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Specific Effects of Room Temperature Ionic Liquids on Cleavage Reactivity: Example of the Carbon−Halogen Bond Breaking in Aromatic Radical Anions

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Specific solvation effects of ionic liquids have been evidenced on the chemical reactivity of radical anions with three different ionic liquids (1-butyl-3-methylimidazolium, trimethylbutylammonium, and triethylbutylammonium cations associated with the same anion (bis(trifluoromethylsulfonyl)imide). Large modifications depending on the localization of the negative charge in the radical anions and, to a less extent, on the nature of the ionic liquids cations are reported. When the charge is spread out over the entire molecule as in the 9-chloroanthracene radical anion, an acceleration of the carbon−halogen bond cleavage when passing from acetonitrile to the ionic liquid is observed. On the contrary, in the case of 4-chlorobenzophenone radical anion where the negative charge is more localized on the oxygen atom of the carbonyl group, a large decrease of the C−Cl cleavage rate occurs in relation with a positive shift of the reduction standard potentials. These effects can be explained by specific ion-pair associations between the radical anion and the cation of the ionic liquid that stabilizes the unpaired electron in the π^* orbital of the aromatic system and thus decreases its presence in the σ^* bond breaking. The experimental results can be rationalized using Marcus-type formalism (Savéant's model describing the dynamics of electron transfers and bond cleavage) and agree well with the calculated ion-pair stabilization energies estimated with density functional theory (B3LYP). Besides the decrease of the cleavage rate, the ion pairing favors the dimerization between two radical anions that prevails over the cleavage reaction, leading to a different mechanism.

Introduction

Room-temperature ionic liquids (RTILs) are receiving increasing interest for their possible use as alternative reaction media to organic volatile solvents.[1] They consist of a combination of organic cations with inorganic or organic anions and are liquid at ambient temperature. Among the numerous available RTILs, the most widely used are probably *N*,*N*-dialkylimidazolium salts and, to a less extent, quaternary ammonium salts with common weakly coordinating anions ($AlCl_4^-$, BF_4^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, etc.) that are usually air and moisture stable.[1] Relative to molecular solvents, these ionic liquids are remarkable because they exhibit negligible vapor pressure and are nonvolatile and nonflammable.[2,3] In addition to good thermal and chemical stabilities, miscibility with several classes of solvents, ability to dissolve a wide range of organic and inorganic compounds, large electrochemical window, and high-ionic conductivity, physical properties such as density, melting point, viscosity, and hydrophobicity can be tuned through variation of anion or cation to tailor particular ionic liquids for a given use. All these properties enhance the interest for the use of ionic liquids as media for synthesis, catalysis, and extraction processes.[1,4] They also present large potential interest as solvents for electrochemical applications because they can be used without the need of any added supporting electrolyte thanks to their inherent ionic conductivity. They have been shown to be suitable media for batteries, fuel cells, photovoltaic devices, or electroplating processes[1] or organic electrosynthesis.[5] Besides direct applications, electrochemical methods have been proved to be powerful tools for probing the chemical reactivities of electrogenerated intermediates.[6] Similar electrochemical investigations can be performed in RTILs (see references for examples).[7,8] All studies demonstrate that the electrochemical patterns remain similar with those observed in organic molecular solvents, confirming first the possibility of using RTILs in electrosynthesis instead of organic solvents, and second, that the classical analysis criteria used in the transient electrochemical methods are valid for mechanistic studies in these new media.[7,8] Considerable ion-pairing association between the electrogenerated charged species and ions of the "solvent" is expected because of their pure ionic nature.[1] As illustrated by numerous studies performed in organic solvent, when small alkali metal salts (typically lithium, sodium, or magnesium salts) are added into the solution, ion pairing can influence the kinetics and nature of reaction mechanisms involving charged reactants.[9−11] In RTILs, modifications of electron-transfer rates or reaction kinetics involving radical ions have been detected using pulse radiolysis techniques[12] or photochemical methods.[13] Tentative approaches were performed to correlate the experimental results with solvent parameters, notably ion-transfer free energies.[12e] In electrochemistry, a recent work describes large and remarkable ion-pairing effects between dialkylimidazolium ions and the dianions electrochemically generated by reduction of dinitrobenzene.[7f]

In a preliminary work, we investigated the effect of ionic liquids on the general reactivity (in terms of lifetimes) of some delocalized aromatic cation radicals that are involved in classical series of electrochemical reactions.[8] In the present work, we focus on the cleavage reactivity of compounds containing a leaving group illustrated by the well-known carbon−halogen bond cleavage reaction in haloaromatic anion radicals.[14] We

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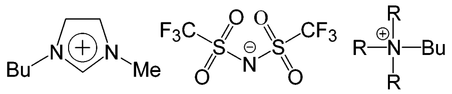
SCHEME 1: Combination of Cations and Anions Used To Form the RTILs



used three different ionic liquids in which the cation was varied (1-butyl-3-methylimidazolium, trimethylbutylammonium, and triethylbutylammonium) while the anion (bis(trifluoromethylsulfonyl)imide) was kept the same for all experiments. Results were systematically compared to those for a conventional electrolytic medium (acetonitrile + 0.1 M Bu_4NBF_4). Two different redox systems were chosen (the reduction of 4-chlorobenzophenone and 9-chloroanthracene) to contrast the possible ionic liquid effects as their radical anions correspond to two opposite situations for the charge delocalization. In the 9-chloroanthracene radical anion,[14e] the negative charge is spread out over the whole molecule, whereas it is more localized (on the oxygen atoms of the CO group) in the halobenzophenone.[14a] Interestingly, these two radical anions exhibit rather low cleavage rates in conventional media, allowing the kinetics changes to be easily observable in ionic liquids by classical transient electrochemical methods. Molecular quantum chemistry (B3LYP density functional theory) was used to evidence the key parameters responsible for the changes in the chemical reactivities in the framework of the Marcus-formalism and the "electron and bond cleavage" model developed by Savéant et al.[15]

Experimental Section

Room-Temperature Ionic Liquids. RTILs ([BMIM][TFSI], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [Me_3BuN][TFSI], trimethylbutylammonium bis(trifluoromethylsulfonyl)imide; [Et_3BuN][TFSI], triethylbutylammonium bis(trifluoromethylsulfonyl)imide) were prepared according to previously published procedures[16] (Scheme 1). Prior to each experiment, RTILs were carefully dried overnight by vacuum pumping and the amount of residual water was measured with Karl Fischer titration (Karl Fischer 652 Metrohm). The presence of water in ionic liquids (even for those which are immiscible in water) is an important parameter because the RTILs can absorb considerable amounts of water that result in large changes in their physical and chemical properties (viscosity and diffusion coefficients, conductivity, and so on).[1,17] The amount of water measured in our samples ranged from 200 to 300 ppm.

Chemicals. 4-Chlorobenzophenone, benzophenone, and ferrocene were from Acros Organics and used without further purification. Anthracene and 9-chloroanthracene from Aldrich were recrystallized prior to experiments. Acetonitrile (ACN) was purchased from SDS and used as received. Tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) was from Fluka (puriss, electrochemical grade).

Electrochemical Experiments. Because of the high viscosity of these media inducing low diffusion coefficients and low electrochemical currents,[7] it was necessary to perform the voltammetric experiments at relatively high concentration of electroactive substance, typically 7×10^{-3} to 1×10^{-2} mol·L^{-1}, in order to get good signal-to-noise ratios. The electrochemical cell was a classical three-electrode setup. The counter electrode was a Pt wire, and an Ag wire (immersed in HNO_3 65% prior to experiments, then rinsed thoroughly with water and ethanol) 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. Potential values are given against the ferrocene/ferrocenium couple. The working electrode was a glassy carbon disk (0.5 mm diameter). The electrode was carefully polished before each voltammetry experiment with 1 μm diamond paste and 0.25 μm alumina suspensions and ultrasonically rinsed in absolute ethanol. Electrochemical instrumentation consisted of a Tacussel GSTP4 programmer and of home-built potentiostat equipped with a positive-feedback compensation device.[18] The voltammograms were recorded with a 310 Nicolet oscilloscope. Experiments were performed at room temperature (20 ± 2 °C).

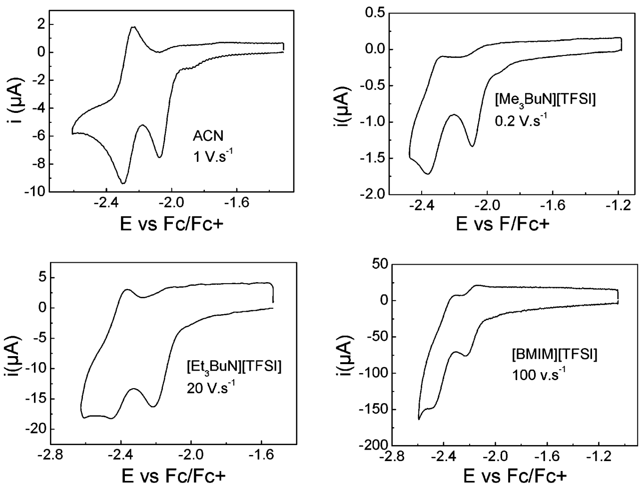


Figure 1. Cyclic voltammograms of the reduction of ClAnt (2×10^{-3} mol·L^{-1}) in ACN (+0.1 mol·L^{-1} Bu_4NBF_4) and ($\approx 1 \times 10^{-2}$ mol·L^{-1}) in [BMIM][TFSI],[Me_3BuN][TFSI] and [Et_3BuN][TFSI] at different scan rates on a 0.5 mm glassy carbon disk.

Numerical simulations of the voltammograms were performed with the BAS DigiSim simulator 3.03 (Bioanalytical Systems), using the default numerical options with the assumption of planar diffusion and a Butler−Volmer law for the electron transfer. The charge-transfer coefficient, α, was taken as 0.5.

Quantum Chemistry Calculations. The calculations were performed using the Gaussian 03W package.[19] Gas-phase geometries and electronic energies were calculated by full optimization without imposed symmetry of the conformations using the B3LYP[20] density functional with the 6-31G* basis set,[21] starting from preliminary optimizations performed with semiempirical methods. We choose B3LYP because of the delocalization of the unpaired electron in the aromatic radical anions that requires an adequate treatment of the electronic correlation.[20] We checked that the spin contamination remains low ($s^2 < 0.76$) for all the open-shell B3LYP calculations (for the pairs involving a radical anion). The effects of the base were previously evaluated in similar situations, and this base and method were suggested as a good compromise between calculation and accuracy.[22] For each cation−anion pair, several optimizations were performed starting from different initial geometries inspired by literature results,[22,23] leading either to the same type of conformers or to higher energy conformers. The conformers with the lower energies were kept in the comparison with experimental data.

Results and Discussion

Electroreduction of 9-Chloroanthracene. Figure 1 displays some typical cyclic voltammograms of the reduction of 9-chloroanthracene (ClAnt) in the three ionic liquids and for comparison in ACN (+ 0.1 mol·L^{-1} Bu_4NBF_4). Similar patterns can be described for the experiments performed in RTILs and

TABLE 1: Electrochemical Data for ClAnt in ACN and Ionic Liquids

	$E°_1$[a] (V)	$E°_2$[a] (V)	$\partial E_p/\partial \log(v)$ (mV/dec)	$k_s/\sqrt{D}$ ($s^{-1/2}$)	D[f] ($cm^2 \cdot s^{-1}$)	k_s ($cm \cdot s^{-1}$)	k_c (s^{-1})
[BMIM][TFSI]	−2.18	−2.39	−31.4[b]	119	$(1.8 \pm 0.9) \times 10^{-6}$	0.16	400−500
[Me$_3$BuN][TFSI]	−2.13	−2.33	−32.6[c]	190	$(5.7 \pm 1.6) \times 10^{-7}$	0.14	1000
[Et$_3$BuN][TFSI]	−2.17	−2.38	−27.2[c]	122	$(4.3 \pm 1.2) \times 10^{-7}$	0.08	800−1000
ACN	−2.19	−2.39	−27.2[d]	1200[e]	2.5×10^{-5} [g]	5−6	200−300[h]

[a] Vs the ferrocene/ferrocenium couple. [b] For $v = 0.1-70$ V·s^{-1}. [c] For $v = 0.1-100$ V·s^{-1}. [d] For $v = 0.1-5$ V·s^{-1}. [e] From ref 28. [f] In RTILs, from linear variation $i_p = f(\sqrt{v})$. [g] From ref 29 and assuming that diffusion coefficients are equal for anthracene and its chloro derivatives. [h] From ref 14e.

ACN. At low and moderate scan rates (0.2−50 V·s^{-1}), the voltammograms exhibit two successive one-electron waves, the first one being chemically irreversible while the second one is reversible.

In the three ionic liquids, we found that the height of the first wave corresponds to a one-electron per molecule stoichiometry by comparison to the reversible wave of ferrocene under the same conditions. The second wave (located at the more negative potentials) displays all the characteristics of the reversible wave of the anthracene/anthracene radical anion system from comparison with an authentic sample of anthracene. Upon increasing the scan rates, this second wave decreases to the point of vanishing as the first wave simultaneously becomes reversible. These observations show that the second cathodic process corresponds to the reduction of the product formed during the first reduction process. In the scan-rate range where the first reduction wave is irreversible, analysis of the first peak potential as a function of scan rate displays a linear variation with a slope close to 29 mV per a 10-fold increase of v, in agreement with a first-order reaction following a fast electron transfer.[6] All these observations are consistent with the well-known mechanism commonly described for the electrochemical reduction of aryl halides and involves the following steps:[6,14]

$$\mathrm{ArX} + e^- \rightleftarrows \mathrm{ArX}^{\bullet -} \qquad E°, k_s, \alpha \tag{1}$$

$$\mathrm{ArX}^{\bullet -} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^- \qquad k_c \tag{2}$$

Ar$^\bullet$ is converted into ArH from a series of fast reactions which does not consume electrons, certainly involving H-atom transfer from the ionic liquid to the radical[24] in agreement with the H-donor ability of the cations considered here.[25] Then, ArH formed during the first process is reversibly reduced at the level of the second wave into its anion radical.

The standard potentials $E°$ for the ClAnt/ClAnt$^{\bullet -}$ couples were derived as the half-sum between the forward and the backward scans from the reversible voltammograms.[6] As seen in Table 1, $E°$ values obtained in the three ionic liquids and in ACN are almost identical,[26] suggesting that if any specific solvation of the ClAnt$^{\bullet -}$ by the RTIL exists, its effects remain negligible. Concerning the electron-transfer rates, the kinetics parameter $k_s/\sqrt{D}$ was estimated from the peak-to-peak potential separations assuming a Butler−Volmer law and a charge-transfer coefficient $\alpha = 0.5$ (where k_s is the standard heterogeneous electron-transfer rate constant uncorrected from the double layer effect and D the diffusion coefficient taken equal for all species).[6,27]

As seen in Table 1, the k_s values are lower by at least 1 order of magnitude in the ionic liquids than in ACN in agreement with our previous studies.[8] The C−Cl cleavage kinetics rate constants k_c were determined by comparison of the experimental voltammograms (variation of the reversibility) with calculated curves for different scan rates.[6] The changes from ACN electrolytic medium to ionic liquids electrolytic media result in a small but significant increase of k_c, the largest increase being found in [Me$_3$BuN][TFSI].

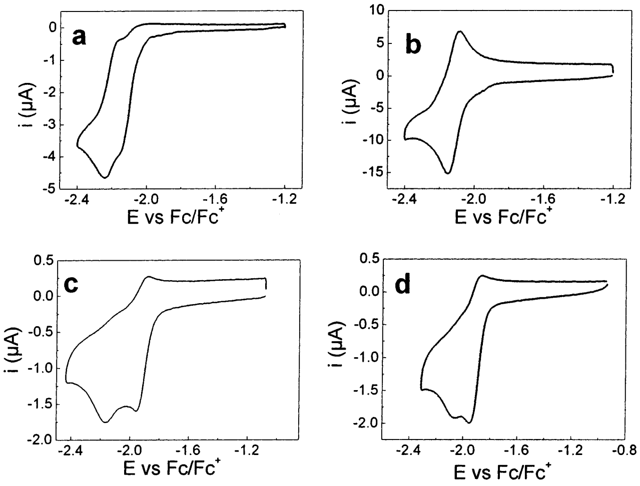


Figure 2. Cyclic voltammograms of ClBz (2×10^{-3} mol·L^{-1}) in ACN at (a) 0.2 V·s^{-1} and (b) 5 V·s^{-1} and ClBz ($\approx 1 \times 10^{-2}$ mol·L^{-1}) in (c) [Me$_3$BuN][TFSI] and (d) [BMIM][TFSI] at 0.2 V·s^{-1} on a glassy carbon disk electrode (0.5 or 1 mm diameter).

Electroreduction of 4-Chlorobenzophenone. In organic solvent (see Figure 2a and b), the reduction of the 4-chlorobenzophenone, ClBz, follows a mechanism similar to that described above for the reduction of ClAnt.[14a,e,30] The first irreversible process corresponds to the reductive cleavage of the carbon−halogen bond in the radical anion ClBz$^{\bullet -}$, leading to the formation of benzophenone with a C−Cl cleavage rate constant k_c reported in the range of 5−10 s^{-1}.[14a,30] The quantitative formation of benzophenone is attested by the presence of the second electrochemical process (reversible in ACN) that corresponds to the formation of the benzophenone radical anion Bz$^{\bullet -}$. Depending on the experimental conditions (acidity, presence of small cations), it is known that Bz$^{\bullet -}$ can become unstable, leading either to the alcohol or to the pinacol (dimerization).[10c,31]

The nature of the mechanism is strongly dependent on the media,[10c,30,31] making this system a sensitive tool for probing the effect of ionic liquids. Indeed, we observed that the reduction of 4-chlorobenzophenone displays very different patterns (Figure 2) in the ionic liquids and in ACN. In the ionic liquids, two one-electron reduction waves are observed as in ACN, but the first wave is now partially reversible whereas the second wave is irreversible (in the scan-rate range 0.05−50 V/s). Moreover, the reversibility of the first reduction wave (i.e., the lifetime of ClBz$^{\bullet -}$) decreases when the initial concentration of ClBz is increased, indicating that the rate-determining step is now a bimolecular reaction involving ClBz$^{\bullet -}$. Simultaneously upon increasing the initial concentration of ClBz, the second irreversible wave tends to disappear. For a given ClBz concentration,

TABLE 2: Electrochemical Data for ClBz in Ionic Liquids and in ACN

	$E°_1{}^a$ (V)	$E^{red}{}_p{}^{a,b}$ (V)	$k_s/\sqrt{D}$ ($s^{-1/2}$)	D^c ($cm^2 \cdot s^{-1}$)	k_s ($cm \cdot s^{-1}$)	k_{dim} ($L \cdot mol^{-1} \cdot s^{-1}$)
[BMIM][TFSI]	−1.91	−2.15	47	$(7.1 \pm 1.3) \times 10^{-7}$	0.04	300−500
[Me_3BuN][TFSI]	−1.89	−2.14	237	$(1.2 \pm 1.4) \times 10^{-7}$	0.08	800−1000
[Et_3BuN][TFSI]	−2.00	−2.35	95	$(2.3 \pm 1.2) \times 10^{-7}$	0.05	3000
ACN	−2.1	−2.8		1.9×10^{-5} [d]	0.7−1.2	

[a] Vs the ferrocene/ferrocenium couple. [b] Reduction peak potential of $ClBz^{\bullet-}$ at $v = 10$ V·s^{-1} [c] Diffusion coefficient D measured from linear variation $i_p = f(\sqrt{v})$. [d] From ref 34 (in tetraethylammonium perchlorate) assuming diffusion coefficients are similar for benzophenone and its chloro derivative.

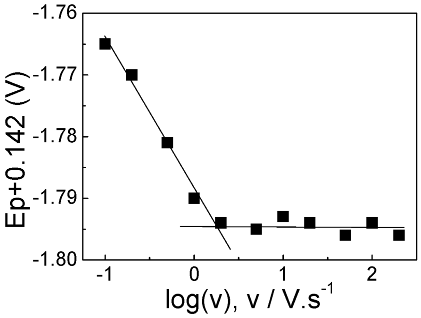


Figure 3. Cyclic voltammetry of 30×10^{-3} mol·L^{-1} ClBz in [Me_3BuN][TFSI] at a 0.5 mm diameter disk glassy carbon electrode. Variation of the reduction peak potential with the logarithm of the scan rates v.

it is possible to recover both the second wave height and the reversibility of the first one upon raising the scan rates (i.e., decreasing the experimental time). For comparison, we also investigated in the ionic liquids the electrochemical reduction of the unsubstituted benzophenone Bz, which displayed the same general behaviors as ClBz (shape of the voltammetric currents, variations with the scan rates and concentrations, and so on), the only difference being a reduction potential about 60−70 mV more positive for ClBz than for Bz. From this similarity, we can conclude that the first monoelectronic reduction of ClBz corresponds to the production of its radical anion without the cleavage of the C−Cl bond, and the second wave to the reduction of $ClBz^{\bullet-}$ into the dianion. At this point, it is worth emphasizing that if two reduction waves are visible both in ACN and in RTILs (compare Figure 2a and b and Figure 2c and d), the second reductions have two different origins (see discussion below). Another observation is the large positive shift in the ionic liquids for the second reduction of the benzophenones (from 450 to 650 mV versus ACN) and the relatively smaller positive shift for the standard potential of the $ClBz/ClBz^{\bullet-}$. It results in an enhancement of the dismutation driving force of the radical anion that is indicative of strong ion pairs that are obviously stronger with a double-charged dianion than a mono-charged radical anion.[7f,32]

For the experiments performed with the largest concentration of ClBz ($C° = 30 \times 10^{-3}$ mol·L^{-1} in [Me_3BuN][TFSI]), the cyclic voltammograms are irreversible until $v \approx 5$ V/s. In such conditions, the peak potential (E_p) varies linearly as a function of log(v) (v in the scan-rate range 0.05−2 V·s^{-1}) with a slope $\partial E_p/\partial \log v = 20.8$ mV per 10-fold increase of v (Figure 3).

The value of $\partial E_p/\partial \log v$ and the variations of the voltammograms' reversibility with the initial concentrations of ClBz (or Bz) are fully consistent with a mechanism involving an irreversible dimerization between two $ClBz^{\bullet-}$ without the occurrence of the C−Cl bond breaking.[33] The reactions occurring in ACN and in RTILs can be summarized in the following mechanistic scheme:

$$\mathrm{ClBz} + e^- \rightarrow \mathrm{ClBz}^{\bullet-} \qquad E_1°, k_s, \alpha \tag{3}$$

$$\mathrm{ClBz}^{\bullet-} + \mathrm{ClBz}^{\bullet-} \rightarrow \mathrm{dimer} \qquad k_{dim} \tag{4}$$

$$\mathrm{ClBz}^{\bullet-} \rightarrow \mathrm{Bz}^{\bullet} + \mathrm{Cl}^- \qquad k_c \text{ (then leads to Bz)} \tag{5}$$

$$\mathrm{ClBz}^{\bullet-} + e^- \rightarrow \mathrm{ClBz}^{2-} \qquad E^{red}{}_p \tag{6}$$

In ACN, the major decay for $ClBz^{\bullet-}$ is the cleavage of the C−Cl bond (reaction 5) whereas the dimerization (4) that does not occur in ACN (+0.1 mol·L^{-1} Bu_4NBF_4) becomes the faster decay route in RTILs. In this last case, when the initial concentration of ClBz is increased, the dimerization rate (reaction 4) is amplified and the competitive reduction of $ClBz^{\bullet-}$ (reaction 6, second voltammetric peak) does not occur anymore.

Taking into account this mechanistic scheme, we extracted the kinetics parameters k_s, k_{dim}, and an upper limit for k_c (See Table 2). The kinetic parameter $k_s/\sqrt{D}$[6,27] and the value for the standard rate constant were measured as described above for ClAnt. For the highest concentrations of ClBz (to favor reaction 4 versus 5), the reversibility of the first reduction allows the determination of k_{dim} by comparison with calculated curves (see Table 2).[6] The dimerization rates correspond to a rather slow process that is slightly sensitive to the nature of the ionic liquid cations in the order $Et_3BuN > Me_3BuN \geq$ BMIM (Table 2).

Similar analysis performed at low ClBz concentration (i.e., when dimerization 4 is the slowest) provides estimation for k_c that was found to be lower than 1 s^{-1} in the RTILs. This value is more than 10 times below the values reported in ACN, showing that the change of mechanism is due not only to an increase of the dimerization rate but mainly to a large decrease of the carbon−halogen cleavage rate.

Estimation of Ion-Pairing Interactions with Molecular Modeling. Ab initio calculations in the gas phase have already been used to characterize the ion-pair clusters between cations and anions involved in the preparation of RTILs. They were proposed as a way for comparing the interaction energies between cation and anion in ionic liquids.[23] Even if these descriptions are only partial since anion−cation clusters are treated as isolated species (gas phase), they provide a reasonable agreement with crystallographic data[35] and remain useful for detecting trends in the experimental data collected in liquid phase.[22,23] The B3LYP density functional method[20] with the 6-31G* base[21] was chosen as a compromise between time and accuracy taking into account the size of the systems. In a simplification purpose, the ion-pair energies were computed on the benzophenone and anthracene radical anions instead of their halogenated analogues. When data were available in the literature (as for the [BMIM][TFSI] cluster), we checked that the calculated conformations were similar to the published results issued from calculations performed at a higher level of

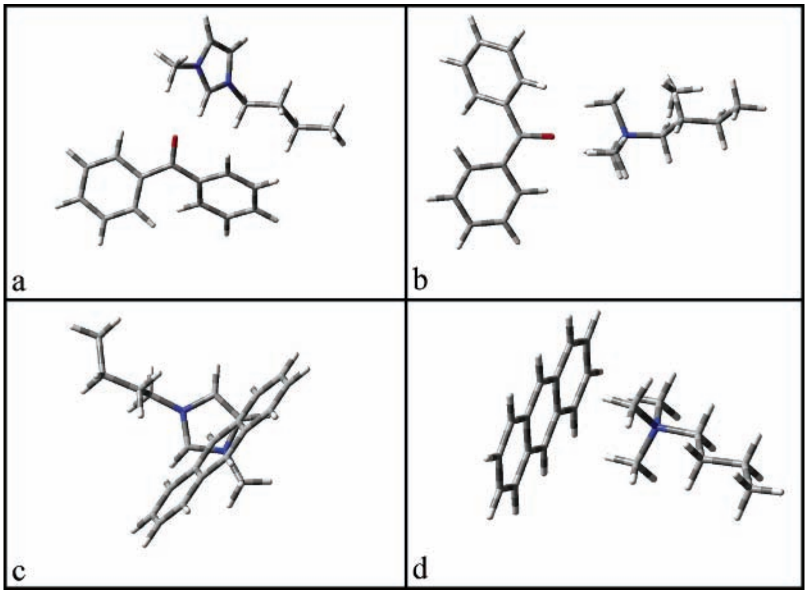


Figure 4. Optimized conformations for benzophenone and anthracene radical anion clusters with cations of ionic liquids. (a) $BMIM^+$, benzophenone$^{\bullet-}$. (b) $Me3BuN^+$, benzophenone$^{\bullet-}$. (c) $BMIM^+$, anthracene$^{\bullet-}$. (d) $Me3BuN^+$, anthracene$^{\bullet-}$.

theory, supporting the choice of the 6-31G* base.[23] For the clusters involving the imidazolium cation, the most stable conformers always display geometries with the anion located near the C−H on the 2-position of the $BMIM^+$. In agreement with X-ray crystallographic data, similar geometries have been reported for clusters between $BMIM^+$ and small anions indicating a strong hydrogen-bonding ability for $BMIM^+$.[35] For clusters with radical anions, we performed several attempts in order to break the H bonding and to favor a possible interaction between the two π-systems by starting the calculations from initial conformations where the aromatic ring of the radical anion was facing the imidazolium ring. In all cases, the optimization converged to a conformer where the anion is localized near the C2-position (even when the radical anion was the anthracene radical anion) demonstrating that these conformations are not stable. When the cation is an ammonium, the most stable conformers simply correspond to geometries where the distance between the nitrogen atom (that carries the charge) and the anion is minimum. (See Figure 4).

Considering the conformers with the lowest energies, we estimated the interaction energy from the difference $\Delta U_{\mathrm{ionpair}} = U_{\mathrm{ionpair}} - U_{\mathrm{cation}} - U_{\mathrm{anion}}$ where the U are the B3LYP electronic energies.

The (B3LYP) $\Delta U_{\mathrm{ionpair}}$ range in 70−80 kcal·mol^{-1} (3.0−3.5 eV) in agreement with previously calculated values for these types of ion associations.[23] We also defined a relative interaction energy $\Delta U_{\mathrm{rel}} = \Delta(\Delta U_{\mathrm{ionpair}} - \Delta U_{\mathrm{solvent}})$ that is the difference between the interaction energies calculated for the clusters formed with the ions of the ionic liquids ($\Delta U_{\mathrm{solvent}}$) on one side and the cations of the ionic liquids and the generated radical anions on the other side ($\Delta U_{\mathrm{ionpair}}$). We suggest that ΔU_{rel} provides a better description of the ion-pairing stabilization, taking into account that the formation of the cluster cation−radical anion competes with the "intra-associations" between the ions of the RTIL. Experimentally, the ion-pairing stabilization of the radical anion $\Delta G°_{\mathrm{ionpair}}$ can be probed through the variations of the $ArX/ArX^{\bullet-}$ couples' standard potentials $E°$ when passing from the organic solvent to the ionic liquids according to $\Delta(E°_{\mathrm{RTIL}} - E°_{\mathrm{ACN}}) \approx -\Delta G°_{\mathrm{ionpair}}$ that can be compared with the calculated ΔU_{rel}.[36] For the delocalized radical anion of the 9-chloroanthracene, the $E°$ shows little change with the media in agreement with theoretical expectations.[26] As seen in Table 3, the corresponding calculated stabilization energies ΔU_{rel} remain small in the three ionic liquids. In contrast, calculations predict large variations of $E°$ for the reduction of the 4-chlorobenzophenone as experimentally observed. The effect is more important in [BMIM][TFSI] and in [Me_3BuN][TFSI] than in [Et_3BuN][TFSI] (Table 3). On the whole, a good correlation is obtained between the calculated ΔU_{rel} and the experimental $\Delta E°_{(\mathrm{RTIL-ACN})}$, supporting the proposition that the largest part of transfer free energy is related to ion-pair associations (see Figure 5).

TABLE 3: Calculated and Measured Ion-Pair Stabilizations

ion pairs	$\Delta U_{\mathrm{ionpair}}{}^{a}$ (kcal/mol)	$\Delta U_{\mathrm{rel}} = \Delta U_{\mathrm{ionpair}} - \Delta U_{\mathrm{solvent}}{}^{a}$ (eV)	$-\Delta E°_{(\mathrm{RTIL-ACN})}{}^{b}$ (eV)
$Me3BuN^+$, $TFSI^-$	−77.2		
$Me3BuN^+$, Benzophenone$^{\bullet-}$	−86.5	−0.40	−0.21
$Me3BuN^+$, anthracene$^{\bullet-}$	−77.4	−0.01	−0.06
$Et3BuN^+$, $TFSI^-$	−75.6		
$Et3BuN^+$, benzophenone$^{\bullet-}$	−82.6	−0.30	−0.10
$Et3BuN^+$, anthracene$^{\bullet-}$	−75.6	0.0	−0.02
$BMIM^+$, $TFSI^-$	−79.4		
$BMIM^+$, benzophenone$^{\bullet-}$	−89.1	−0.42	−0.19
$BMIM^+$, anthracene$^{\bullet-}$	−80.9	−0.06	−0.01

[a] Calculated for H-aromatic molecules (see text). [b] Measured for halogenated aromatic molecules.

Considering only the two quaternary ammoniums, the $ClBz^{\bullet-}$ is more stabilized in [Me_3BuN][TFSI] than in [Et_3BuN][TFSI]. Since this last one is the bulkiest ammonium-based ionic liquid, it induces a larger cation−anion distance in the pair leading to a lower electrostatic stabilization. In the case of [BMIM][TFSI], the bulkiness should be over-compensated by the ability of the imidazolium cation to form an H bond with the C=O of the carbonyl that is evidenced from its position near the C2-H of $BMIM^+$. This interaction is also enhanced by the charge localization on the carbonyl group (highest B3LYP calculated charges in anthracene and benzophenone radical anions are −0.35 and −0.62, respectively).[37]

The next question concerns the effect of ion pairing on the electron-transfer kinetics. This point is fundamental for the use of RTILs as it concerns the production rates of the reactive

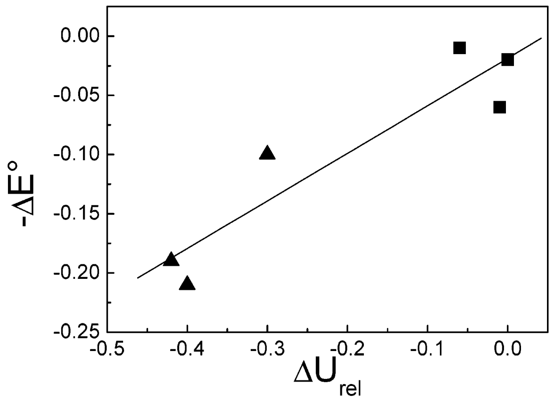


Figure 5. Comparison between experimental and theoretical ion-pair stabilization energies in eV. (▲) Benzophenone. (■) Anthracene. (Linear regression: $-\Delta E° = 0.402 \times \Delta U_{rel} - 0.019$ V.) Experimental error on $\Delta E° = \pm 10$ mV.

intermediates in the RTILs. A simple treatment of the electron-transfer dynamics with ion pairing as in RTILs is to consider the ion-pair association as a fast postequilibrium following the electronic transfer.[10b] In such a case, the ion pair is characterized by its thermodynamic formation constant $K_{ionpair} = \exp(-F\Delta G°_{ionpair}/RT)$. The formal kinetics for this situation has already been described for various situations in terms of EC_{rev} mechanisms (see ref 10 and the references therein). Increasing the value of $K_{ionpair}$ makes the electron transfer more irreversible because the reverse electron transfer is annihilated by the transformation of the free radical anion into the ion pair.[10b] As we did for the electron-transfer thermodynamics, we can estimate $\Delta G°_{ionpair}$ from the variations of the $E°$ as a function of the media. With stabilization energies $\Delta G°_{ionpair}$ around 0.1 and 0.2 eV, we expect decreases of the activation energies of 0.05−0.1 eV and thus decreases of k_s by a factor of 10−50.[11] These expectations are in the range of what is experimentally observed, but do not explain the relative trends between anthracene and benzophenone, as the k_s variations do not correlate the standard potential shifts. However, because we only measure apparent standard kinetics constants k_s uncorrected from the double layer effect,[6] these discrepancies may also reveal different structures of the electrode/solution interface in the ionic liquids as compared to that encountered in more conventional electrolytic media (variation of the double-layer structure of electrode).

Carbon−Halogen Cleavage Rates. The evolutions of the cleavage reactivity with the media are completely different for the two types of radical anions. A small increase of the C−Cl cleavage rate is observed for the 9-chloroanthracene radical anion whereas a large decrease is found for the 4-chlorobenzophenone radical anion. Concerning the driving force of the process, the free energy of the cleavage reaction in the radical anion can be expressed as[15]

$$\Delta G° = D_{ArX} + E°_{ArX/ArX^{\bullet-}} - E°_{X^{\bullet}/X^{-}} - T\Delta S \qquad \text{(I)}$$

where D is the homolytic dissociation energy of the Ar−X bond, $E°$ the standard potentials for the ArX/ArX$^{\bullet-}$ and X$^{\bullet}$/X^{-} couples, and $T\Delta S$ an entropic term. For both radical anions, the bond dissociation energies are not expected to vary much with the solvent.[10c] Concerning the activation energy of the process, the model of the dissociative electron transfer developed by Savéant[15] was successfully adapted to the case of the carbon−halogen bond cleavage in radical anion.[38] In this model, the bond cleavage is described as a concerted process with an intramolecular electron transfer of the unpaired electron from the π^* orbital of an aromatic ring into the C−X σ^* orbital. In the framework of this model, the activation free energy $\Delta G^{\ddagger}$ is related to the standard free-energy of the reaction $\Delta G°$ by Marcus-type quadratic relationship where $\Delta G^{\ddagger°}$ is the intrinsic activation barrier (i.e., a barrier for $\Delta G° = 0$):

$$\Delta G^{\ddagger} = \Delta G^{\ddagger°}\left(1 + \frac{\Delta G°}{4\Delta G^{\ddagger°}}\right)^2 \qquad \text{(II)}$$

The intrinsic activation barrier is given by

$$4\Delta G^{\ddagger°} = D_{ArX} + E°_{ArX/ArX^{\bullet-}} - E°_{Ar^{\bullet}/(Ar^{\bullet})^{\bullet-}} - T\Delta S^{\ddagger} + \lambda_0 \qquad \text{(III)}$$

where λ_0 is the solvent reorganization energy. In the latter expression, the excited state $(Ar^{\bullet})^{\bullet-}$ is formed from $Ar^{\bullet}$ by injecting one electron into the π^* orbital of $Ar^{\bullet}$. As discussed previously, a mutual compensation between the variations of the two standard potentials is expected because the distribution of the negative charge should be similar in both anions.[10c] It follows that the intrinsic barrier should not vary much from ACN to the RTILs, and the sources of the kinetics changes have to be found in variations of the driving force. For the reduction of the 9-chloroanthracene, we found that the formal potential $E°_{ArX/ArX^{\bullet-}}$ does not vary appreciably when passing from ACN to the ionic liquids. According to the previous equations, the decrease of $\Delta G°$ (and the acceleration of the cleavage rate in ClAnt$^{\bullet-}$) is thus related to a better stabilization of the leaving chloride ion due to ion pairing with the cations of the ionic liquids. The interactions of the RTIL cations with the small Cl^{-} ion are expected to be stronger than those involving the bulky and delocalized chloroanthracene radical anion. When discussing the intrinsic barrier (eq III), the solvent reorganization energy term λ_0 is usually neglected in conventional media for most aryl halides because its contribution is small relative to the other factors. One may suggest that λ_0 values are larger in ionic liquids than in conventional media taking into account that RTILs exhibit a higher degree of molecular organization[39] and ion-pair associations. However, such an increase of λ_0 would result in a decrease of the cleavage rate, meaning that, if this effect exists, it is overcompensated by the stabilization of the leaving Cl^{-}.

The situation is completely different for 4-chlorobenzophenone reduction. A large increase of the reduction potential is observed, leading to the conclusion that the driving force for the C−Cl cleavage is less favorable in the RTILs by around 0.2 eV. Considering a Marcus-type variation, this variation leads to an increase of the activation energy of 0.1 eV and a decrease of the cleavage rate around 50 corresponding to kinetics constants k_c in the range of 0.1−0.2 s^{-1}. These expectations are fully consistent with the experiments ($k_c < 1$ s^{-1}) but are below the current limit of measurement due to the concomitant increase of the dimerization rate. On the whole, the behavior observed in ionic liquids has the same origin as the variations reported for the electroreduction of benzophenone derivatives in the presence of small cations in organic aprotic solvents.[10c,30] The stabilization of the radical anion becomes the major effect that completely overcomes the stabilization of the leaving Cl^{-}. The acceleration of the pinacolization kinetics was also explained by the existence of strong ion-pair associations with the electrogenerated anion radicals that facilitate the coupling between two charged radical anions.[10c,31] However, this behavior that is mainly observed with small cations in organic media exists in a larger amount with the bulky cations of the ionic liquids in the RTILs.

Conclusion

The reactivity of radical anions is considerably affected when passing from an organic solvent to an ionic liquid as illustrated with the variation of the cleavage reactivity in halogenated radical anions. The effects are mainly dependent on the charge delocalization in the radical anion. When the negative charge is spread out over the whole molecule as for 9-chloroanthracene radical anion, the carbon−halogen bond cleavage accelerates due to specific interaction between the cation of the ionic liquid and the small leaving ion. In radical anions where the negative charge is more concentrated on a small area of the molecule (mostly on the oxygen atom of the carbonyl group), a large decrease of the cleavage reactivity occurs. In this case, the stabilization of the leaving group still exists but is largely overcompensated by the stabilization of the radical anion in agreement with the positive shift of the reduction potential. As explained previously,[10c] the ion pair association stabilizes the π^* orbital where the unpaired electron is located and thus decreases its ability to be transferred into the σ^* of the breaking bond.

Quantum chemistry calculations of the relative ion pair stabilization energies agree well with the experimental variations of the standard potentials. This demonstrates the ion-pair character of the stabilization in the ionic liquid and provides a way for predicting the modifications in the cleavage reactivity. These modifications can be accompanied by a total change of mechanism as other reactions like the dimerization between two charged radical anions are greatly favored by the ion-pair associations and can easily overrun the cleavage reaction.

On the whole, our results fall in line with the reported effects of the addition of small cations (Li^+, Mg^{2+}) in organic solvents but are notably larger. This last point is worth being noticed regarding the bulkiness of the ionic liquid cations (large tetraalkylammonium or imidazolium cations) since the ion-pairing strength rapidly decreases as the size of the cations increase.[10] By definition, ionic liquids contain a cation at very high concentration and thus offer the opportunity to generate unusually strong ion-pairing association. Moreover, the ion-pairing effect considered here is actually different from that encountered in conventional solvents where the ion-pair association is built between a discrete ion surrounded by solvent molecules and another solvated species. In ionic liquids, there is no molecular solvent present to solvate the ionic species. Consequently, the solvent shell is ionic and an electrogenerated ionic species would always be coordinated by one or more counterions from the ionic liquids that should explain the large and unusual effect observed in this media.

It is worth emphasizing that these general conclusions, illustrated here with the 4-chlorobenzophenone and 9-chloroanthracene radical anions, are not limited to haloaromatic compounds. The same key effects are expected to influence the cleavage steps that are involved in practical organic synthesis in ionic liquids and also for different types of leaving groups.

Supporting Information Available: Drawings of the optimized geometries at the B3LYP/6-31G* level with the corresponding Cartesian coordinates and calculated electronic energies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) The literature about ionic liquids is rapidly growing. For a general view about current research in the field, see: *Ionic liquids as green solvents. Progress and prospects;* Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 856; American Chemical Society: Washington, DC, 2003.

(2) See general comments from R. D. Rogers and K.R Seddon in the preface of ref 1 about unknown toxicity of RTIL and precautions when using ionic liquids.

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(24) Several reports show that the outcome of Ar$^•$ is strongly dependent on the considered solvent.[14b−d] For example, in ACN, aryl radicals that are good H-atom scavengers, abstract a hydrogen atom from the solvent. The resulting radical of the solvent undergoes then a series of fast reactions (reduction, deprotonation, oxidation) that does not, on the whole, consume electrons. Even if a detailed discussion about the conversion of Ar$^•$ to ArH is beyond the scope of the present article as the rate-determining step is the cleavage of the radical anion ArX$^{•-}$, it is noticeable that the one-electron stoichiometry found here demonstrates that the conversion of Ar$^•$ into ArH involves a fast H-atom abstraction from the ionic liquid (cation or anion) by the aromatic radical.[25]

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(26) We assume that the passage from acetonitrile to ionic liquid does not considerably influence the standard potential of the ferrocene/ferrocenium couple (used as an internal reference for potential standardization).[7g]

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(33) In ionic liquids, the production of pinacol has been reported in the photochemical reduction of several substituted benzophenones in competition with the benzhydrol formation.[13a] However, care should be taken when comparing photochemistry and electrochemistry. First, the photochemical reaction involves a different mechanism starting with H-atom transfer to the benzophenone. Second, reactive intermediate concentrations are several orders higher in electrochemical production than in photochemistry that greatly favors second-order reaction pinacolization.

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