Kinetic Study of the Addition of Trihalides to Unsaturated Compounds in Ionic Liquids. Evidence of a Remarkable Solvent Effect in the Reaction of ICl_2^-

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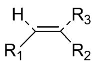
The kinetic constants and activation parameters for the reactions of Br_3^- and ICl_2^- with some alkenes and alkynes have been determined in the ionic liquids [bmim][PF_6], [emim][Tf_2N], [bmim][Tf_2N], [hmim][TF_2N], [bm_2im][Tf_2N], and [bpy][TF_2N] (where emim = 1-ethyl-3-methylimidazolium, bmim = 1-butyl-3-methylimidazolium, hmim = 1-hexyl-3-methylimidazolium, bm_2im = 1-butyl-2,3-dimethylimidazolium, bpy = butylpyridinium, PF_6 = hexafluorophosphate, and Tf_2N = bis(trifluoromethylsulfonyl)imide) and in 1,2-dichloroethane. The rates of both reactions increase on going from 1,2-dichloroethane to ILs. Evidence suggests that, while the hydrogen bonding ability of the imidazolium cation is probably the main factor able to increase the rate of the addition of ICl_2^- to double and triple bonds, this property has no effect on the electrophilic addition of Br_3^- to alkenes and alkynes. Furthermore, in the case of the ICl_2^- reaction, the hydrogen bonding ability of ILs can be exploited to suppress the unwanted nucleophilic substitution reaction on the products by the Cl^- anion.

Introduction

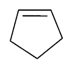
Recently, room-temperature ionic liquids (ILs) have gained a great deal of attention due to their excellent electrochemical properties, as well as their promise as new green reaction media in organic synthesis.[1] Because of the potential importance of ILs as solvents for various industrial processes, we have begun a systematic study of their effects on rate constants of some representative elementary reactions occurring through ionic intermediates, including electrophilic additions to double and triple bonds,[2] aliphatic nucleophilic substitutions,[3] aromatic electrophilic substitutions.[4]

In the present study, we examine the effect of some widely employed ionic liquids on the kinetic behavior of the addition of Br_3^- and ICl_2^- to alkenes and alkynes. The electrophilic properties of Br_3^- have been studied extensively in chlorinated solvents,[5] where this species is generally produced by reaction of Br_2 with a tetraalkylammonium bromide. At variance, only few data about the use of ICl_2^- as an electrophile have been reported[6] also in molecular solvents. Recently, we have shown[2c] that trihalide ILs can be generated by addition of a proper halogen (Br_2 or ICl) to an imidazolium halide and that they can be used as reagent−solvents for the stereospecific halogenation of double and triple bonds in ILs. The addition of both trihalides to alkenes and alkynes proceeds with complete anti stereoselectivity, while the regioselectivity, observable in the case of the ICl_2^- addition, depends on the alkene or alkyne structure.[2] Aryl-substituted double or triple bonds give exclusively the Markovnikov adducts, while alkyl-substituted alkenes give mixtures of Markovnikov or anti-Markovnikov adducts, the percentage depending on the relative steric hindrance of the substituents.[2c]

Herein, we report the kinetic constants and the activation parameters for the reactions of Br_3^- and ICl_2^- with some alkenes and alkynes (compounds **1**−**3**) in six different ILs and in a typical molecular solvent for these reactions, 1,2-dichloroethane (DCE).



1a-e



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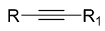

3a-b

a: R_1 = n-C_3H_7, R_2 = H, R_3 = H
b: R_1 = Ph, R_2 = H, R_3 = H;
c: R_1 = Ph, R_2 = H, R_3 = COOEt
d: R_1 = C_2H_5, R_2 = H, R_3 = CH_3
e: R_1 = C_2H_5, R_2 = CH_3, R_3 =H

a: R = Ph, R_1 = H;
b: R = Ph, R_1 = CH_3

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TABLE 1. Second-Order Rate Constants for the Reaction of Br_3^- with Alkenes and Alkynes in Ionic Liquids and DCE at 25 °C[a]

solvent	**1a** $k_{Br_3^-}$ (M^{-1} s^{-1})	**1b** $k_{Br_3^-}$ (M^{-1} s^{-1})	**1c** $k_{Br_3^-}$ (M^{-1} s^{-1})	**3a** $k_{Br_3^-}$ (M^{-1} s^{-1})	**3b** $k_{Br_3^-}$ (M^{-1} s^{-1})
[bmim][PF_6]	3.4×10^{-2}	6.7×10^{-2}	2.7×10^{-4}	9.3×10^{-4}	1.8×10^{-3}
[emim][TF_2N]	1.2×10^{-1}	nd[b]	5.4×10^{-4}	9.5×10^{-4}	3.2×10^{-3}
[bmim][TF_2N]	1.5×10^{-1}	1.2×10^{-1}	1.9×10^{-4}	6.4×10^{-4}	2.8×10^{-4}
[hmim][TF_2N]	8.4×10^{-2}	7.6×10^{-2}	1.3×10^{-4}	4.3×10^{-4}	1.5×10^{-4}
[bm_2im][TF_2N]	4.2×10^{-2}	4.1 a 10^{-2}	1.2×10^{-4}	2.7×10^{-4}	1.3×10^{-4}
DCE	nd[b]	nd[b]	1.8×10^{-5}	5.6×10^{-5}	2.6×10^{-4}

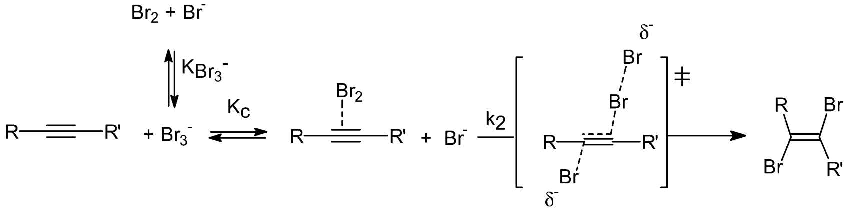
[a] Standard deviations in the values of $k_{Br_3^-}$ were always less than 5% and more usually between 2 and 3% of the quoted values. [b] Too fast to be measured using a UV−vis spectrophotometer. nd = not determined.

TABLE 2. Apparent Activation Parameters for the Reaction of Br_3^- with 1c and 3a[a]

		$k_{Br_3^-}$ (298 K) (M^{-1} s^{-1})	$E_{a,obsd}$ (kJ mol^{-1})	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J K^{-1} mol^{-1})
1c	DCE	1.8×10^{-5}	69.6 (4)	67.1 (4)	−111 (2)
	[bmim][Tf_2N]	1.9×10^{-4}	68.2 (4)	65.7 (4)	−95 (2)
	[bpy][Tf_2N]	6.2×10^{-4}	56.1 (4)	53.6 (4)	−127 (4)
3a	DCE	5.6×10^{-5}	67.8 (4)	65.3 (4)	−104 (2)
	[bmim][PF_6]	9.3×10^{-4}	57.8 (3)	55.3 (3)	−118 (3)
	[emim][TF_2N]	9.5×10^{-4}	55.7 (4)	53.2 (4)	−124 (2)
	[bmim][TF_2N]	6.4×10^{-4}	60.5 (4)	58.0 (4)	−113 (2)
	[bm_2im][TF_2N]	2.7×10^{-4}	61.7 (4)	59.2 (4)	−116 (2)

[a] Standard deviations are given in parentheses.

SCHEME 1



The different kinetic behavior characterizing the two addition reactions is discussed considering a different charge development in the two transition states.

Results and Discussion

Bromination Rates. The kinetic constants for bromination of several alkenes and alkynes, 1-pentene (**1a**), styrene (**1b**), ethyl *trans*-cinnamate (**1c**), 1-phenylacetylene (**3a**), and phenylpropyne (**3b**), using [bmim][Br_3^-] as a halogenating agent, were determined in six ionic liquids, [bmim][PF_6], [emim][Tf_2N], [bmim][Tf_2N], [hmim]-[TF_2N], [bm_2im][Tf_2N], and [bpy][TF_2N] (where emim = 1-ethyl-3-methylimidazolium, bmim = 1-butyl-3-methylimidazolium, hmim = 1-hexyl-3-methylimidazolium, bm_2im = 1-butyl-2,3-dimethylimidazolium, bpy = butylpyridinium, PF_6 = hexafluorophosphate, and Tf_2N = bis(trifluoromethylsulfonyl)imide). In all examined ILs, the reaction gave the corresponding dibromo adducts arising from an anti stereospecific addition process.

The reaction rates were measured spectrophotometrically, under pseudo-first-order conditions (in the presence of a large excess of alkyne or alkene), by monitoring the disappearance of Br_3^-. All reactions obeyed the second-order rate law of eq 1

$$-d[Br_3^-]/dt = k_{Br_3^-}[Br_3^-][S] \qquad (1)$$

where [S] is the substrate (alkene or alkyne) concentration. The $k_{Br_3^-}$ values at 25 °C are reported in Table 1. The rate constants for bromination of substrates **1c**, **3a**, and **3b** with tetrabutylammonium tribromide ([Bu_4N]-[Br_3]) in DCE are also reported in Table 1.

All the reactions were followed for at least two half-lives. It is immediately evident that the reactions in ILs are slightly accelerated (5−30 times) in comparison to the molecular solvent (DCE) and that the values of kinetic constants depend on the IL structure. In Table 2 are reported the activation parameters related to the reaction of alkene **1c** and alkyne **3a**.

Kinetic and product distribution data[2] suggest a very similar mechanism for the reaction in ILs and in the molecular solvent.

In chlorinated solvents (DCE, chloroform, dichloromethane) it has been shown[5,7] that the addition of Br_3^- to alkenes and alkynes takes place through a concerted mechanism, reported in Scheme 1. The process involves as a first step an equilibrium between two complexes of bromine, that bearing to Br_3^- and that giving the 1:1 alkyne−Br_2 π-complex ($K_{\pi-complex}$). The equilibrium constant K_C is given by the ratio of the formation constants of the two species; $K_C = K_{\pi-complex}/K_{Br_3^-}$. The product- and the rate-determining nucleophilic attack of the bromide ion on the initially formed alkene− or alkyne−Br_2 π-complex gives directly the anti addition product. Practically no intermediate is formed in this reaction; the bond-making and bond-breaking steps are indeed con-

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certed, although not necessarily simultaneous. Almost pentacoordinated carbon atoms characterize the charge-diffuse rate-determining transition state.

This mechanism is completely different from that characterizing the addition of Br_2 to alkenes and alkynes in chlorinated solvents, which occurs through the formation of an ionic intermediate, a bromiranium (or bromirenium), or β-bromocarbenium tribromide ion pair.[5,7] Although Br_2 is a much better electrophile than Br_3^-, due to the high formation constant of the tribromide ion in chlorinated solvents,[5,7] the addition of free Br_2 is not able to compete with the addition of Br_3^-. Also in ILs the charge-diffuse Br_3^- anion is much more stable than the Br^- species;[8] practically no free bromine is present in solution,[2c] and Br_3^- is the sole electrophile both in DCE and ILs.[2c] In DCE, an aprotic solvent of medium polarity, the electrophile (Br_3^-) and the nucleophilic species (the formed Br^- anion or the same Br_3^- anion) are surely present in solution as ion pairs with the tetrabutylammonium cation. Since the activation parameters in ILs are very similar to the parameters characterizing the reaction of $[Bu_4N][Br_3]$ in DCE, much like in the ionic media the anions are coordinated by one or more cations of the ionic liquid, forming species very similar to ion pairs. The presence of ion pairs in ILs has been proposed[9] also by Welton and co-worker on the basis of the kinetic behavior of nucleophilic substitution reactions in some ILs and dichloromethane.

Although we propose the same mechanism in the two media (ionic and molecular), it is evident from the data reported in Table 1 that the reactions in ILs are generally faster that in DCE, showing that ILs are able to affect the stability of reactants and/or transition state, probably the latter being more important.

In a previous study on bromination of alkynes (including **3a** and **3b**) in [bmim][Br], a very viscous IL, we have proposed[2b] the hypothesis that the viscosity of the reaction medium might affect the rate of Br_3^- addition. Particularly, viscosity seemed[2b] to increase the kinetic constant when, as in the case of alkyne **3a** ($k_{Br_3^-} = 1.25 \times 10^{-3}$ $M^{-1}s^{-1}$), the substrate structure favored an earlier transition state, in which bond making is favored with respect to bond breaking. Since the viscosity of the ionic liquids used in this work has been recently determined,[10] we first checked if, also under the new conditions, the viscosity played a main role in the bromination of **3a**. At 25 °C, the order of increasing viscosity is $[emim][Tf_2N] < [bmim][Tf_2N] \cong [bpy][Tf_2N] < [hmim][Tf_2N] < [bm_2im][Tf_2N] < [bmim][PF_6] \ll [bmim][Br]$. The data reported in Table 1 for alkyne **3a** clearly show that the reaction rates do not depend on the viscosity of the ionic liquid alone. A trend may be found only considering a more homogeneous class of ILs, $[emim][Tf_2N] < [bmim][Tf_2N] < [hmim][Tf_2N]$, although in this case the reaction rates increase as the solvent viscosities decrease. Actually, the viscosity can have opposite effects on the reaction rate; indeed it favors bond making but disfavors bond breaking.[11] In a reaction of the type of Br_3^- addition, in which both bond making and bond breaking occur in the transition state, the effect of the viscosity depends on the position of the transition state. At variance with the situation characterizing the addition in all the other ILs, in [bmim][Br] the reaction occurs in the presence of a large excess of Br^-. This anion is probably the true nucleophile of the addition process, and its presence in a large excess may affect the position of the transition state; bond making may prevail over bond breaking. Viscosity can in this case enhance the reaction rate. At variance, in all the other ILs a later transition state is more probable and the effect of the viscosity decreases, becoming the opposite if the bond breaking is more advanced with respect to the bond making.

The values of the kinetic constants and activation parameters, which are really apparent activation parameters being $k_{Br_3^-}$ the product of two constants (K_C and k_2), cannot give direct information about the properties of ILs. Anyway, the comparison with the values related to the reaction in molecular solvents may be useful for increasing the knowledge of these new reaction media.

In chlorinated solvents, the reaction rate increases on going from more polar DCE to less polar chlorinated solvents, in agreement with the formation of a transition state having more charge delocalization than the reactants. Furthermore, reaction rate is positively affected by the ability of the solvent (for example, chloroform) to give hydrogen bonding.[5] In particular, it was suggested[5] that the electrophilic solvatation by hydrogen bonding to the leaving bromide ion is the main factor affecting reactivity when the reaction is carried out in chloroform. Using solvatochromic dyes and partition methods, Welton et al. have shown that the examined ILs have a different hydrogen bonding acidity; $[bmim][Tf_2N]$ should be among the employed ILs, having the higher hydrogen bonding ability.[12] Actually, the data reported in Table 2 show that the activation parameters are very similar in all investigated ILs. Therefore, they seem to be not significantly affected by the different ability of the investigated ILs to give hydrogen bonding, although generally the activation enthalpies are lower in ILs than in DCE. The apparent lower ability of the ionic liquids, with respect chloroform, to affect reactivity through hydrogen bonding can be a consequence of the fact that this effect is due to the IL cation. Cation exerts the hydrogen bonding donor ability both on the leaving and on the entering Br^- anion. If bond making and bond breaking occur simultaneously in the rate-determining step, the hydrogen bonding ability of the IL has practically no effect. At variance, in chloroform the nucleophilic Br^- is present in solution as a tight ion pair with the counteranion, the tetraalkylammonium cation, and therefore the formation of hydrogen bonding between the entering Br^- and the solvent is not important. The solvent can instead hydrogen bond with the liberated leaving group (the Br^- anion), favoring the Br−Br bond breaking. Therefore, although we hypothesize the same mechanism in molecular and ionic

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TABLE 3. Second-Order Rate Constants for the Reaction of ICl_2^- with Alkenes and Alkynes in Ionic Liquids and DCE at 25 °C[a]

solvent	**1a** $k_{ICl_2^-}$ ($M^{-1}\ s^{-1}$)	**1b** $k_{ICl_2^-}$ ($M^{-1}\ s^{-1}$)	**1d** $k_{ICl_2^-}$ ($M^{-1}\ s^{-1}$)	**1e** $k_{ICl_2^-}$ ($M^{-1}\ s^{-1}$)	**2** $k_{ICl_2^-}$ ($M^{-1}\ s^{-1}$)	**3a** $k_{ICl_2^-}$ ($M^{-1}\ s^{-1}$)
[bmim][PF_6]	7.1×10^{-4}	5.8×10^{-4}	1.8×10^{-3}	7.0×10^{-3}	2.6×10^{-3}	3.4×10^{-5}
[emim][TF_2N]	4.1×10^{-3}	1.6×10^{-3}	1.0×10^{-2}	1.1×10^{-2}	nd[b]	7.7×10^{-5}
[bmim][TF_2N]	5.3×10^{-4}	7.8×10^{-4}	4.7×10^{-3}	7.2×10^{-3}	7.3×10^{-3}	3.1×10^{-5}
[hmim][TF_2N]	1.0×10^{-3}	2.8×10^{-4}	3.6×10^{-3}	5.2×10^{-3}	4.9×10^{-3}	2.9×10^{-5}
[bpy][TF_2N]	1.8×10^{-3}	9.6×10^{-4}	7.6×10^{-3}	1.1×10^{-2}	1.0×10^{-2}	5.9×10^{-5}
DCE	1.1×10^{-4}	nd[c]	3.6×10^{-4}	5.9×10^{-4}	7.5×10^{-4}	nd[c]

[a] Standard deviations in the values of $k_{ICl_2^-}$ were always less than 5% and more usually between 2 and 3% of the quoted values. [b] Too fast to be measured using a UV–vis spectrophotometer. [c] Rapid darkening of the solution prevented the evaluation of the kinetic constant.

solvents, the hydrogen bonding between Br^- and the solvent can play a different role in the two media.

Iodination Rates. The kinetic behavior of the addition of ICl_2^- to several alkenes (1-pentene, **1a**; styrene, **1b**; *trans*-2-pentene, **1d**; *cis*-2-pentene, **1e**; cyclopentene, **2**) and to phenylacetylene, **3a**, has been examined both in ILs and DCE, using in this latter case tetrabutylammonium ICl_2^- ([Bu_4N][ICl_2]) as an iodochlorinating agent. The kinetics of iodochlorination were measured spectrophotometrically by monitoring the disappearance of ICl_2^- at 336 nm (absorption maximum of ICl_2^- in ILs). They were carried out under pseudo-order conditions, working in the presence of at least a 10-fold excess of the substrate. All reactions obeyed the second-order rate law of eq 2

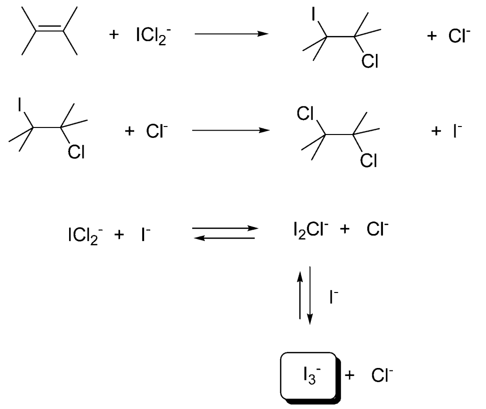
$$-d[ICl_2^-]/dt = k_{ICl_2^-}[ICl_2^-][S] \qquad (2)$$

where [S] is the substrate (alkene or alkyne) concentration. The $k_{ICl_2^-}$ values at 25 °C are reported in Table 3. The rate constants for iodochlorination of substrates **1a**, **1d**, **1e**, and **2** with [Bu_4N][ICl_2] in DCE are also reported in Table 3. All the reactions carried out in ILs were followed for at least two half-lives. At variance, only the initial rate constants (<10% of conversion) could be measured in the case of the reactions performed in DCE, due to the progressive darkening of the solutions. In the case of **1b** and **3a**, the darkening of the solutions was so fast that also the initial rate constants could not be evaluated. This phenomenon has been attributed to the formation of I_3^-. The formation of this species is probably a consequence of the reaction of Cl^- with the addition product(s), the iodochloro adduct(s). This substitution reaction gives the corresponding dichloro derivative(s) and an increase in the amount of I^- (see Scheme 2). The formation of small amounts of dichloro adducts has been evidenced frequently in the reactions of ICl_2^- addition to alkenes, in particular when the alkene structure favors the substitution process (arylalkenes).

The I^- anion reacts with ICl_2^- to gives I_3^-, through the multiequilibria pathway reported in Scheme 2. The formation of I_3^- has been confirmed by the appearance of the corresponding absorption band in the UV spectrum. This anion has in ILs a peculiar absorption band centered at 365 nm. Therefore, on the basis of these newer results, we attribute the very low reaction rates, previously observed[2c] using [Bu_4N][ICl_2^-] as a reagent in chlorinated solvents, to the partial transformation of the ICl_2^- species in I_3^-.

On the contrary, the substitution reaction is not able to compete significantly with the addition process in ILs.

SCHEME 2



While the rates of the electrophilic addition of ICl_2^- to double and triple bonds increase on going from DCE to ILs, the substitution reactions are generally slower in these latter media. In particular, the decomposition of the ICl_2^- species may be completely repressed performing the reaction in the ILs having the higher hydrogen bonding donor ability. These solvents not only increase the rate of the addition process but also reduce the nucleophilicity of Cl^- anion, reducing the rate of the substitution process, in agreement with the recently reported data about nucleophilic substitution reactions in ILs.[9] In these ILs, it is therefore generally possible to isolate the corresponding iodochloro derivatives in high yield, without observation of reactant decomposition and formation of the corresponding dichloro adducts.

The complete anti stereoselectivity,[2c] which characterizes this reaction as well as the addition of Br_3^-, associated with the similar kinetic behavior suggests for this reaction a mechanism analogous to that proposed for the addition of Br_3^-. However, the increase in the reaction rate observed for the addition of ICl_2^- on going from DCE to ILs is generally higher than the increase characterizing the addition of Br_3^- in the same solvents. This is in agreement with a different charge distribution in the two transition states or a different stabilization of the two ground states.

Also for the addition of ICl_2^- the reaction rates do not correlate with IL viscosity alone. Furthermore, at variance with the Br_3^- addition, the activation parameters (reported in Table 4 for the reaction of olefin **1d**) show a higher dependence on the IL structure, although the activation energy values, $\Delta G_{298}^{\ddagger}$, are very similar in all examined ILs.

The constancy of $\Delta G^{\ddagger}$ may be explained considering the possibility of having in these solvents an isokinetic

TABLE 4. Apparent Activation Parameters for the Reaction of ICl_2^- with 1d[a]

	$K_{ICl_2^-}$ (298 K) (M^{-1} s^{-1})	$E_{a,obsd}$ (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G_{298}^{\ddagger}$ (kJ $mol^{-1)}$
DCE	3.6×10^{-4}	30.6 (3)	28.1 (3)	−215 (2)	92
[emim][TF_2N]	1.0×10^{-2}	33.3 (5)	30.8 (5)	−178 (1)	84
[bmim][TF_2N]	4.7×10^{-3}	17.8 (1)	15.3 (1)	−238 (1)	84
[bm_2im][TF_2N]	1.8×10^{-3}	44.8 (3)	42.3 (3)	−159 (1)	89.5
[bpy][Tf_2N]	7.6×10^{-3}	28.4 (3)	25.9 (3)	−198 (3)	86
[bmim][PF_6]	1.8×10^{-3}	78.0 (6)	75.5 (6)	−26 (1)	83

[a] Standard deviations are given in parentheses.

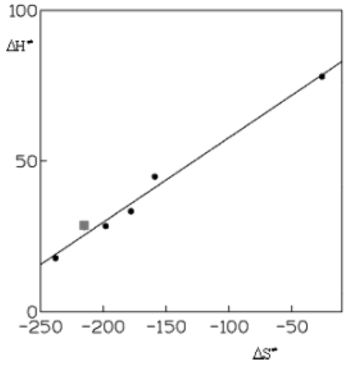


FIGURE 1. Enthalpy-entropy compensation plot for the reaction of **1d** with ICl_2^- in ILs (•) and DCE (■).

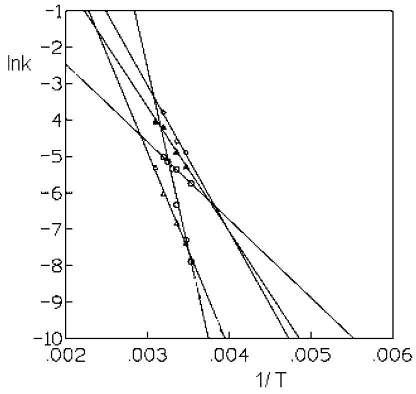


FIGURE 2. Arrhenius plots for the reaction of **1d** with ICl_2^- in ILs.

relationship (IKR) and/or a compensation effect. Similarities and differences between these two concepts have been recently discussed.[13]

According to the definition, the linear correlation found between enthalpies and entropies of activation (Figure 1) for the reaction of **1d** with ICl_2^- in the examined ILs and DCE clearly illustrates the presence of a compensation effect.

A correlation of this type has been recently found also for a diffusion-controlled process carried out in several imidazolium ILs and some molecular solvents.[14] However, such linear correlations between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are often coincidental or are the fruit of an inappropriate or incomplete description of the kinetic model, and therefore caution is required in their interpretation. A true test of the existence of an IKR is generally considered[13] the behavior shown by the Arrhenius plots. An IKR would result in a convergence of the Arrhenius lines to a single point, referred as the isokinetic temperature (IKT), where the difference among the rate constants is at a minimum.

Examination the Arrhenius plots for the reaction of **1d** in the investigated ILs (Figure 2) shows a convergence of the lines with a similar intersection point for [emim][Tf_2N], [bmim][Tf_2N], and [bpy][Tf_2N], but deviations can be evidenced for [bmim][PF_6] and [bm_2im][Tf_2N], which present another intersection point.

Since the two points are not very far from each other, a program for linear regressions with a common point of intersection has been applied to establish if the deviations may be due to experimental errors.[15] Calculation seems to indicate that IKR does not exist, or if existing it is not inclusive of all the solvents. The existence of an isokinetic relationship is usually taken to mean that the reaction parameter that is varied, in this case the solvent, is operating on only one type of interaction in the system, while the absence can point to a complex interplay of effects.

In our case the presence of two intersection points seems to indicate that not only the hydrogen bonding ability but also at least another factor are able to affect the rate of ICl_2^- addition. Considering the physicochemical properties of the examined ILs, we may hypothesize, as explained below, that the hydrogen bonding donor ability of the IL is the main or sole factor affecting reactivity in [emim][Tf_2N], [bmim][Tf_2N], and [bpy][Tf_2N], while in the other two solvents there is the additional contribution of the viscosity. The viscosities of [bmim][PF_6] and [bm_2im][Tf_2N] are indeed significantly different from those of the other ILs.

With more detailed examination of the activation parameters, it emerges that in [bmim][Tf_2N], at variance with the behavior in the other ionic solvents, the activation enthalpy is strongly reduced, while the $\Delta S^{\ddagger}$ value is significantly increased. Considering that this is the IL having the relatively higher hydrogen bonding donor ability, the activation parameters seem to suggest that this solvent property is probably the main factor affecting the reaction rate. In agreement with this hypothesis, the activation enthalpy increases (and the activation entropy decreases) when the reaction is performed in an ionic liquid having a cation less suitable to give hydrogen bonding such as [bm_2im] or [bpy]. In the imidazolium salts, the presence of a methyl group at C-2 significantly reduces the hydrogen bond acidity of the imidazolium cation. Analogously, the pyridinium cation is expected to form weaker, if any, hydrogen bonds. Furthermore, it

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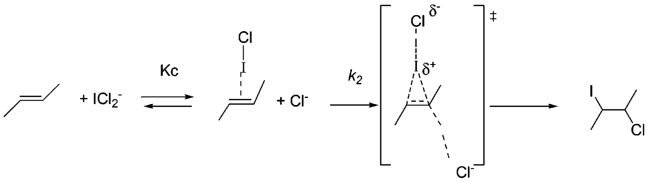
SCHEME 3



is more frequently claimed[16] that a strong anion−cation association such as that characterizing [bmim][PF$_6$] is able to reduce the cation hydrogen bonding ability. It is worth noting that the reaction in this latter IL is characterized by the higher value of the activation enthalpy but by the lower activation entropy. This behavior may be attributed to the greater cross-linking that distinguishes the ILs bearing the [PF$_6$]$^-$ anion compared to [Tf$_2$N]$^-$. A similar behavior has been observed[14] also previously for the triplet energy transfer from triplet benzophenone to naphthalene.

Finally, it must be remarked that the activation parameters for the reaction in [emim][Tf$_2$N] are quite different from those related to the same reaction in [bmim][Tf$_2$N], despite the structural similarity between these two ILs, suggesting a different ability of the two cations to give hydrogen bonding. This may be attributed to a different anion−cation interaction.

In conclusion, the solvent effect in the addition of ICl$_2^-$ to double bonds can be explained by the degree of stabilization of the leaving chloride ion via hydrogen bonding to the cation of the ionic liquid. The different sensibility showed by the two investigated reactions (addition of ICl$_2^-$ and Br$_3^-$) toward the hydrogen bonding ability of the IL may be related to a different charge distribution in the respective transition states, which is probably a consequence of the different hydrogen bonding acceptor ability of the two departing halides. The interaction IL cation···chloride should be stronger than cation···bromide.

We retain therefore that in the case of ICl$_2^-$ addition, the bond breaking precedes bond making, the transition state has greater iodiranium character (in this case, we cannot exclude the formation of a iodiradium intermediate), and the attack by chloride is not in itself the rate-determining step, although it might be part of a concerted process. In this situation, the ability of the IL to form hydrogen bonding with the leaving Cl$^-$ plays a main role (Scheme 3).

Conclusion

In conclusion, this work shows that ICl$_2^-$ may be a useful electrophile for the functionalization of double or triple bonds in particular when it is used in ionic liquids, where the higher stability of the product(s) toward substitution reaction reduces or avoids the formation of dichlorides and the decomposition of the reactant.

Furthermore, it supports the more recent data showing that not all ionic liquids are the same, the replacement of a conventional solvent with a single ionic liquid not necessarily implying that the new conditions are the best ones. The ability of the ionic liquids to affect the reaction rate depends, however, on the reaction; the addition of ICl$_2^-$ is more affected by the ionic liquid structure than the analogous reaction of Br$_3^-$, although both are faster in ionic liquids than in molecular solvents.

Finally, important information about the features of ionic liquids and on the correlation between structure−solvent properties can be obtained from kinetic study of well-known reactions. These results show the potential effects of the cations of the ILs as hydrogen bonding donors in electrophilic addition reactions in ionic liquids and corroborate previous data[17] showing that the capability of imidazolium ILs for hydrogen bonding can be exploited to suppress unwanted substitution reactions.

Experimental Section

Preparation of [bmim][Br$_3$] and [bmim][ICl$_2$]. An appropriate amount of [bmim][Cl] or [bmim][Br] was weighed in a calibration flask, and the IL was refrigerated at 0 °C. An equimolar amount of ICl or Br$_2$ was added at the same temperature, and the trihalide ionic liquid obtained was stored in the dark. Attention was paid to avoid contamination of the solution from atmospheric humidity.

Kinetic Measurements. Solutions of [bmim][Br$_3$] or [bmim]-[ICl$_2$] in ILs were prepared by weighing the halogenating species into known volumes of the desired ionic liquid. Analogously, solutions of [Bu$_4$N][Br$_3$] in DCE were prepared by weighing the reagent into known volumes of the solvent. Solutions of [Bu$_4$N][ICl$_2$] in DCE were prepared adding an equimolar amount of ICl to solutions of [Bu$_4$N][Cl] in DCE. Concentrations were also checked by UV measurements.

All these solutions were prepared shortly before use, protected from daylight, and adjusted to twice the desired initial concentrations in the kinetic runs. Aliquots of these prethermostated solutions were mixed with equal volumes of prethermostated solutions of the unsatured compounds of suitable concentrations.

The reactions of compounds **1a**, **1b**, **1d**, **1e**, **2**, and **3d** with [bmim][ICl$_2$] in ionic liquids or with [Bu$_4$N][ICl$_2$] in DCE were carried out at halogen concentrations ranging from 1 x 10^{-2} to 1 x 10^{-1} M in the presence of at least a 10-fold excess of the unsatured compound, following the disappearance of the dichloroiodate at 336 nm. For the reactions of compounds **1a**−**c** and **3a**,**b** with [bmim][Br$_3$] in ionic liquids or with [Bu$_4$N][Br$_3$] in DCE, a halogen concentration ranging from 1 x 10^{-3} to 1 x 10^{-2} M was used and the disappearance of the halogen was followed at 336 nm. The experiments were repeated at least in triplicate and accepted on condition of a 5% maximum difference of the respective absorption/time curves. The second-order rate costants, $k_{\mathrm{Br_3^-}}$ and $k_{\mathrm{ICl_2^-}}$, obtained by fitting the absorption/time data to the appropriate integrated rate equation, are reported in Tables 1 and 3. The apparent activation parameters, reported in Tables 2 and 4, were obtained from Arrhenius plots.

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Supporting Information Available: General experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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