deeply unlike IL–amine interactions. Nevertheless, structurally similar amines (i.e., secondary cyclic) should interact with IL in a comparable manner and the aqueous pK_{BH^+} values constitute a good starting point for analyzing the reactivity trend.

For reactive amines a quantitative study was undertaken. To make a comparison with conventional organic solvents, a kinetic measurement of the elimination reaction of **1a** in dioxane (the cosolvent used for reaction in IL solution, see Section 4) in the presence of pyrrolidine (7.5×10^{-3} M) as a model amine was carried out. The elimination reaction was very slow ($k_{obs}<5.5\times10^{-7}\ s^{-1}$). In IL solution, the above reaction was faster and the complete course of the absorbance as a function of the time is shown in Figure 2.

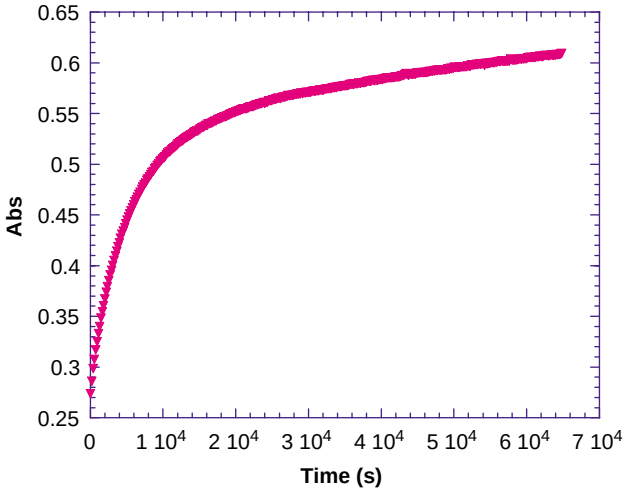

Figure 2. Experimental plot of Abs versus time for the elimination reaction of **1a** in the presence of pyrrolidine (0.0304 M) in [BMIM][BF_4] at 298.1 K and λ=280 nm.

It can be seen that the curve does not show a typical trend of a simple kinetic process. It seems that at least two kinetically relevant steps are responsible for the observed trend. In fact, first- or higher-order kinetic equations do not fit the experimental trace. From a careful analysis of the system we found that the absorbance of the IL–pyrrolidine mixture, for each of studied ILs, changed as function of the time. Furthermore a slow variation in the UV–vis spectrum of IL, induced by some of the used amines, was observed. For example, in Fig. 3, the spectra of IL in the presence of heptamethyleneimine, collected over a time range (48 h), are reported.

Data previously obtained by us seem to exclude that the observed variation could be a consequence of an acid–base equilibrium between the acidic imidazolium ion and the amine. Indeed, in this case, the observed variation of UV–vis spectrum is fast.[7]

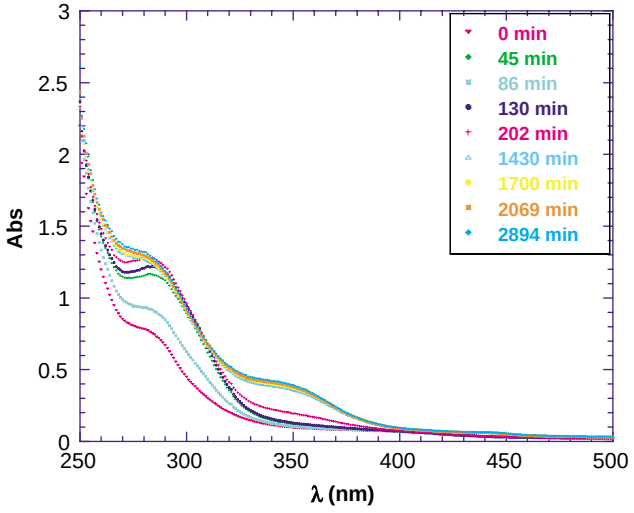

Figure 3. UV–vis spectra of [BMIM][BF_4] in the presence of heptamethyleneimine 0.0304 M collected in 48 h.

The variation in UV–vis spectrum cannot be accounted as well for the occurrence of an amino demethylation of imidazolium cation. Indeed, this reaction occurs with scarce yields to 398 K.[8] To confirm of this, the IL–amine mixture, after some days from mixing, was extracted with diethylether. The extract, analyzed by HPLC and GC–MS, did not show the presence of methylamine or other reaction products.

The IL–amine interaction was also studied by ^{1}H NMR spectroscopy recording the spectra of a mixture IL–heptamethyleneimine during a time range. Firstly, we analyzed the effect of dioxane addition to IL and a significant variation of the NMR spectrum was observed. For example, the signal due to the H-2 proton was split in a couple of signals of different intensity, the more shielded signal had the lesser intensity and was broad. The same splitting, but with opposite relative intensity and shape of signals, was observed for adding of a solution of amine in dioxane (see Fig. 4)

However, as can be observed, every signal is affected by amine solution addition and after 5 min, all the signals result enlarged and lose the multiplicity.

The signals splitting can be easy explained considering that two different ion-pairs are present in the IL–amine mixture.

This hypothesis perfectly agrees with both the formation of ion-pairs in imidazolium-based ionic liquids,[9] and with the observed variations induced by trace amounts of water in the ^{1}H NMR spectrum of [BMIM][BF_4].[10] However, the shape of signals changes slowly in the time. For example, the signals at 7.34 and 7.29 ppm due to H-4 and H-5, respectively, (see Fig. 5 spectrum **A**) change. In fact, in a first time (60 min, see Fig. 5 spectrum **B**) they seem to collapse, later (180 min, see Fig. 5 spectrum **C**) they return as two distinct signals.

The spectrum acquired after 8 days show distinct signals for the heterocyclic hydrogen atoms but broad signals for aliphatic ones (see Fig. 5, spectrum **D**).

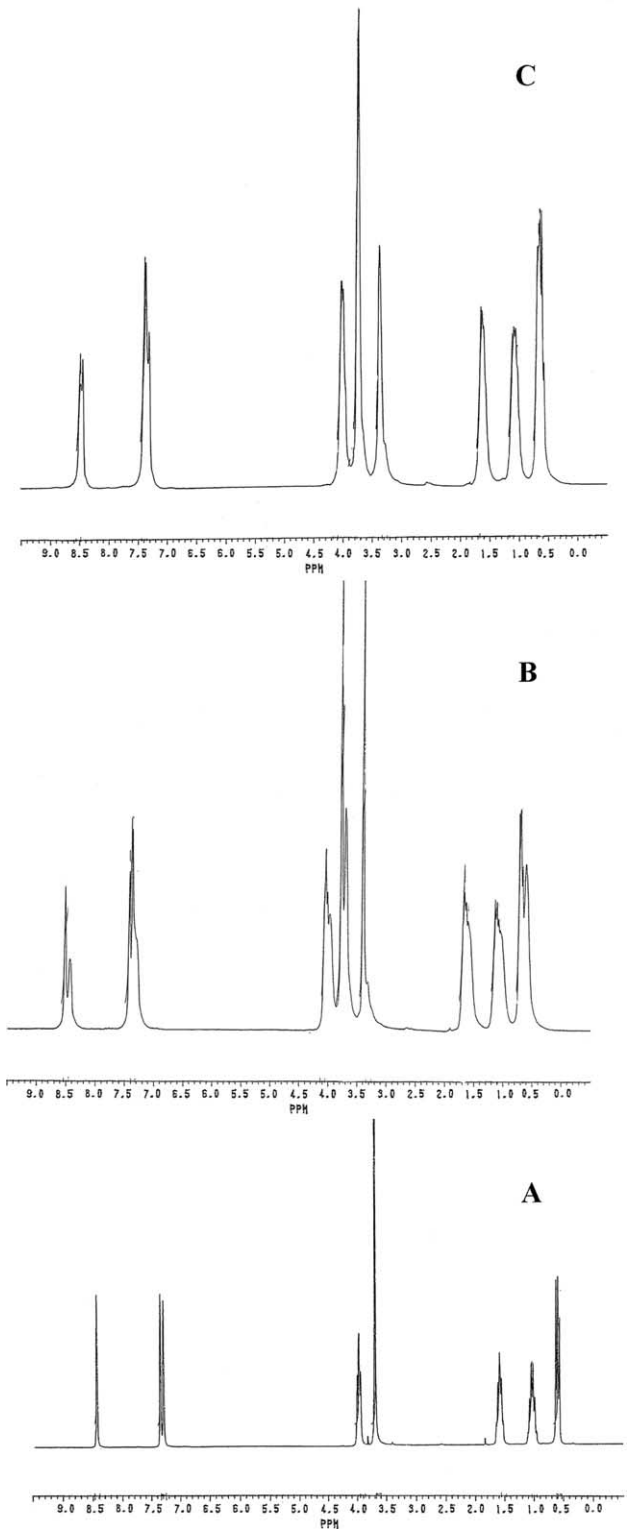

Figure 4. ^{1}H NMR spectra of: (A) neat [BMIM][BF_4]; (B) [BMIM][BF_4] in the presence of 50 μL of 1,4-dioxane; (C) [BMIM][BF_4] in the presence of a dioxane solution of heptamethyleneimine (0.0304 M) at $t=0$ min.

The above picture could be a consequence of a little and slow reorganization of molecules of IL; the different and variable interactions between two imidazolium rings could explain the variation in NMR and UV–vis spectra. To verify if the reorganization process is operative only for

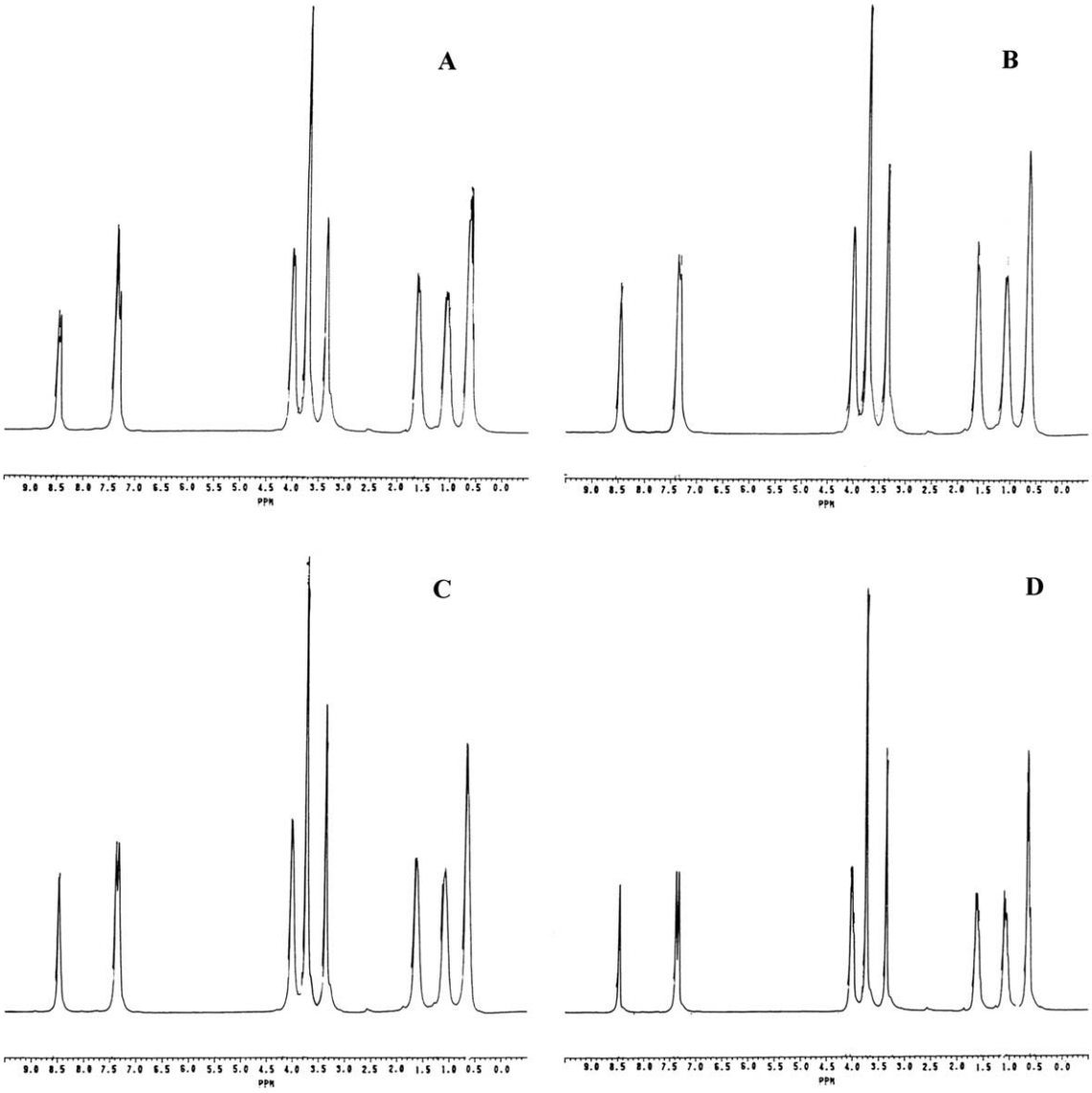

Figure 5. ^{1}H NMR spectra of: (A) [BMIM][BF_4] in the presence of a dioxane solution of heptamethyleneimine (0.0304 M) at $t=0$ min; (B) at $t=1$ h; (C) at $t=3$ h; (D) at $t=8$ days.

amines for which a variation in UV–vis spectrum was observed, we collected NMR spectra of an IL–piperidine mixture in a range of time. A very similar behavior was observed. However, it must be remarked that no signal due to transformation products of IL and amines was detected. Furthermore, the ratios among integrals relative to different signals were constant in the time. It is noteworthy that both variations in UV–vis and ^{1}H NMR spectra can not be related to a deficiency in homogeneity of IL–amine mixtures. Indeed, these were perfectly clear.

2.1. Kinetic data

In order to avoid invalidating the kinetic data by variations in UV–vis spectrum of the IL–amine mixture, the kinetic runs were registered using a sample of IL containing the same amine concentration of the kinetic run as reference. In this manner, excellent pseudo first-order curves were obtained (Fig. 6).

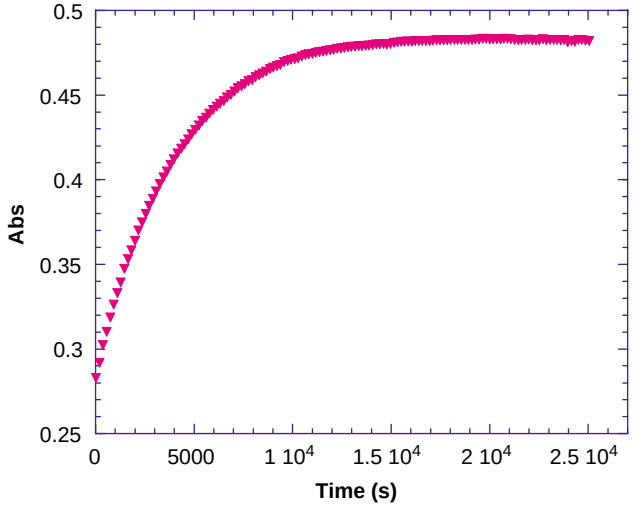

Figure 6. Experimental plot of Abs versus time for the elimination reaction of **1a** in the presence of pyrrolidine (0.0304 M) in [BMIM][BF_4] at 298.1 K and $\lambda=280$ nm recorded by using the [BMIM][BF_4]–amine mixture as reference.

To verify that the effect of the IL–amine mixture on the studied reaction was not a function of IL reorganization time, a kinetic run was carried out adding the substrate solution to an equilibrate (after 3 h from mixing) of IL–amine mixture. The observed kinetic constant was equal to that collected with a typical methodology (see Section 4).

The kinetic data for the elimination reaction of **1a** to **2a** induced by different IL–amine mixtures are reported in Table 2 (data collected at different amine concentration are available in Supplementary data: Table 4).

The secondary cyclic amines namely pyrrolidine, piperidine, hexamethyleneimine and heptamethyleneimine (five, six, seven and eight membered rings, respectively) were able to induce the elimination reaction. Similar results were previously reported by Yadav et al.[11] The geometry of amine seems to be one of the determinant factors for their reactivity. Indeed, for example, the opposite behavior of butylamine (unable to induce the elimination in **1a**) and heptamethyleneimine, bases with comparable pK_{BH^+} values (10.68 and 10.78, respectively), could be attributed to their different conformational freedom. This, higher for the butylamine than for the hexamethyleneimine, should disturb the ionic liquid organization with the consequent loss of its activating effect. However, for amines having comparable geometry and flexibility, large differences in basicity, as for piperidine and morpholine ($pK_{BH^+}=11.12$ and 8.33, respectively) are, of course, responsible of the unlike behavior. Also, the steric hindrance can change the reactivity as in the case of piperidine and 2,2,6,6-tetramethylpiperidine that have barely different basicity ($pK_{BH^+}=11.12$ and 11.07, respectively), the same geometry and flexibility but very different reactivity.

The above data show that the elimination reaction, in IL solution, is very sensitive to the amine structure (i.e., flexibility and steric hindrance). In contrast, the base strength plays a minor part. Then, it is possible to think, on the grounds of literature reports,[12] that the mechanism proceeding by an $E1_{cb}$ (in MeOH)[4] will be moved in the E2 direction in IL solution. Indeed, the E2 mechanism involving a highly crowded activated complex should be more affected than the $E1_{cb}$ mechanism by steric effects. Changes in reaction mechanism going from conventional organic solvents to IL are well documented. For example, in a nucleophilic displacement reaction, a change in mechanism was proposed on the grounds of a different nucleophilicity order observed going from conventional solvents to IL.[13]

For reactive amines, an excellent linear dependence of k_{obs} (collected values are reported in Supplementary data: Table 4) on amine concentration was found according to Eq. 1.

$$k_{obs} = a + (k_{II})_{amine}[Amine] \quad (1)$$

Significant 'negative' intercept values were calculated for [BMIM][BF_4]. They were related to an acid–base interaction between the acidic imidazolium ion and the amine as previously reported.[7]

The k_{II} values show that reactivity of **1a** decreases on going from pyrrolidine to piperidine to hexamethyleneimine to heptamethyleneimine in the order 22.7:3.1:2.7:1. The ability of amines to induce the elimination seems to be a function of their flexibility (i.e., higher flexibility, lower reactivity), due to the ring dimension, rather than of nitrogen basicity. Indeed, this changes in the order 3.1:2.2:1.3:1 on going from pyrrolidine to piperidine to heptamethyleneimine.

It is noteworthy that pyrrolidine induced elimination of **1a** ($k_{II}=9.16\times10^{-3}\ M^{-1}\ s^{-1}$) is faster than the methoxide/methanol reaction ($k_{II}=8.3\times10^{-3}\ M^{-1}\ s^{-1}$) despite the difference in basicity between the two considered bases, and that [BMIM][BF_4] and methanol have comparable polarity. Indeed, the E_{NR} values for [BMIM][BF_4] and methanol are 217.2 and 217.7, respectively.[14] This is surely indicative that the IL has an activating effect on the reaction that only the polarity is not able to explain. Probably, this effect could be a consequence both of the electrostatic interactions (bromine–imidazolium ion) and π–π interactions. The positive effect of electrostatic interactions can be explained by the E2 mechanism where an assistance to bromine departure by IL cation owing to its donor hydrogen bond ability is important. Also, Chiappe et al. studying the bromination of alkynes in ILs, accounted the possibility that

Table 2. Calculated second order rate constants and third order rate constants at 298.1 K for the elimination reaction of **1a** and **1b**, in ionic liquids solution, in the presence of amines[a,b]

IL	Substrate	Amine	k_{II} ($M^{-1}\ s^{-1}$)	k_{III} ($M^{-2}\ s^{-1}$)	i	n	R
[BMIM][BF_4]	**1a**	Pyrrolidine	0.00916 (0.00038)		-4.88×10^{-5} (8.48×10^{-6})	7	0.996
		Piperidine	0.00124 (0.00010)		-3.33×10^{-6} (2.28×10^{-6})	7	0.983
		Hexamethyleneimine	0.00109 (2.20×10^{-5})		-5.21×10^{-6} (4.87×10^{-7})	7	0.999
		Heptamethyleneimine	0.000404 (2.71×10^{-5})		1.42×10^{-6} (6.00×10^{-7})	7	0.989
[BMIM][PF_6]	**1a**	Piperidine	0.000851 (1.65×10^{-5})		2.21×10^{-6} (3.54×10^{-7})	7	0.999
[BdMIM][BF_4]	**1a**	Piperidine		0.0633 (0.014)		6	0.996
[BMIM][BF_4]	**1b**	Piperidine	0.000372 (3.02×10^{-5})		-1.11×10^{-6} (6.31×10^{-7})	7	0.987

[a] The values of k_{obs}, from which the k^{II} and k_{III} values were obtained, were reproducible within ±3%.
[b] Standard deviations are given in parenthesis.

the imidazolium cation could assist the bromine–bromine bond breaking, in the 1:1 π complex, to give a bromirenium bromide intermediate.[15] On the other hand, π–π interactions are able to increase the coplanarity between aromatic rings then favoring the conjugation and stabilizing the transition state. The relevance of π–π interactions in IL media has been previously reported by Atwood et al. according to the hypothesis that the high solubility of aromatic compounds in ILs could be related to some kind of clathrate formation.[16]

It is noteworthy that the imidazolium cation acidity, as well as, its hydrogen bond ability could negatively affect the reaction owing to a decrease in free amine concentration. However, the data collected show that the activating assistance to bromine departure seems to be predominant.

In order to study the effect of a different structure of IL cation or anion, the piperidine induced elimination of **1a** was also carried out in [BMIM][PF_6] and in [BdMIM][BF_4].

The reaction was faster (1.45 times) in [BMIM][BF_4] than in [BMIM][PF_6]. A similar reactivity trend in these ionic liquids was recently observed. Chi attributed this trend to a lower solubility of nucleophile in hexafluorophosphate than in tetrafluoroborate.[17] Welton claimed that changing the anion affected the halide nucleophilicity.[18] Recently we, studying an heterocyclic rearrangement, explained the higher reactivity in [BMIM][BF_4] than in [BMIM][PF_6], as a consequence of a different 'packing' of two ionic liquids. This determines a different catalytic effect.[7] Probably the same explanation could be used for the data reported herein, as the present elimination reaction seems more influenced by steric or stereoelectronic factors rather than by basicity of amines.

A more interesting behavior was found in [BdMIM][BF_4] solution; in fact, in this case the observed kinetic rate constant shows a dependence on second order amine concentration, that is, $k_{obs}=(k_{III})_{amine}$[Amine].[2] The observed trend could be a further support to the occurrence of the E2 mechanism. Indeed, the lesser donor hydrogen bond ability of the [BdMIM][BF_4] that hampers the assistance to bromine departure, causes the intervention of a second amine molecule to favor product formation. The effect of imidazolium cation in BMIM and BdMIM due to different hydrogen bond donor ability is well documented. Welton et al. reported a decrease in nucleophilicity of chloride anion, going from BdMIM to BMIM, owing to its stabilization via hydrogen bonding.[19] Also the *endo*-selectivity for Diels–Alder reaction between methyl acrylate and cyclopentadiene, in IL, was influenced by hydrogen bond ability of the cations.[20] At last, conversions and reaction rates of Tsuji–Trost allylic substitution, in BMIM and BdMIM, were explained considering the different nature of cations used.[21]

Previously, it was reported that the elimination of 1,1,1-trihalo-2,2-bis(phenyl-substituted)ethanes was affected by steric effects. In fact, the *ortho*-substituted derivatives were found to be less reactive than the corresponding unsubstituted derivatives as a consequence of the hindrance to conjugation between aromatic ring and π-electrons of the forming double bond.[4b] As ionic liquids are organizing media, we verified if they were able to decrease the entity of steric effects. So we carried out the piperidine induced elimination of **1b** in [BMIM][BF_4]. Effectively, the kinetic results show that the **1b** reactivity in IL is less affected by steric effects and prevalently determined by electronic effects. In fact, the reactivity ratio $(k_{II})_{1a}/(k_{II})_{1b}$ is only 3.3 in IL compared to 600 calculated for methanol solution;[22] this high value was attributed to the fact that steric effects were, in determining the different reactivities, more important than electronic ones. Indeed, the latter should equally act in both substrates. So the result obtained for reaction of **1b** in IL–piperidine mixture can be interpreted as due to a decrease in steric effects. The IL, by means of π–π interactions, constrains the aryl rings in **1b** to a coplanar conformation despite the *ortho*-methoxy groups.

2.2. Activation parameters

It is well known that, for kinetics carried out in ILs, in some cases, a significant curvature in Arrhenius or Eyring plots can be observed as a consequence of structural changes in the solvent.[23] So for a careful analysis of the temperature effect, the elimination reaction was carried out at five temperatures going from 293.1 K up to 313.1 K. For each amine and IL, an excellent linear correlation of log (k_{obs}/T) versus $1/T$ was obtained. This indicates that, in the analyzed range, the above upsetting effect is not operative. So the calculated activation parameters are only dependent on the elimination process. The activation parameter values are reported in Table 3, for an useful comparison the values for methoxide/methanol induced elimination are also reported (data collected at different temperatures are available in Supplementary data: Table 5).

The enthalpy values range from 47.4 kJ/mol up to 64.7 kJ/mol, whereas the entropy values range from −180 J/K mol up to −119 J/K mol. The collected values show that, with respect

Table 3. Activation parameters for the elimination reaction of **1a** and **1b**, in ionic liquids solution, in the presence of amines[a]

IL	Substrate	Base	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (kJ/mol)
MeOH	**1a**	MeO^-	71.9[b]	−72[b]
[BMIM][BF_4]	**1a**	Pyrrolidine	54.9 (3.2)	−135 (10)
		Piperidine	47.4 (2.2)	−180 (7)
		Hexamethyleneimine	59.0 (2.8)	−138 (9)
		Heptamethyleneimine	52.1 (4.9)	−165 (16)
[BMIM][PF_6]	**1a**	Piperidine	60.5 (2.4)	−132 (8)
[BdMIM][BF_4]	**1a**	Piperidine	64.7 (4.6)	−119 (15)
[BMIM][BF_4]	**1b**	Piperidine	36.7 (2.8)	−220 (9)

[a] Standard deviations are given in parenthesis.
[b] See Ref.4a.

to that induced by methoxide, the elimination induced by amines is enthalpy favored but entropy disfavored. These differences could be due to the fact that in methanol, compared to the IL, stronger interactions and more extensive solvation of initial state with respect to the transition state are operative. This causes a larger enthalpic contribution but a less unfavorable entropic one.

In IL, the particularly unfavorable entropic contribution is according to both the E2 mechanism and not relevant differences in solvation between initial state and transition state.

The activation parameter values trend for elimination induced by piperidine in [BMIM][BF_4], [BdMIM][BF_4] and [BMIM][PF_6] can be explained considering that different cation–anion interactions are operative. Welton claimed that a charge-separated activated complex from neutral starting materials can induce a disruption of the ionic liquid structure leading to a less negative entropy value.[24] The main contributions to this effect could be due to the degree of cation–anion interaction and to hydrogen-bond acceptor and donor ability of ionic liquid. It is noteworthy that the outcome of the reaction depends on the balance of the above factors that can also act in opposite directions.

In the studied reaction the above effects could be a consequence of the interaction between the anion and the ammonium acid proton in the activated complex. A careful analysis of entropy values seems to indicate that only the β solvent parameter is unable to explain the observed trend. The [BMIM][BF_4] having the higher β value shows the more negative $\Delta S^{\neq}$ value. Thus the strong interaction cation–anion should be responsible of the scarce disruption of ionic liquid structure. This can only be a partial explanation, as [BdMIM][BF_4], having similar β value, shows a less negative entropy value. Furthermore, [BMIM][PF_6] having the lowest β value shows an intermediate entropy value. Also the other solvent parameters do not explain the variation of activation parameters as a function of IL. This could be a consequence of the fact that the solvent parameters for ILs are probably inadequate. Indeed, it is well known that it is questionable whether the empirically derived measurements of solvent properties could be exclusively referred to room temperature ionic liquids or whether they are also affected by the nature of the tested compounds.[25] However, the entropy increase, going from an IL to another, could be attributed to an easier disruption of ionic liquid structure owing to weaker electrostatic interactions between cation–anion pairs, according to that previously reported by Welton et al.[17]

The above discussion is also supported by enthalpy values, that are higher for [BMIM][PF_6] and [BdMIM][BF_4] than [BMIM][BF_4].

Activation parameter values for **1b** show that the piperidine induced elimination is enthalpy but not entropy favored with respect to **1a**. The decrease in enthalpy could be related to a gain in energy due to an increase, going from initial state to transition state, in conjugation between the aromatic rings and π-electrons of the forming double bond, which favors the reaction of **1b**.

The same factor could cause the highly negative entropic contribution as a forcedly ordered activated complex, entropically hampered, is needed.

3. Conclusions

The data collected herein confirm the idea that ionic liquids represent an intriguing solvent system that can not be only described by means of the usual solvent parameters. Indeed, most of the obtained results seem to be a consequence of the order as well as the organizing ability of these systems. For example, the addition of a small quantity of amine solution induces a reorganization of ionic liquid structure as detected by NMR experiments. In addition, the structure rather than amine basicity determines the occurrence of the reaction. This seems to indicate that ionic liquids induce, for the studied reaction, a shift of mechanism from $E1_{cb}$ (in MeOH) versus E2 (in ionic liquid). However, it is probable that in ionic liquid deep changes in amine structure could correspond to significant variations in amine basicity, so the observed reactivity could reflect the basicity in ionic liquids. Unfortunately the lack of basicity data in ionic liquid does not allow to verify this hypothesis. The activating effect of ionic liquid on elimination of **1a** could be a consequence both of the electrostatic interactions (bromine–imidazolium ion) and π–π interactions.

The data collected show that the reaction rate is influenced by dimension and charge distribution in ionic liquid anion as well as by the hydrogen bond ability of cation that could assist the bromine departure. Finally, in the case of **1b**, the organizing ability of ionic liquids is able to minimize the unfavorable steric effects, operative in conventional organic solvents.

4. Experimental

4.1. Materials

1,1,1-Tribromo-2,2-bis(3,4-dimethoxyphenyl)ethane (**1a**) and the corresponding 1,1-dibromo-2,2-bis(3,4-dimethoxyphenyl)ethene (**2a**) were prepared according to a procedure reported.[26]

4.1.1. 1,1,1-Tribromo-2,2-bis(2,5-dimethoxyphenyl)-ethane (1b). To a stirred solution of 1,4-dimethoxybenzene (4.25 g, 0.03 mol) and bromal (1.68 g, 0.006 mol) in glacial acetic acid (20 mL), 98% sulfuric acid (7.5 mL) was added dropwise, while the temperature was maintained below 30 °C. After standing at room temperature overnight, the mixture was poured on to crushed ice and the precipitate was filtered, neutralized and dried. The product was purified by chromatography over silica gel employing a mixture of light petroleum–ethyl acetate (10/1) and crystallized from ethanol (yield 1.93 g). White crystals, mp: 118–120 °C.

IR (Nujol) ν_{max} 1059, 1284 cm^{-1}. ^1H NMR δ_H (250 MHz; $CDCl_3$): 3.76 (s, 6H, 2OCH_3); 3.83 (s, 6H, 2OCH_3); 5.40 (s, 1H); 6.70–6.83 (m, 4H, Ar); 7.10 (d, 2H, J=2.7 Hz, Ar); ^{13}C NMR δ_C (250 MHz; $CDCl_3$): 48.3; 52.9; 55.6; 56.2; 112.1; 112.3; 115.9; 130.3; 151.3; 153.3. Anal. Calcd for

$C_{18}H_{19}Br_3O_4$: C, 40.10; H, 3.55; Br, 44.47%. Found: C, 40.15; H, 3.48; Br, 44.70%.

4.1.2. 1,1-Dibromo-2,2-bis(2,5-dimethoxyphenyl)ethene (2b). 1,1,1-Tribromo-2,2-bis(2,5-dimethoxyphenyl)ethane (2.14 g, 0.004 mol) (**1b**) was dehydrobrominated by heating under reflux with a solution of CH_3ONa (0.43 g, 0.008 mol) in dry CH_3OH (10 mL). The crude dehydrohalogenated was purified by chromathography over silica gel employing a mixture of light petroleum–ethyl acetate (15/1) and crystallized from ethanol (yield 1.0 g). White crystals, mp: 115–116 °C.

IR (Nujol) ν_{max} 1053, 1309, 1583 cm^{-1}. ^1H NMR δ_H (250 MHz; $CDCl_3$): 3.72 (s, 6H, 2OC*H*$_3$); 3.77 (s, 6H, 2OC*H*$_3$); 6.77–6.87 (m, 4H); 7.05 (s, 2H); ^{13}C NMR δ_C (250 MHz; $CDCl_3$): 55.7; 56.5; 112.7; 112.9; 116.7; 130.1; 140.3; 151.3; 153.4. Anal. Calcd for $C_{18}H_{18}Br_2O_4$: C, 47.19; H, 3.96; Br, 34.88%. Found: C, 47.40; H, 3.85; Br, 34.79%.

All other products were commercial. [BMIM][BF_4], [BdMIM][BF_4] and [BMIM][PF_6] were purchased from Solvent innovation, were dried on a vacuum line at 60 °C at least for 2 h and stored in a dryer under argon and over calcium chloride. 1,4-Dioxane (for fluorescence) was purchased from Fluka and was used without further purification. Amines (Aldrich) were freshly distilled before use. UV–vis spectra and kinetic measurements were carried out by using a Beckman DU 800 spectrophotometer equipped with a peltier temperature controller, able to keep the temperature within 0.1 K. NMR spectra were collected on a Bruker AC-E Series 250 spectrometer.

4.2. Measurements and calculations

In NMR measurements 500 μL of IL were added to a 5 mm NMR tube, under argon. 75 μL of 1,4-dioxane or 75 μL of amine solution were added to IL, by a syringe. A stem coaxial capillary tube, loaded with DMSO-d_6, was inserted into the 5 mm NMR tube and this solvent was used as external lock.

All UV–vis spectra of IL–amine solutions were recorded against air.

Kinetic runs were carried out over the temperature range 293.1–313.1 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 **1** in 1,4-dioxane, and then 25 μL of a concentrated solution of amine in 1,4-dioxane, previously thermostated. The concentration of **1** was constant and equal to 0.00019 M, and the amine concentration ranging from 0.008 up to 0.0304 M. To avoid that the reorganization process of IL, induced by amine solution, affected the kinetic run, all measurements were carried out by using as reference a sample prepared injecting into a quarz cuvette 500 μL of IL, 50 μL of 1,4-dioxane and then 25 μL of a concentrated solution of amine in 1,4-dioxane. In this manner, the net absorbance at $\lambda=280$ nm for **1a** and at $\lambda=270$ nm for **1b** was plotted versus time and showed a simple exponential dependence. The reactions were all studied over 6 half-lives or more. In all cases the correlation coefficient was higher than 0.9998.

To evaluate the possibility of reusing ILs, 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 IL 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 IL.

All kinetic data were analyzed by means of the KALEIDAGRAPH 3.0.1 software.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.11.061.

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