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Dimerization of ion radicals in ionic liquids. An example of favourable "Coulombic" solvation†

Fabien André,[ab] Philippe Hapiot[ab] and Corinne Lagrost*[ab]

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The irreversible dimerization of the acetophenone radical anion, chosen as an example of a carbon–carbon coupling reaction between two charged species, was investigated in a series of 1,3-dialkylimidazolium and 1,2,3-trialkylimidazolium ionic liquids. Indeed, such ion dimerizations which display slow kinetics despite small activation energies, are controlled by a subtle competition between bond formation, Coulombic repulsion and solvation. The effects of viscosity, "polarity" and ionic solvation on the reactivity of the radical anions were examined. The dimerization rate constants were demonstrated to be only weakly affected by the high viscosity of the medium or its apparent polarity. When the acetophenone radical anion is "solvated" in imidazolium-based ionic liquids, a strong interaction between the negatively-charged intermediates and the imidazolium cation occurs. The ensuing charge stabilization allows a fast dimerization step in all the ionic liquids used. The kinetic effect is even enhanced in the 1,3-dialkylimidazolium salts as compared to the 1,2,3-trialkylimidazolium ones because the interaction between the radical anions and the 1,3-dialkylimidazolium cations are stronger, probably due to the formation of H-bond. The reactivity of the ion radical is demonstrated not only to be mainly dominated by electrostatic interactions, but also that the nature of the ionic liquid cations with respect to that of the ion radical is a major factor that affects the reaction kinetics.

Introduction

Room-temperature ionic liquids (ILs), which typically consist of bulky asymmetric onium-type cations and charge-diffuse anions, form a novel class of solvents with remarkable properties that can be tuned by variation of the cation and anion. As such, they became increasingly popular and nowadays cover a wide range of applications including synthetic chemistry,[1,2] catalysis,[3] electrochemistry,[4,5] and material science.[6,7]

As an alternative to molecular solvents, ILs were found to be media able to increase selectivities, reaction rates, catalyst recyclability or to facilitate product recovery.[3] However, despite their extensive applications, the nature of the solvation process in ILs as well as the relationship of their structure and the reaction outcomes remain marginally understood, certainly because these could not be simply interpreted on the basis of the usual theories of molecular solvents.[8]

It is now well-established that ILs, despite apparent similarities with molecular polar liquids, are particularly complex media. The key difference between molecular liquids and ILs is the significant electrostatic interactions occurring between the components of the liquid. In addition to the negligible vapour pressure so characteristic of ionic liquids, these electrostatic interactions may result in larger stabilisation of dissolved charged species and contribute to a significant ordering in the solution. Much of the crystal structure of the salt was then demonstrated to endure in the liquid.[9–11] However, it has been demonstrated that ILs are not homogeneous media. and they are better described as nanostructured fluids where separate nanoscale domains co-exist in the ionic medium.[12–14] Thus, the transfer of potentially useful chemical processes from molecular solvents to IL media may be not straightforward. From a kinetic point of view, ILs could affect the activation energy, through solvent–solute interactions, dynamic solvent effects, as well as the entropic term because of the strong structuration of the media. Many studies, both in electrochemistry and in chemistry to a general sense, have been undertaken to understand the differences in the kinetics in these solvents.[4,15–21] Accelerations of the reaction rates,[17,19,22] as well as lower or identical kinetics were equally highlighted.[18,23–26]

The present work aims to extend our observations on the influence of ionic liquids on the kinetics of dimerization of ion radicals, underlining the ILs' complex solvation effects with respect to the molecular electrolyte.[27]

The dimerization of electrochemically generated ion radicals is a reaction whose mechanism and reactivity factors were intensively discussed.[28–30] Besides the importance of such processes on the industrial scale (Baizer–Monsanto reaction), the mechanism and reactivity factors gave rise to puzzling

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issues and controversy. Although the activation energy may be very small, these processes are often characterized by slow dimerization kinetics (far slower than the diffusion limit) in polar solvents. As rationalized by Costentin and Savéant,[30] the solvation is an essential factor to counteract the Coulombic repulsion between the two ion radicals. This concerns not only the thermodynamics of the reaction, making exergonic a reaction that would have been strongly endergonic in the gas phase, but also its kinetics, because solvation allows a substantiate energy gain, rendering the activation energy "*vanishingly small*".[30] *The payback is however a strong negative contribution of solvation to the entropy of activation*,[30] leading to slow kinetics, quite unusual for barrierless reactions. These reactions appear particularly interesting for kinetic investigations in ionic liquids to characterize the peculiarities that differentiate ionic liquids from molecular solvents because they are particularly sensitive to solvation.

As a reaction model system, we chose the electrochemical reduction of aromatic carbonyl compounds (acetophenone) where two anion radicals couple to give the pinacolate that protonates further to pinacol.[31] In a previous work, we found that the coupling of the radical anions was slowed down in the viscous trialkylbutylammonium bis(trifluoromethylsulfonyl) amide salts.[27] These results were rationalized through electrostatic interactions between the ionic liquid cations and the electrogenerated ion radicals. However, other solvent parameters, including polarity, viscosity, and more specifically to ionic liquids, ionic concentrations were not taken into account. The present work undertakes a more careful examination of the solvent parameters that affect the reactivity of the acetophenone anion radicals. A systematic study was performed in a series of six imidazolium salts sharing the same anion. Because imidazolium salts are the most widely studied among the ionic liquids, their physico-chemical data are readily available. Within this family of imidazolium salts, the viscosity and the ion-pairing ability could be fine tuned by varying the length of the alkyl chain and by introducing an additional methyl group at the 2-position in the cation, without any significant modification of either the static dielectric constants,[32] or the ionic concentration.[33] The dimerization reaction of the radical anions was scrutinized in the six media, and the results were also compared with those obtained in a previous work.[27] We tried to correlate the dimerization rate constants determined in the six imidazolium salts with different parameters, including viscosity, polarity, ionic concentration, ion-pairing ability. The results clearly evidenced that, if the reactivity of the anion radical was mainly dominated by electrostatic interactions, the nature of the ionic liquid cations with respect to that of the ion radical was a major factor that affects the reaction kinetics.

Results and discussion

Assessment of a radical–radical dimerization reaction

Cyclic voltammetry experiments monitoring the reduction of acetophenone were performed at different scan rates v, between 0.1 V s^{-1} and 100 V s^{-1} in the six imidazolium-based ionic liquids, namely 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm][NTf_2]), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([PMIm][NTf_2]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([BMIm][NTf_2]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HexMIm][NTf_2]), 1-butyl-2,3-methylimidazolium bis(trifluoromethylsulfonyl) amide ([BMMIm][NTf_2]), 1-ethyl-2,3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMMIm][NTf_2]. Fig. 1 displays some typical cyclic voltamogramms (CVs) in [EMIm][NTf_2], [PMIm][NTf_2], [HexMIm][NTf_2] and [BMMIm][NTf_2]. For scan rates $v < 20$ V s^{-1}, an irreversible reduction peak is observed at −2.3 to −2.45 V *vs.* Fc/Fc^+ (Table 1). Plotting the corresponding peak currents *versus* $v^{1/2}$ was checked to yield a linear variation, showing that the currents are under diffusion-control for the six ionic liquids. The slopes of the variation provide estimations of the diffusion coefficients of acetophenone.[34] As frequently reported for similar organic redox couples, the diffusion coefficients (D) are about two orders of magnitude lower than those obtained in conventional organic electrolytes (Table 1).[4,15] As expected, the diffusion coefficients of acetophenone decrease as the viscosity of the ionic liquid increases, being fully consistent with a slower rate of mass transport to the electrode in a viscous medium.

In the six ionic liquids, the electrochemical processes remain irreversible at low and moderate scan rates (0.1–20 V s^{-1}). Upon increasing the scan rates, the voltammograms become reversible (Fig. 3). Note that similar patterns are observed in more conventional electrolytes such as acetonitrile + 0.1 mol L^{-1} Bu_4NPF_6. This electrochemical behaviour could be ascribed to the formation of a radical anion upon the electronic transfer, associated to a subsequent coupling reaction to form the corresponding pinacol compound (2,3-diphenylbutane-2-3-diol), as previously reported.[27]

A first point to address concerns the determination of the mechanism. Indeed, such coupling reaction trigerred by the electronic transfer may occur either at the level of the primary ion radical or at the level of radicals produced from the primary radical by means of an acid–base reaction.

The cyclic voltammetry analysis allows a clean distinction between the two possibilities, namely a radical–radical

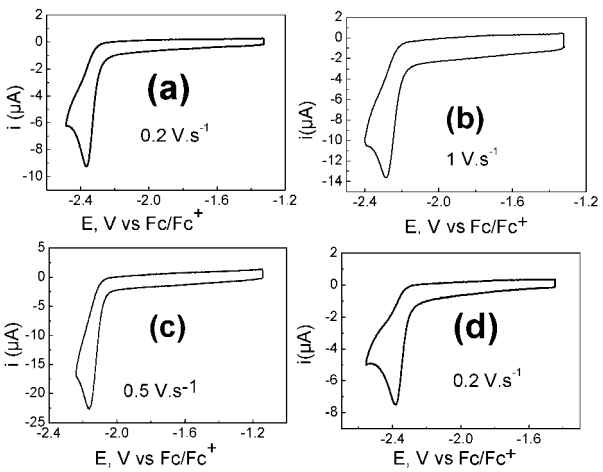

Fig. 1 Cyclic voltammetry of 4–7 × 10^{-3} mol L^{-1} acetophenone at a glassy carbon electrode in (a) [EMIm][NTf_2], (b) [PMIm][NTf_2], (c) [HexMIm][NTf_2] and (d) [BMMIm][NTf_2].

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Table 1 Key results for acetophenone reductive coupling in the six imidazolium ionic liquids. Comparison with the data recorded in conventional organic electrolyte and $[Et_3BuN][NTf_2]$

Medium	E°/V *vs.* Fc/Fc+	$\partial Ep/\partial(\log v)$/mV dec^{-1}	D/cm^{-2} s^{-1}	k_{dim}/L mol^{-1} s^{-1}
$[EMIm][NTf_2]$	−2.31	21.6	$(1.5 \pm 0.4) \times 10^{-6}$	1.5×10^6
$[PMIm][NTf_2]$	−2.26	19.5	$(8.0 \pm 0.2) \times 10^{-7}$	1.0×10^6
$[BMIm][NTf_2]$	−2.27	22.7	$(6.4 \pm 0.3) \times 10^{-7}$	2.0×10^6
$[HexMIm][NTf_2]$	−2.21	21.9	$(5.4 \pm 0.3) \times 10^{-7}$	$0.8–0.9 \times 10^6$
$[BMMIm][NTf_2]$	−2.38	22.1	$(3.4 \pm 0.2) \times 10^{-7}$	$0.8–1 \times 10^5$
$[EMMIm][NTf_2]$	−2.42[b]	25.0[b]	$(6.5 \pm 0.3) \times 10^{-7}$[b]	2.0×10^5[b]
Conventional electrolyte	−2.52[d]	—	1.84×10^{-5}[c]	2×10^5[d]
$[Et_3BuN][NTf_2]$[a]	−2.46	20.7	$(6.8 \pm 0.4) \times 10^{-7}$	$3–5 \times 10^5$

[a] From ref. 27. [b] At T = 26 °C. [c] From ref. 39 in DMF + 0.1 mol L^{-1} Bu_4NPF_6. [d] From ref. 40 in EtOH + 0.1 mol L^{-1} Bu_4NOH.

dimerization or radical-substrate dimerization. Indeed, the variation of the peak potential as a function of the scan rates and initial concentration of acetophenone are expected different for the different kind of mechanism.[35,36] In the scan-rate range where the reduction process is irreversible, the peak potential varies linearly as a function of the logarithm of the scan rate v with a slope close to 20 mV per a 10-fold increase in v, for any of the ionic liquids under consideration (two examples are shown on Fig. 2).

A linear variation is also found for the variation of the peak potential with the logarithm of the initial concentration of acetophenone with a slope close to −20 mV for a 10-fold increase in concentration.[37] These results unambiguously show that the rate-determining step is a coupling process involving two radical anions that are formed in an earlier, rather fast electron transfer (Scheme 1).[35,36]

Determination of the dimerization rate constants

It is remarkable that the scan rate corresponding to the apparition of the reversibility depends on the "nature" of the ionic liquids. For the 1,3-dialkylimidazolium salts, partial reversibility becomes visible for scan rates, v, higher than 100 V s^{-1} while this occurs for $v > 20$ V s^{-1} for the 1,2,3-trialkylimidazolium salts (Fig. 3).

Qualitatively, these differences reflect the variations in the radical anion–radical anion dimerization kinetics, in relation with the nature of the imidazolium ionic liquids. In order to quantify these observations, the apparent dimerization rate constants (k_{dim}) were derived from comparisons at different scan rates of the experimental voltammograms (variation of the reversibility) with calculated curves using DigiElch software.[53] Numerical simulations of the voltammograms were performed according to the mechanism described above (Scheme 1) and by assuming an irreversible dimerization. Concerning the electron-transfer rates, the kinetic parameter $k_s/D^{1/2}$ was

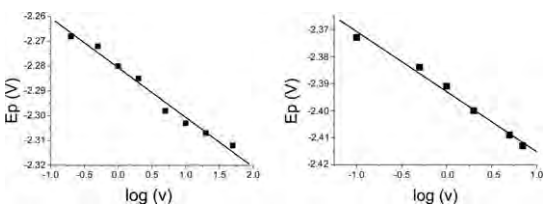
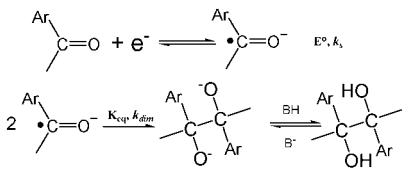


Fig. 2 Cyclic voltammetry of $\approx 5 \times 10^{-3}$ mol L^{-1} acetophenone at a glassy carbon electrode. Variation of the peak potential in V *vs.* Fc/Fc$^+$ with the logarithm of the scan rate in $[PMIm][NTf_2]$ (left) and in $[BMMIm][NTf_2]$ (right).



Scheme 1 Radical–radical dimerization mechanism involved in the electrodimerization of acetophenone

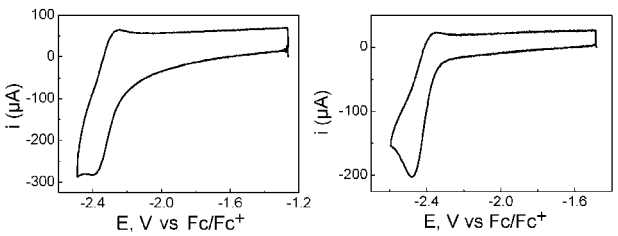


Fig. 3 Cyclic voltammetry of $\approx 5 \times 10^{-3}$ mol L^{-1} acetophenone showing reversibility. Left, in $[EMIm][NTf_2]$ at 200 V s^{-1}. Right, in $[EMMIm][NTf_2]$ at 30 V s^{-1}.

evaluated to be around 15–30 s^{-1}, where k_s is the standard heterogeneous rate constant uncorrected from the double layer effect.[38] The results obtained from the analyses of the cyclic voltammetric data are inserted in Table 1.

For comparison purposes, data obtained in conventional solvents and in ammonium-based ionic liquid are added. The dimerization rate constants in the 1,3-dialkylimidazolium salts are found to be approximately constant within one order of magnitude, $k_{dim} \approx 10^6$ L mol^{-1} s^{-1} in the whole series of dialkylated salts. In a parallel manner, a similar observation could be made in the case of the trialkylimidazolium salts where $k_{dim} \approx 10^5$ L mol^{-1} s^{-1}, these values being close to that obtained in the ammonium-based ionic liquid. Interestingly, these values are equal or even larger than those reported in conventional alkaline ethanolic medium (Table 1). The dimerization rate constants are quite high in the ionic liquids despite the high viscosity of the media. Now, such a bimolecular reaction with small activation energy should suffer particularly from the high viscosity of the ionic liquids. This observation highlights the potential beneficial use of ionic liquids to run ion dimerization processes allowing C–C bond formation.

What are the solvent parameters that influence the kinetics?

The static dielectric constant ε_s is a convenient parameter to scale the polarity of a solvent. In ILs ε_s is evaluated as

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the zero-frequency limit of the frequency-dependant dielectric dispersion. However, because of its complexity, the solvent polarity in Ils is usually not very well described by macroscopic parameters such as the dielectric constant.[41] Here ε_s could be conveniently used as a standard tool to compare a series of ionic liquids within a group of similar "solvents". Generally, ILs are classified as moderately polar solvents with dielectric constants of the order of ε_s = 10–12 (Table 2). Heinze and co-workers have shown that the dimerization of ion radicals (equally charged) becomes faster as the polarity of solvent increases and the Smoluchowski–Debye equation for the bimolecular rate constant varies as a function of dielectric constant.[29] Because the concept of polarity is not easily transposable from molecular solvents to ILs, we only tried to qualitatively correlate the dimerization rate constant k_{dim} with the static dielectric constant. Despite the fact that they vary in a narrow range for the considered ILs, there is no clear tendency for the dependence on the static dielectric constants in ILs (Fig. 4, top). For example, we could observe that the dimerization kinetics is ten times lower in [BMMIm][NTf_2] than in [BMIm][NTf_2], although the two ILs exhibit a similar ε_s value.

Viscosity, η, is a parameter of importance that could influence on the kinetics of bimolecular reaction especially when the activation energy is small. Fig. 4, bottom displays the variations of the dimerization rate constants measured in the different imidazolium ionic liquids with their viscosity (Table 2), including previous kinetics analyses obtained in the ammonium-based ionic liquid.[27] One could observed some diminution of k_{dim} on the whole series of investigated ILs when increasing η. However, this parameter does not appear to be a critical factor. For instance, within the dialkylimidazolium salts series, by increasing the alkyl chain length from ethyl to hexyl, the viscosity considerably increases whereas the dimerization rate constants show no significant variation. Moreover, because the experiments were run at T = 26 °C

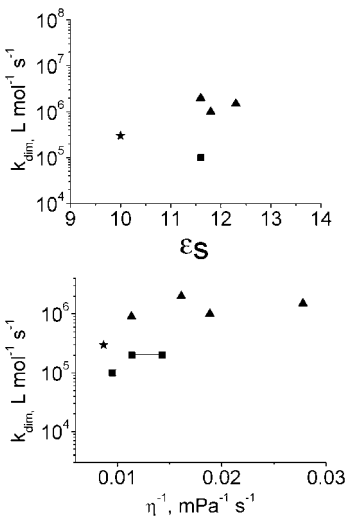

Fig. 4 Variations of k_{dim} with ILs static dielectric constant (top) and the inverse of viscosity of ILs (bottom). (▲) marks the 1,3-dialkylimidazolium-based salts, (■) the 1,2,3 trialkylimidazolium-based salts and (★) the ammonium salt. The value for the viscosity of the [EMMIm] salt was considered to be in the range [88–70] mPa s.[43]

Table 2 Viscosity, static dielectric constant and ionic concentration for the ionic liquids used in the work

Medium	η/cP (21 °C)	$\varepsilon_s^{b,c}$	C_i^a/mol L^{-1}
[EMIm][NTf_2]	36[a]	12.3	3.88
[PMIm][NTf_2]	53[b]	11.8	3.66
[BMIm][NTf_2]	62[a]	11.6	3.41
[HexMIm][NTf_2]	88[a]	—	3.07
[BMMIm][NTf_2]	105[a]	11.6	—
[EMMIm][NTf_2]	88[a]	—	3.65
[Et_3BuN][NTf_2]	115[a]	10[d]	3.18

[a] From ref. 33. [b] From ref. 32. [c] From ref. 42. [d] This value is for [Et_3PN][NTf_2].[42]

in [EMMIm][NTf_2], it is reasonable to consider that the viscosity of the medium would be less than 88 cP, ranging between the viscosities of [BMIm][NTf_2] and [HexMIm][NTf_2]. However, the dimerization kinetics in [EMMIm][NTf_2] are found to be lower than those in [BMIm][NTf_2] and [HexMIm][NTf_2].

An interesting feature is the clear decrease (about a factor of ten) of the dimerization rate constants when passing from the 1,3-dialkylimidazolium ionic liquids to the 1,2,3-trialkylimidazolium ones. As mentioned above, this phenomenon cannot result either from a higher viscosity of the 1,2,3-trialkylimidazolium salts or from a polarity effect. To characterize this effect, the variation of the dimerization kinetics within the two families of imidazolium ionic liquids was studied as a function of ΔE°, that is the difference between the standard potential values for the acetophenone/acetophenone radical anion couple measured in the ILs (E°_{RTILs}) and in conventional media (DMF +0.1 mol L^{-1} NBu_4PF_6) (E°_{CONV}).

The E° value for the acetophenone/acetophenone radical anion couples were derived as the half-sum between the forward and the backward scans from the reversible voltammograms, that is, at the highest scan rates.[36,44] As compared to the E° value in an organic electrolyte, a large positive shift (between 100 and 300 mV) is observed for the standard potential of the acetophenone/acetophenone$^{\bullet-}$ in the six imidazolium-based ionic liquids. This shift is indicative of a better stabilization of the electrogenerated acetophenone radical anion in ionic liquids probably through electrostatic associations with the cation of the ionic liquids.[45] Similar formal potential shifts have been reported for various compounds,[46] including benzaldehyde,[25] nitrobenzene derivatives,[47,48] or benzophenone compounds.[22,49] Obviously, such a stabilization of the radical anion is favored by a small cation–anion distance and for charge-localized solutes. This is the case for the acetophenone radical anion where the negative charge is mostly concentrated on the oxygen atom of the carbonyl group. Furthermore, the planar geometry of the imidazolium ring allows the oxygen atom of the carbonyl group to closely face the cationic ring, hence minimizing again the cation–anion distance in the pair. Then a strong interaction between the radical anion and the imidazolium cation is observed, as exemplified by the positive shift of the E° values. We could also notice that in the series of 1,3-dialkylimidazolium salts, the E° values are more positively shifted than those corresponding to the 1,2,3-trialkylimidazolium media (Table 1). In the case of the 1,3-dialkylimidazolium ionic liquids, the interaction between the acetophenone radical anion and the

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imidazolium cation could be even enhanced by the ability of such cations to form H-bond at the C_2 position with the $C^{\bullet}$–O^{-} of the carbonyl group.[22] In the case of 1,2,3-trialkylimidazolium salts, an extra stabilization of the ion-pair is precluded from the absence of the C_2H proton in the 1,2,3-trialkylimidazolium cation, thus leading to $E^{\circ}_{\text{dialkylimidazolium}} > E^{\circ}_{\text{trialkylimidazolium}}$.

Concerning the variations of k_{dim} with ΔE°, we could observe a clear correlation between the potential shift and the acceleration of the dimerization reaction (Fig. 5). On the whole, the more easily acetophenone is reduced, the better the radical anion is "stabilized", the faster the reaction. Similar accelerating effects have already been described for the dimerization of ketones or aldehydes radical anion in conventional organic polar electrolytes, provided that the radical anions were stabilized by ion-pairing or better solvation.[31,50,51] Similarly, we could conclude that the radical anions are better solvated in the 1,3-dialkylimidazolium through ion-pairing associations with the imidazolium cation because the ion-pair is strengthened by hydrogen-bonding to the carbonyl oxygen, thereby facilitating the coupling of two negatively charged species. The ionic solvation related to ion-pairing-like interaction appears to be favorable for the dimerization of ion radicals. However, similarly to what has been reported in molecular solvents,[29,30] the reaction is slower than the diffusion limit, probably due to a negative contribution of the ionic solvation to the entropy of activation. Yet, considering that the diffusion-controlled limit rate is estimated to be around 10^8 L mol^{-1} s^{-1} in ILs,[52] it emerges that the dimerization rate for the acetophenone radical anions are not so slow, relative to the reported values in molecular solvents.[53] We might speculate that the entropic cost could be smaller in ionic liquids than in molecular solvents, probably because of the significant quasimolecular organisation of the ILs that modifies the dynamics of activation in those media as suggested previously.[8,21]

Finally, the marked difference between the dimerization kinetics observed in the dialkylated imidazolium salts and the kinetics obtained in the trialkylated ones deserves further comment. As demonstrated before, the influence of ILs on the reaction rate is dominated by the solvent–solute electrostatic interaction. The interaction between the cations of the ILs and the anion radical allows the Coulombic repulsion between two ion radicals to be overcome. This is probably the reason why the dimerization rate constants in imidazolium salts as well as in ammonium salts are even significantly higher than (or at least, comparable to) those reported in a conventional alkaline ethanolic medium.[40] This effect might be simply explained by regarding the high ionic concentration of the media (Table 2). Then it is reasonable to invoke a charge-shielding effect, in relation to the ionic nature of the ILs, that helps two charged transient species to couple. Then, such a charge-shielding effect would equally occur in all ionic liquids whatever the nature of the combination cation/anion, providing that the ionic concentration is quite similar. Considering that the ionic concentration of the ionic liquids used in that work remain quite similar, this charge-shielding rationale failed to fully account for the larger k_{dim} values in the dialkylimidazolium salts ($\approx 10^6$ L mol^{-1} s^{-1}) than those in the trialkylimidazolium ones ($\approx 10^5$ L mol^{-1} s^{-1}). Actually, the nature of the IL cation with respect to that of the electrogenerated charged species has a major impact on the reaction kinetics by driving the strength of the electrostatic interactions. The coupling of the two ion radicals is considerably facilitated when a strong tight ion-pairing association between the anion radical and the ILs cations is possible, as is the case for the 1,3-dialkylimidazolium ILs. In that situation, the imidazolium cation could accommodate electron density from the radical anion *via* electron delocalisation. As a consequence, the dimerization reaction would involve a more pronounced neutral-like radical coupling.

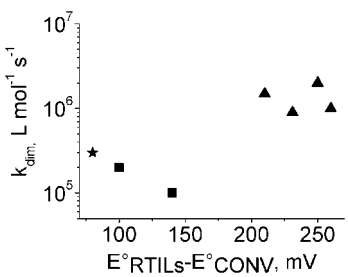

Fig. 5 The observed variation of k_{dim} with the standard potential of the acetophenone radical anion/acetophenone redox couple in the ILs, relative to that in conventional media. (▲) marks the 1,3 dialkylimidazolium-based salts, (■) the 1,2,3 trialkylimidazolium-based salts and (★) the ammonium salts.

Conclusion

The reactivity of electrogenerated acetophenone radical anions was investigated in two families of imidazolium bis(trifluoromethylsulfonyl)amide salts. Despite its diffusion-controlled character, the kinetics of the dimerization of the acetophenone radical anions was found to be only weakly sensitive to the polarity or to the high viscosity of the medium.

When the acetophenone radical anion is "solvated" in imidazolium-based ionic liquids, a strong interaction between the negatively-charged intermediates and the imidazolium cation takes place and the ensuing charge stabilization allows a fast dimerization step. The kinetics of the dimerization is found to be significantly increased in 1,3-dialkylimidazolium salts as compared to 1,2,3-trialkylimidazolium salts, probably because the ion-pair interaction between the 1,3 dialkylimidazolium cations and the acetophenone radical anion is strengthened due to the formation of an H-bond at the C_2 position in the cation. When they are possible, such strong and tight ion associations allow charge density delocalisation over the ion-pair, amounting the dimerization to a coupling of neutral-like radicals rather than charged radicals. In that sense, ionic liquids are not only media with ionic character particularly suitable for carrying out ion radical dimerization but the type of ions that compose the solvent should be carefully chosen: their nature could strongly influence the reaction rates.

Experimental

Chemicals

[EMIm][NTf_2], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [PMIm][NTf_2], 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [BMIm][NTf_2],

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1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [HexMIm][NTf_2], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [BMMIm][NTf_2], 1-butyl-2,3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [EMMIm][NTf_2], 1-ethyl-2,3-methylimidazolium bis(trifluoromethylsulfonyl)amide, were prepared from their corresponding chloride or bromide precursors salts and $LiN(CF_3SO_2)_2$ (Solvionic, France) aqueous solutions according to previously published procedures.[54,55] The samples were purified by extensive repeated washing with deionized H_2O, filtered over SiO_2/neutral alumina. Prior to each experiment, RTILs were carefully dried overnight by vacuum pumping at 50 °C and the amount of residual water was measured with Karl Fischer titration (Karl Fischer 652 Metrohm). The amount of water measured in our samples ranged from 200 to 300 ppm.

Acetophenone (99%, Aldrich) was used as received.

Electrochemical experiments

Because of the high viscosity of RTILs inducing low diffusion coefficients and thereby, low electrochemical currents, the voltammetric experiments need to be performed at a relatively high concentration of electroactive substance, typically 5×10^{-3} to 10^{-2} mol L^{-1}, in order to get a good signal-to-noise ratio. The electrochemical cell was a classical three-electrode set-up. The counter electrode was a Pt wire, and a Pt wire coated with polypyrrole was used as a quasi-reference. Ferrocene was added to the electrolyte solution at the end of each series of experiments, and the ferrocene/ferrocenium couple (E° = 0.405 V/SCE in ACN +0.1 mol L^{-1} Bu_4NBF_4) served as an internal probe. To allowing comparisons between measurements in the ionic liquids and in conventional electrolytes, all potential values are given against the ferrocene/ferrocenium couple as several works recommend its use as reference system.[56–58] A glassy carbon disk (1 mm diameter) was used as a working electrode. The electrode was carefully polished before each voltammetry experiment with 1 μm diamond paste and 0.25 μm alumina suspensions and ultrasonically rinsed in acetone. Electrochemical instrumentation consisted of a Tacussel GSTP4 programmer and of home-built potentiostat equipped with a positive-feedback compensation device.[59] Since ionic liquids are more resistive media than the conventional organic solvent/supporting salts electrolyte, Ohmic drop compensation must be cleanly achieved to avoid distortion of the Faradaic current, especially when employing high scan rates. The voltammograms were recorded with a 310 Nicolet oscilloscope. Experiments were performed at room temperature (20 ± 2 °C) under N_2 blanket, except for [EMMIm][NTf_2] where experiments were run at 26 °C.

Digital simulations with the DigiElch software (version 3, Elchsoft) were used to simulate the reduction of acetophenone in the different ionic liquids and at different scan rates, by using the default numerical options.[60] A planar diffusion and that the Butler–Volmer law applied for the electron transfer was assumed. The charge-transfer coefficient was taken as 0.5.

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