J. Phys. Chem. A **2003,** *107,* 745−752

Reactivities of Some Electrogenerated Organic Cation Radicals in Room-Temperature Ionic Liquids: Toward an Alternative to Volatile Organic Solvents?

C. Lagrost, D. Carrié, M. Vaultier, and P. Hapiot*

Synthèse et Electrosynthèse Organiques, UMR CNRS 6510, Institut de chimie de Rennes,
Université de Rennes 1, Campus de Beaulieu, Av. Gal. Leclerc, 35042 Rennes CEDEX, France

Received: September 4, 2002; In Final Form: November 5, 2002

Four different ionic liquids, based on 1-alkyl-3-methylimidazolium or quaternary ammonium cations, were used as reaction media for several typical electrochemical reactions with a strict control of the residual water concentration. The oxidation of organic molecules (anthracene, naphthalene, durene, 1,4-dithiafulvene, and veratrole) for which the cation radicals undergo first and second-order kinetics reactions were investigated in ionic liquids and compared with their behavior in acetonitrile. From the analysis of the voltammetric current responses, the reaction mechanism was established and the thermodynamic and kinetics parameters were extracted. The most interesting result is that the nature of investigated mechanisms is almost unchanged in ionic liquids as compared with conventional organic media. A decrease of the electron-transfer kinetics from the aromatic molecules to the electrode (around 1 order of magnitude) is observed for all of the studied molecules, indicating an higher solvent reorganization during the charge transfer. The kinetics of the chemical reactions triggered by the electron transfer are slightly affected by the use of ionic liquid. The only noticeable effect is a decrease of the bimolecular reactions rates partly due to a lowering of the limiting diffusion-controlled kinetics rate constant together with a specific solvation effect of reactants in these special media. These preliminary electrochemical experiments appear as encouraging results for the use of ionic liquids in a "green" electrochemistry.

Introduction

Room-temperature ionic liquids (RTILs) are attracting an increasing attention in diverse fields of chemistry because of their special physical and chemical properties (stability at high temperature, negligible vapor pressure, low toxicity, nonflammable, nonvolatile, etc.).[1,2] Among these neoteric solvents, simple room-temperature ionic liquids are obtained by the combination of large organic cations (*N*,*N*-dialkylimidazolium, quaternary ammoniums, phosphonium, pyridinium, etc.) with a variety of anions ($AlCl_4^-$, PF_6^-, BF_4^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, etc.). (For a review, see, for example, refs 1 and 2.) Most recent works in which ionic liquids were used concern catalysis, extraction processes, and organic synthesis,[1,2] and RTILs were proposed as "green" alternatives to volatile organic solvents (VOS), offering the great advantages to be environmentally friendly and to limit hazardous problems in chemical plants or laboratories. In electrochemistry, because of their desirable properties, RTILs were considered as versatile electrolytes for diverse technologies such as electroplating of base metals, rechargeable batteries, photoelectrical cells, electrochemical devices.[3,4] Several electrochemical investigations considering different RTILs have shown that some of them present a good ionic conductivity and a wide potential window (up to 5V).[5−8] Although the use of room-temperature ionic liquids in electrochemistry is not new (see for example the pioneering work of Hurley and Wier in the late 1940s),[9] few fundamental studies have focused on the reactivity of the electrogenerated organic species. For example, the potentialities of ionic liquids in electrosynthesis of organic materials have been investigated for the electropolymerization of conducting polymers.[10,11] In 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid, different electrochemical studies considering silver, nickel salen, ferrocene, and tetrathiafulvalene have been reported.[3,12,13] Recently, the effects of water on the redox properties of three well-known redox couples have been investigated in two imidazolium-based PF_6^- and BF_4^- ionic liquids.[14] More recently, studies of the electrochemical behavior of $Ru(bpy)_3^{2+}$ were performed in both imidazolium and tetraalkylammonium-based ionic liquids to probe the electrochemical and solvation properties of these ionic liquids,[15] whereas the direct electrochemical reduction of hemin (protoporphyrin IX iron (III) chloride) was investigated in imidazolium-based PF_6^- ionic liquids.[16] In the same field, recent works have reported on several electron-transfer reactions triggered via pulse radiolysis: the reaction kinetics were investigated from a fundamental point of view to describe the effects of solvation and of these special media on elementary radical reactions.[17] Because ionic liquids, being both electrolytes and solvents, would appear to be very attractive for organic electrochemistry, it seems of interest to increase the amount of fundamental studies on the electrochemistry of organic compounds in these nonconventional media in order to fully evaluate their potentiality in organic electrosynthesis, that is their possibilities for a "green" electrochemistry and/or new classes of electrochemical reactions.

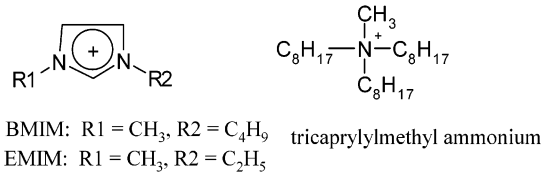
Thus, our idea was to explore some known classical electrochemical reactions, from the simple reversible process to more complicated ones for which chemical reactions (protonation, nucleophilic attack, radical−radical coupling, etc.) are associated with electron transfer. In this connection, we electrogenerated several cation radicals of aromatic (or polyaromatic) molecules in two types of RTILs that have been shown

---

* To whom correspondence should be addressed. E-mail: philippe.hapiot@univ-rennes1.fr.

10.1021/jp026907w CCC: $25.00

SCHEME 1: Cations Used to Prepared the RTILs



to exhibit good electrochemical stability,[14,15] allowing high anodic window limit (2.2−2.4 V/SCE under our experimental conditions).[18] Thus, the RTILs used in this work were based both on long alkyl chain quaternary ammonium and on 1-alkyl-3-methylimidazolium cations (alkyl = ethyl and butyl) in combination with different nonnucleophilic counteranions (PF_6^- and $N(SO_2CF_3)_2^-$). These RTILs that are air and water stable are good solvents for a wide range of organic molecules, and their viscosity remains compatible with electrochemical experiments at room temperature. Consequently, the stability of the electrogenerated cation radicals was investigated by cyclic voltammetry at low and high scan rates, and the current responses were analyzed in detail to extract the corresponding thermodynamic and kinetics parameters. The results are discussed on the basis of comparison with the behaviors observed in classical organic solvents (acetonitrile, dimethylformamide, dichloromethane, etc.).

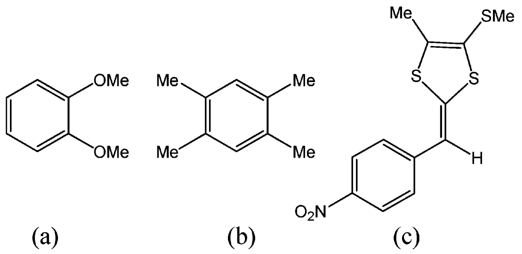
Experimental Section

Ionic Liquids. RTILs (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTf$_2$]; 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM][NTf$_2$]; 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$]; and tricaprylylmethylammonium bis(trifluoromethylsulfonyl)imide, [$(C_8H_{17})_3NCH_3$][NTf$_2$], were prepared according to previously published procedures (Scheme 1).[19] Prior to each experiment, RTILs were dried overnight (Kugel-Rohr), and the amount of residual water was determined with Karl Fischer titration (Karl Fischer 652 Metrohm). Even for ionic liquids such as [EMIM][NTf$_2$], [BMIM][NTf$_2$], or [BMIM][NTF$_2$], which are immiscible with water, these RTILs can absorb considerable amounts of water resulting in changes in their physical or chemical properties (viscosity and diffusion coefficients, conductivity, etc.).[1,2,5,14,20−22] The presence of water in the ionic liquids may also accelerate the deprotonation reaction, with the water acting as a weak base. The amount of water measured in the samples at the end of each experiment ranged from 300 to 500 ppm, except in the case of anthracene oxidation where slightly higher amount of water were used to favor the formation of anthraquinone (1500 ppm).

Chemicals. Durene, ferrocene, naphthalene, and anthracene were received from Aldrich and purified by recrystallization prior to experiments. Anthraquinone was from Janssen Chimica and purified by recrystallization prior to experiments. Veratrole (1,2-dimethoxybenzene) was from Aldrich and used as received. DTF−NO$_2$ was a gift of Prof. D. Lorcy (University of Rennes 1) and was synthesized according to a previously published procedure (Scheme 2).[23]

Electrochemical Experiments. Solutions of durene, anthracene, naphthalene, veratrole, ferrocene, or DTF−NO$_2$ in ionic liquids were prepared from stock solutions in dichloromethane that were added under strong stirring. The dichloromethane was subsequently removed under low pressure. In a first test, the absence of residual dichloromethane was checked by the absence of an NMR signal corresponding to CH_2Cl_2. In a second time, we checked that similar electrochemical behaviors are observed when the product is directly dissolved (in the case of anthracene). Because of the high viscosity of these media inducing low diffusion coefficients and low electrochemical currents,[1,2,5] it was necessary to carry out the voltammetric experiments at relatively high concentration of electroactive substance, typically 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 an iron wire, and a Pt wire coated with polypyrrole was used as a quasireference. This quasireference was checked against the ferrocene/ferricinium couple ($E° = 0.405$ V/SCE) used as an internal probe. For low scan rate cyclic voltammetry (0.1−1000 V s^{-1}), the working electrode was a platinum wire (0.3 mm or 1 mm diameter) sealed in soft glass. 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 a home-built potentiostat equipped with a positive-feedback compensation device.[24] The voltammograms were recorded with a 310 Nicolet oscilloscope. For high scan rate cyclic voltammetry, the ultramicroelectrode was a platinum wire (25 or 10 μm diameter) sealed in soft glass. The signal generator was an Agilent 33250A, and the data were acquired with an Agilent Infiniium oscilloscope (500 MHz, 1 Gsample/s). Experiments were performed at room temperature (20 ± 2 °C).

SCHEME 2: General Formula of Organic Molecules Considered in This Work (Veratrole (a), Durene (b), and DTF−NO$_2$ (c))



Numerical simulations of the voltammograms were performed with the BAS DigiSim simulator 3.03.

In contrast to experiments with DTF−NO$_2$ and veratrole for which clear electrochemical signals due to the DTF−NO$_2$ dimer or veratrole trimer were observed, only a weak reversible electrochemical wave was visible for the reduction of the authentic ionic liquids solutions of anthraquinone as well as for the reduction of the products obtained by oxidation of 1×10^{-2} mol L^{-1} anthracene in ionic liquids, probably because of the lack of solubility of anthraquinone in RTILs. To check the nature of the produced compound, we performed a potentiostatic electrolysis of anthracene (at 1.2 V/SCE) in ionic liquids. The yellow reaction mixtures were treated with dichloromethane and passed on a small silica gel column to extract the electrolysis product from the ionic liquids. The presence of anthraquinone was qualitatively checked by TLC, using dichloromethane as eluent.

Results and Discussion

Preliminary Experiments: Electrochemical Behavior of Ferrocene in Ionic Liquids. To check the possibility of detailed analysis of the electrochemical current response, we first focused on a fully reversible redox couple with the monoelectronic oxidation of ferrocene. To limit the interference of the residual ohmic drop with experimental measurements due to the working

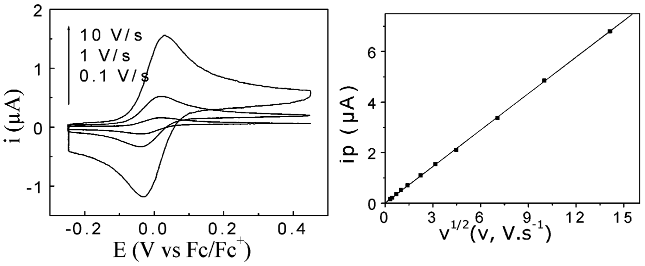


Figure 1. Cyclic voltammetry of the oxidation of ferrocene ($C° = 1 \times 10^{-2}$ mol L^{-1}) in [EMIM][NTf_2] on a 0.3 mm diameter disk platinum electrode (left). Variation of the anodic peak current with the square root of the scan rate (0.1−200 V s^{-1}; right).

electrode resistance, special care was taken to compensate the residual ohmic drop due to working electrode resistance, especially for the highest scan rates (>50 V s^{-1}). Although ionic liquids are “pure” electrolytes, we found that they require much more ohmic drop compensation (compensated resistances between 2.5 and 28 kΩ)[25] than in more conventional media such as acetonitrile + $Bu_4NBF_4^-$ (0.4−0.8 kΩ), indicating that the RTILs media are more resistant despite their ionic characters.[24] The resistance values with imidazolium-based ionic liquids were low enough to be fully compensated by our equipment, whereas the higher resistance values obtained for [$(C_8H_{17})_3NCH_3$][NTf_2] make detailed mechanistic studies in this latter medium more difficult. Under these conditions, cyclic voltammetry experiments of the oxidation of ferrocene to ferricinium (Fc/Fc^+) in RTILs were performed with scan rates ranging from 0.1−1000 V s^{-1}. Well-defined waves were observed for the whole range of scan rates, and the couple Fc/Fc^+ was found to be electrochemically reversible (see Figure 1, for example, in [EMIM][NTf_2]).[26] The behavior is similar to that observed for the well-known one-electron oxidation of ferrocene in more conventional media (acetonitrile, for instance) and can be compared with the electrochemical reversibility previously reported in other ionic liquids.[3a] Peak-potential differences (ΔE) between the forward and backward scans were measured as 57 and 73 mV at scan rates of 0.1 and 1000 V s^{-1}, respectively, corresponding to a reversible redox couple with relatively fast electron-transfer kinetics. The peak currents i_p for the reduction/oxidation of ferrocene were found to vary linearly with the square root of the scan rate ($r^2 \geq 0.9993$) between sweep rates of 0.1 and 1000 V s^{-1}, showing that the electrochemical process is diffusion-controlled (Figure 1). From the slope $i_p = f(v^{1/2})$, the diffusion coefficient of ferrocene in [EMIM][NTf_2] is estimated to be 6.3×10^{-8} cm^2 s^{-1}, that is, 100−300 smaller than that in a typical solvent-electrolyte system.[27] This result is in agreement with other reported studies[3,15,16,22] and can be ascribed to the high viscosity of the ionic liquids (52 cP and 34 cP for [BMIM][NTf_2] and [EMIM]-[NTf_2],[5] and 319 cP for [BMIM][PF_6][17]),[28] as the diffusion coefficients and viscosity are directly related.[29] These preliminary experiments with ferrocene confirm that (i) ferrocene diffuses according to a semi-infinite regime and (ii) detailed investigations of the reactivity of organic compounds from the analysis on the cyclic voltammetry response (competition between the diffusion rate and the chemical reactions kinetics) could be performed in RTILs.[30]

The peak-potential difference between the cathodic and the anodic processes recorded at different scan rates gives a measurement of the kinetics parameters for the heterogeneous electron transfer: $k_s/\sqrt{D}$ where k_s is the apparent heterogeneous standard electron-transfer rate constant (uncorrected from the double-layer effect).[30] We found $k_s/\sqrt{D} = 630$ $s^{-1/2}$ that leads to $k_s = 0.15{-}0.2$ cm s^{-1} with $D = 6.3 \times 10^{-8}$ cm^2 s^{-1}. This value is in the range of that previously reported in basic chloroaluminate melts.[31] We have to compare this result to the k_s values obtained in organic electrochemical media. For instance, values of $k_s = 5.5$, 3, and 0.95 cm s^{-1} were measured by fast cyclic voltammetry with ultramicroelectrodes in acetone, propionitrile and butyronitrile (with 0.3 mol L^{-1} Bu_4NPF_6), respectively, where the diffusion coefficient values are reported as 2×10^{-5} cm^2 s^{-1} in acetone, 1.8×10^{-5} cm^2 s^{-1} in propionitrile, and 0.87×10^{-5} cm^2 s^{-1} in butyronitrile.[32] Therefore, the k_s values are considerably smaller in RTILs, showing a slower electron-transfer reaction in ionic liquids.

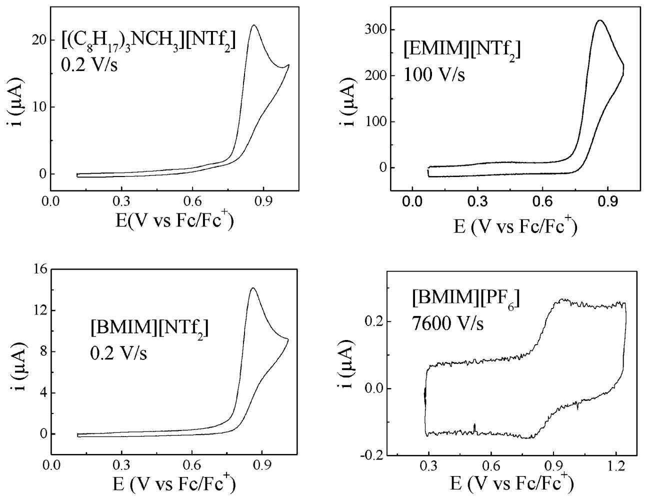


Figure 2. Cyclic voltammograms of anthracene ($C° = 1 \times 10^{-2}$ mol L^{-1}) in [$(C_8H_{17})_3NCH_3$][NTf_2] [EMIM][NTf_2], [BMIM][NTf_2], and [BMIM][PF_6] at different scan rates (0.2, 100 V s^{-1}) on a 1 mm platinum disk electrode and (7600 V s^{-1}) on 10 μm diameter disk platinum microelectrode.

Reactivity of Aromatic Hydrocarbon Radical Cations in Ionic Liquids. Electron-transfers involving aromatic hydrocarbons have been widely studied in molecular electrochemistry because the resulting cation or anion radicals participate in a large variety of reaction types or mechanisms such as electrophilic, nucleophilic, or free-radical substitutions, additions, or eliminations.[33] In oxidation, the resulting cation radicals generally exhibit dramatic changes of reactivity as compared to the parent molecule, becoming much stronger electrophilic, oxidizing, or acidic species, mainly depending on the charge delocalization on the aromatic core. The corresponding reaction mechanisms have been studied in detail in organic solvents. Thus, they appear as good examples to investigate the effects of RTILs on the reactivity of cation radicals by changing the size of the molecule and localization of the unpaired electron. Three examples in this family have been chosen, namely, the oxidations of anthracene and naphthalene on one hand and the oxidation of durene on the other hand.

Among the examples dealing with the electrochemical oxidation of aromatic molecules, the oxidations of anthracene and its derivatives have been the object of numerous publications[34] (some of them very recently) and are classically used as test systems for new electrochemical methods.[35] Anthracene (and naphthalene) cation radicals are known to be weaker acids as compared to alkylbenzene cation radicals that display lifetimes in the millisecond range. Then, a nucleophilic attack by residual water (nucleophilic species that are present in solution) that leads to the ring oxidation to produce the corresponding quinone occurs preferably to a deprotonation reaction leading to a side-chain oxidation.[34,36] Figure 2 displays the voltammograms

TABLE 1: Electrochemical Characteristics for Anthracene in RTILs and in Acetonitrile

	$E°$ (V/SCE)	$\partial E_p/\partial \log(v)$ (mV/dec)	$k_s/\sqrt{D}$ ($s^{-1/2}$)[d]	D (cm^2/s)	k_s (cm s^{-1})
[BMIM][NTf_2]	1.27	20.2[a]	300	$(2.8 \pm 0.8) \times 10^{-7e}$	0.1−0.2
[EMIM][NTf_2]	1.27	22.1[b]	800	$(5.3 \pm 1.7) \times 10^{-7e}$	0.6−0.7
[$(C_8H_{17})_3NCH_3$][NTf_2]	1.26	25.8[c]			
[BMIM][[PF_6]	1.27	20.5[b]	280	$(5.6\pm 1.8) \times 10^{-7e}$	0.2−0.3
ACN (+ Et_4NPF_6)	1.25	21.4[a]		$2.5 \times 10^{-5\,f}$	3−5[g]

[a] For $v = 0.1{-}100$ V s^{-1}. [b] For $v = 0.1{-}50$ V s^{-1}. [c] For $v = 0.1{-}10$ V s^{-1}. [d] Using the DigiSim program with $D = 10^{-5}$ cm^2 s^{-1}. [e] From the linear variation $i_p = f(\sqrt{v})$. [f] From ref 41. [g] From ref 42.

recorded for the oxidation of anthracene in [EMIM][NTf_2], [BMIM][NTf_2], and [BMIM][PF_6] and [$(C_8H_{17})_3NCH_3$][NTf_2] at different sweep rates on a millimeter-sized electrode and on an ultramicroelectrode. Irreversible oxidation waves were observed for scan rates in the range 0.1−100 V s^{-1}. Karl Fischer titration indicated that the amount of water present in the solutions was 1500 ppm, and such a considerable amount of water was used to favor the formation of anthraquinone. Indeed, a small electrochemical signal (reversible wave) appeared on the reverse scan at a much more cathodic potential (the difference between the two oxidation peak potentials was 2 V) and was ascribed to the reduction/oxidation of anthraquinone produced upon oxidation of anthracene (see Experimental Section).[34]

The peak currents exhibit a linear variation with the square root of the scan rate (v) for all studied ionic liquids, showing that a diffusion-controlled electrochemical process occurs at the electrode as previously found for the oxidation of ferrocene. Microelectrodes were used to record high scan rate voltammograms and to observe the chemically reversible cyclic voltammograms. A partial reversibility appears for scan rates above 3000−5000 V s^{-1}. From these reversible voltammograms, assuming a Butler−Volmer law for electron-transfer kinetics and a charge-transfer coefficient $\alpha = 0.5$, the kinetics parameter $k_s/\sqrt{D}$ was estimated from the peak separations.[30] The same experiments allow us to measure the diffusion coefficient D and to derive the value for the standard electron-transfer rate constant (uncorrected from the double layer effect) k_s. We found values between 0.7 and 0.1 cm s^{-1} depending on the ionic liquid (Table 1). These values are about 10 times lower than those observed in more conventional media. For comparison purposes, parallel experiments were performed in acetonitrile. The shapes of the voltammograms were similar, and the reversibility appeared in the same range of scan rates indicating that the radical cation of anthracene displays similar lifetimes in both types of solvent.[37] To get more insight into the nature of the mechanism occurring in the different ionic liquids, we examined the variation of the peak potential as a function of scan rate (v). The peak potential (E_p) was found to vary linearly as a function of log(v). Slopes close to 20 mV/log(v) were found when the solvent was an ionic liquid, indicating that the reaction step consecutive to the formation of the anthracene cation radical involves a second-order pathway (Table 1).[38] Cyclic voltammetry investigations of anthracene oxidation in acetonitrile, in the range 0.1−50 V s^{-1} gave similar results. In particular, a slope of 21.4 mV/log(v) was found for the linear variation of the peak potential as a function of the scan rate. We also observed a linear variation of the peak potential as a function of log(c) with a slope close to −20 mV for a 10-fold increase of the initial concentration of anthracene (c; varying between 10^{-2} and 10^{-4} mol L^{-1}). No unambiguous mechanism can be found to explain the overall reaction for the electrochemical oxidation of anthracene to anthraquinone in the presence of water. However, our results can be compared with recent work concerning the homogeneous oxidation of anthracene by [Ru(bpy)$_3$]$^{3+}$ (bpy = 2,2′-bipyridine) in acetonitrile.[39] The authors report second-order kinetics for the decay of the radical cation of anthracene that corresponds to the intermediate formation of an adduct that can formerly be written (Ant-H_2O)$^{2+}$. By analogy, we propose the same mechanism as that reported in ref 39, and the variations observed for the peak potentials are in agreement with a “DISP2-type electrochemical mechanism”[40] that can be written according to the simplified mechanism:

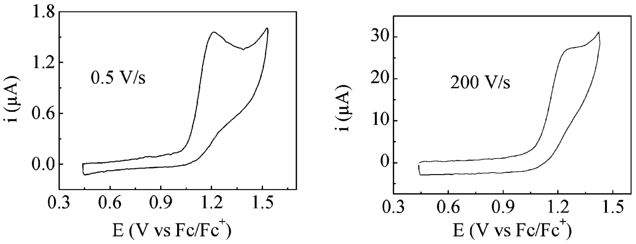


Figure 3. Cyclic voltammograms at different scan rates (0.5, 5, and 200 V s^{-1}) for 1×10^{-2} mol L^{-1} naphthalene in [EMIM][NTf2] on a 0.3 mm diameter platinum electrode.

$$\text{Ant} \underset{}{\overset{k_s}{\rightleftarrows}} \text{Ant}^{\bullet +} + e^- \qquad (0)$$

$$\text{Ant}^{\bullet +} + H_2O \overset{K}{\rightleftarrows} (\text{Ant-}H_2O)^{\bullet +} \qquad (1)$$

$$(\text{Ant-}H_2O)^{\bullet +} + \text{Ant}^{\bullet +} \overset{k_2}{\rightleftarrows} (\text{Ant-}H_2O)^{2+} + \text{Ant} \qquad (2)$$

The electrochemical oxidation process starts with a rapid electron transfer between anthracene (Ant) and the electrode to produce the corresponding cation radical, which reacts with H_2O to form a hydroxy adduct, (Ant-H_2O)$^{\bullet +}$, reaction 1 acting as an unfavored preequilibrium prior to the fast irreversible homogeneous electron transfer (2) (DISP2 mechanism).[40] The electron-transfer disproportionation between (Ant-H_2O)$^{\bullet +}$ and Ant $^{\bullet +}$ occurs to give Ant and a hydroxy dication adduct (Ant-H_2O)$^{2+}$. Because this adduct is a strong electrophile, it will react rapidly with H_2O and will lose protons to produce a dihydroxy adduct that will finally be oxidized to anthraquinone.[39] **[4142]**

Identical trends were found for the oxidation of naphthalene. For example, cyclic voltammetry experiments performed in [EMIM][NTf_2] showed irreversible anodic waves, at 1.65 V/SCE,[43] similar to what is observed in acetonitrile (Figure 3).

As described above for anthracene oxidation, the oxidation peak potential varies linearly as a function of v with a slope of 22.8 mV per 10-fold increase of v, whereas a slope close to 19 mV/dec was determined in acetonitrile. On the basis of the experimental errors (±3 mV), these results indicate that the follow-up reaction to the oxidation step obeys second-order kinetics in ionic liquids as well as in classical organic solvents. We tried to obtain voltammograms showing at least a partial reversibility by increasing the scan rates up to 10000 V s^{-1}, but no return peak could be found with microelectrodes. As

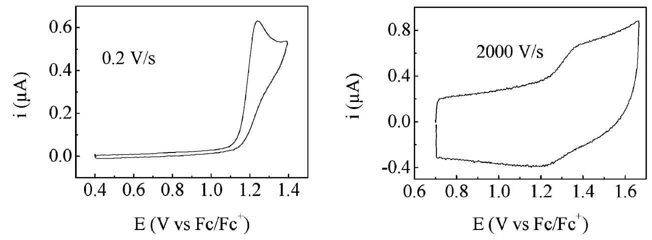


Figure 4. Cyclic voltammograms of durene (10^{-2} mol L^{-1}) in [EMIM][NTf_2] for different sweep rates on a 0.3 mm diameter disk platinum electrode (0.2, 2, and 20 V s^{-1}) and on a 10 μm diameter disk platinum electrode (2000 V s^{-1}).

expected, the naphthalene radical cation displays a higher reactivity than that of anthracene.[44] Consequently, we conclude from these first experiments concerning the oxidation of large aromatic molecules (anthracene and naphthalene) that no significant modification of mechanistic aspect appears when passing from classical organic solvents to ionic liquids.

In contrast to anthracene and naphthalene, the cation radicals of alkylbenzene exhibit a tremendous C$-H^+$ acidity, and the deprotonation from the cation radical is the predominant type of decay.[45-47] We investigated the electrochemical oxidation of durene in [BMIM][NTf_2] and in [EMIM][NTf_2] by varying the scan rate between 0.1 and 200 V s^{-1}. Figure 4 displays some representative cyclic voltammograms obtained in [EMIM][NTf_2]. In the whole scan-rate range, the waves remained irreversible with a peak potential at about 1.6 V/SCE.[43] This value is less positive than the anodic peak potential of durene in acetonitrile reported previously (1.79 V/SCE),[45] indicating an increase of the cation radical stabilization due to a better solvation in RTILs.

We measured, in both investigated ionic liquids, the linear scan-rate dependence of the peak potential $\partial E_p/\partial \log v \approx 30$ mV per decade that reflects a first-order character for the follow-up reaction. The same experiments performed with an acetonitrile solution of 2×10^{-3} mol L^{-1} durene (+ 0.2 mol L^{-1} Et_4NPF_6) lead to similar variation and slope. These results support the obeyance of a classical ECE-DISP1 mechanism in both types of solvent where the rate-determining step is the deprotonation step following the first electron transfer:

$$\mathrm{ArCH_3} \xrightleftharpoons{E°,\, k_s} \mathrm{ArCH_3}^{+\bullet} + e^- \tag{3}$$

$$\mathrm{ArCH_3}^{+\bullet} \xrightarrow{k_1} \mathrm{ArCH_2}^{\bullet} + H^+ \tag{4}$$

$$\mathrm{ArCH_2}^{\bullet} \rightleftarrows \mathrm{ArCH_2}^{+} + e^- \tag{5}$$

$$\text{or } \mathrm{ArCH_2}^{\bullet} + \mathrm{ArCH_3}^{+\bullet} \rightleftarrows \mathrm{ArCH_2}^{+} + \mathrm{ArCH_3} \tag{5'}$$

Cyclic voltammograms recorded at scan rates above 2000 V s^{-1} in [EMIM][NTf_2] showed a partial reversibility, allowing the measurement of k_s and $E°$. The diffusion coefficients D of durene in the ionic liquids were determined from the slope of the linear variation of the peak current with the square root of the scan rate. Thus, we found $D = (4.4 \pm 1.3) \times 10^{-7}$ cm^2 s^{-1} and $D = (2.7 \pm 0.9) \times 10^{-7}$ cm^2 s^{-1} for [BMIM][NTf_2] and [EMIM][NTf_2], respectively. Using these values and assuming $\alpha = 0.5$, simulations of the experimental results according to this mechanism allow us to estimate $k_s = 0.06-0.05$ cm s^{-1} (from $k_s/\sqrt{D} = 79$ s$^{-1/2}$ for [BMIM][NTf_2] and 110 s$^{-1/2}$ for [EMIM][NTf_2]) together with the first-order chemical rate constant (deprotonation) $k_1 = 10^4$ s^{-1}. High scan-rate cyclic voltammetry (2000 and 4000 V s^{-1}) of an acetonitrile solution of 2×10^{-3} mol L^{-1} durene was also performed. Using the ECE-DISP mechanism described above, simulations of experimental voltammograms, assuming $D = 10^{-5}$ cm^2 s^{-1} and $\alpha = 0.5$, give a k_s value of 0.3 cm s^{-1} ($k_s/\sqrt{D} = 95$ s$^{-1/2}$) and a deprotonation rate constant $k_1 = 10^4$ s^{-1}. Similar to what we observed for ferrocene, the apparent electron-transfer rates appear to be slower in RTILs than those in acetonitrile for both aromatic systems, anthracene and naphthalene on one hand and durene on the other hand. Besides, the first-order deprotonation rate constant k_1 of the durene cation radical was found to be identical in both [EMIM][NTf_2] and [BMIM][NTf_2] as well as in acetonitrile (+Et_4NPF_6) medium, showing that no effect can be evidenced in the kinetics on the consecutive first-order reaction because of the use of RTILs.

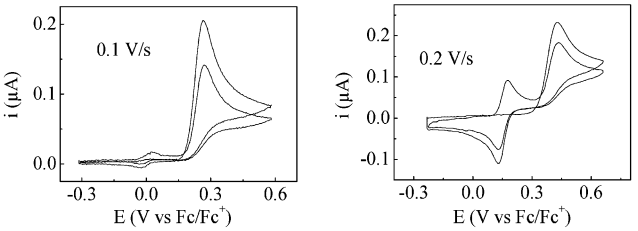


Figure 5. Cyclic voltammetry of 1×10^{-2} mol L^{-1} DTF$-NO_2$ solution in [BMIM][NTf_2] (left) and [BMIM][PF_6] (right) at a 0.3 mm diameter disk platinum electrode.

Electrodimerization Processes in Ionic Liquids. Electrodimerization and electropolymerization (that is the occurrence of several electrodimerization steps) are an important class of reaction involved in the design of organic materials such as conducting polymers.[48] These electrochemical processes are complex as they involve several electron transfers, carbon–carbon bond formation generally from the reaction between two cation radicals and deprotonation reactions.[49] We investigated two systems in ionic liquids that are known to undergo oxidative electrocoupling: the electrodimerization of 1,4-dithiafulvene (DTF) and the trimerization of veratrole.[50,51] The mechanism of the electrochemical dimerization of substituted DTF into TTF vinylogues is now a well-known process that has been studied in detail.[50] The first step involves the formation of cations radicals $\mathbf{AH}^{+\bullet}$ that couple rapidly to form the protonated dication $^{+}\mathbf{HAAH}^{+}$. This dication slowly deprotonates to give the final TTF (dimer). The deprotonation step corresponds to the departure of two protons together with a rearomatization of the system to form the dimer **AA**.

$$\mathrm{AH} \xrightleftharpoons{E°,\, k_s} \mathrm{AH}^{+\bullet} + e^- \tag{6}$$

$$\mathrm{AH}^{+\bullet} + \mathrm{AH}^{+\bullet} \xrightarrow{k_{\mathrm{dim}}} {}^{+}\mathrm{HAAH}^{+} \tag{7}$$

$${}^{+}\mathrm{HAAH}^{+} \xrightarrow{k_{\mathrm{H}}} \mathrm{AA} + 2\,H^+ \tag{8}$$

In this respect, the nature of this deprotonation step is different from that encountered in the deprotonation reaction of the durene radical cation (to give a neutral methylarene radical) because it involves a nonradical dicationic species. Several experiments to investigate the electrochemical reactivity of DTF$-NO_2$ in [BMIM][NTf_2], [EMIM][NTf_2], [BMIM][PF_6], and [$(C_8H_{17})_3NCH_3$][NTf_2] were performed (see Figure 5 for typical voltammograms in ionic liquids).

At a low scan rate (0.1–0.2 V s^{-1}) and on the first anodic scan, an irreversible peak is visible. During the reverse cathodic scan, a reversible process corresponding to the produced TTF appears at a less positive potential with a pattern similar to the

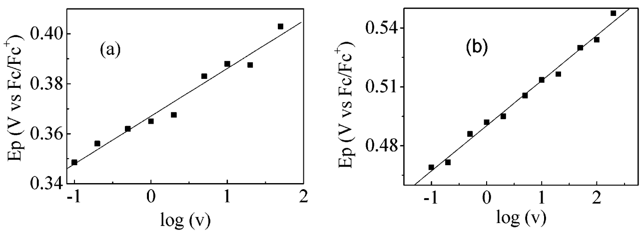
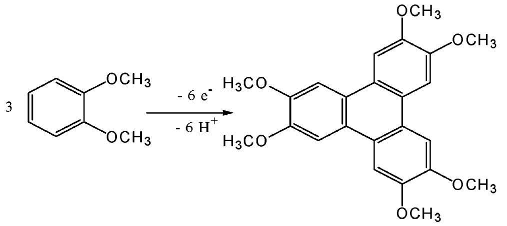


Figure 6. Cyclic voltammetry of 1×10^{-2} mol L^{-1} DTF$-$NO$_2$ in (a) [EMIM][NTf$_2$] and (b) [BMIM][NTf$_2$] at a 0.3 mm diameter disk platinum electrode. Variation of the oxidation peak potential Ep with the logarithm of the scan rates, v in V s^{-1}.

one observed in organic solvents.[50] The oxidation process remained irreversible for scan rates up to 1000 V s^{-1}. To check the nature of the first reaction step, the variation of the peak potential (E_p) with the scan rate (v) was examined (Figure 6).

For [BMIM][NTf$_2$], [EMIM][NTf$_2$], and [BMIM][PF$_6$], the oxidation peak potential varies linearly with log(v) with a slope close to 19 mV per decade, as previously reported for the oxidation of DTF in acetonitrile.[50] This result confirms that the carbon$-$carbon bond is formed by coupling between two cation radicals formed via a fast electron transfer from DTF$-$NO$_2$.[52] In the case of [(C$_8$H$_{17}$)$_3$CH$_3$N][NTf$_2$], we found a slope of 58.5 mV/log(v) for the linear variation of the peak potential as a function of log(v), indicating a control of the global kinetics by the first electron transfer that impedes the investigations of the follow-up reactions. When the scan rate is increased above 4000 V s^{-1}, by use of an ultramicroelectrode, a partial reversibility of the oxidation wave of DTF$-$NO$_2$ appeared, indicating a lifetime of the generated transient species in the range of several microseconds in the ionic liquid. A value of $k_s = 0.1-0.2$ cm s^{-1} ($k_s/\sqrt{D} = 400$ s$^{-1/2}$) is derived from this experiment. As previously noticed for the other investigated redox couples, it is about 10 times lower than that determined in acetonitrile. From the same experiments, the dimerization rate constant could be estimated by comparison with a series of simulated curves.[50] A value $k_{\mathrm{dim}} = 1-2 \times 10^7$ L mol^{-1} s^{-1} is found, which is around 10 times lower than that obtained in acetonitrile (Table 2). It is worth outlining that the peak currents for the electrogenerated dimer are quite small compared to the anodic peak current of the monomer, showing that only a small quantity of dimer is produced during the scan time. When the scan rates are increased, the height of the reversible redox system (TTF dimer), relative to the oxidation peak of DTF$-$NO$_2$, decreased and almost disappeared for scan rates higher than 5, 0.2, and 1 V s^{-1} for [BMIM][PF$_6$], [BMIM][NTf$_2$], and [EMIM][NTf$_2$], respectively. In agreement with the slope of 19 mV/log(v) found above, these results support the conclusion of the formation of a cation radical as a first intermediate and indicate that the first reaction step is the formation of the carbon$-$carbon bond via a radical$-$radical coupling, followed by a deprotonation step which corresponds to the departure of two protons as is the case in acetonitrile.[50] The deprotonation step is much slower than the coupling reaction, and the quantity of dimer produced during the voltammetric scan is a measure of its kinetics. This point can be verified if one adds a base (2,6-lutidine) to the solution: a clear increase of the height of the reversible system (in the range 2$-$500 V s^{-1}) corresponding to the formation of the TTF$-$NO$_2$ is observed, whereas the height of the anodic peak remains quite unchanged, showing that more dimers are produced in the presence of the added base (Figure 7). However, no significant effect is observed on the reversibility of the fast-scan voltammograms in the range 1000$-$10 000 V s^{-1}, indicating that the addition of base does not modify the lifetime of the cation radical. Without base, the relative quantity of dimer formed during the oxidation of the DTF$-$NO$_2$ increases in the order [BMIM][PF$_6$] > [EMIM][NTf$_2$] ≥ [BMIM][NTf$_2$].[53] Because no variation on the reversibility of the oxidation of the cation radical (and thus of k_{dim}) was observed as a function of the nature of the RTILs, we conclude that the deprotonation reaction kinetics vary in the same order. Quantitatively, simulations of the voltammograms with the mechanism proposed above (eqs 6$-$8) allow an estimation of k_H in the different ionic liquids (Table 2).[50] As is reflected by the values of k_H, the kinetics of the deprotonation reaction seems to be only slightly affected by the nature of the cation (see results in [BMIM][NTf$_2$] and in [EMIM][NTf$_2$]). On the contrary, the rate constants k_H decrease considerably when the anion is NTf$_2^-$ that appears as the best medium to stabilize cationic species (certainly in relation with a lower basicity of NTf$_2^-$).

The second example investigated in this part was the oxidation of the 1,2-dimethoxybenzene (veratrole). The anodic oxidative coupling of this aromatic diether leads to the formation of hexamethoxytriphenylene (HMT) but requires a strictly non nucleophilic medium.[51a,54] In this connection, the low nucleophilicity of RTILs is a great advantage for the electrosynthesis of columnar materials.The key intermediate during the electrochemical generation of HMT is a dimer resulting from a first oxidative coupling of dimethoxybenzene that is rapidly followed by different electrochemical/chemical reactions leading to the final trimer. Cyclic voltammetry experiments were performed in [EMIM][NTf$_2$] and in [BMIM][NTf$_2$] at increasing scan rates from 0.1 to 4000 V s^{-1} (Figure 8). In these experiments, both a "classical" electrode (0.3 mm of diameter) and ultramicroelectrodes were used. For low scan rate (0.2 V s^{-1}), an irreversible wave at about 1.35$-$1.4 V/SCE is visible on the first anodic scan, and a reversible redox system appears at a less positive potential during the reverse cathodic scan. Direct comparison with experiments performed in dry organic solvent[54] allowed us to describe this electrochemical behavior as follows: the oxidation of veratrole produced the corresponding trimer which is oxidized at a less positive potential than that of the starting monomer.[55] In the scan-rate range from 0.1 to 20 V s^{-1}, the peak potential (E_p) varies linearly as a function of log(v) with a slope close to 20 mV/log(v) for both ionic liquids. It shows that the first dimer is produced by a cation$-$radical$-$cation radical coupling mechanism similar to that described for DTF$-$NO$_2$. For scan rates higher than 1000 V s^{-1}, a slight reversibility of the oxidation of the veratrole appeared and became clearly visible when the scan rate was increased above 4000 V s^{-1}, indicating that the radical cation of veratrole has a lifetime in the range of several microseconds. Because similar results are obtained in organic solvents, it turns out that the nature of the overall reaction mechanism is not influenced by the use of ionic liquids such as [BMIM][NTf$_2$] or [EMIM][NTf$_2$]. From simulation of the voltammograms, taking into account a first dimerization step similar to that described for DTF$-$NO$_2$, similar heterogeneous electron-transfer (k_s) and dimerization (k_{dim}) rate constants were found in [EMIM][NTf$_2$]



(9)

TABLE 2: Electrochemical Oxidation of DTF−NO$_2$ and TTF−NO$_2$ in RTILs and Acetonitrile

	$E^{ox}_{\mathrm{DTF-NO2}}$ (V/SCE)[a]	$E°_{\mathrm{TTF-NO2}}$ (V/SCE)	$\partial E_p/\partial \log(v)$ (mV/dec)	k_s (cm s^{-1})	D^f (cm^2 s^{-1})	k_{dim} (L mol^{-1} s^{-1})	k_H (s^{-1})
[BMIM][NTf$_2$]	0.832	0.47	23[b]	−	6.7×10^{-8}		0.03−0.04
[EMIM][NTf$_2$]	0.754	0.39	19.1[c]	0.1−0.2	3.9×10^{-8}	$1-2 \times 10^7$	0.05−0.06
[EMIM][NTf$_2$] + lutidine	0.753	0.43	22.8[g]		−		20
[(C$_8$H$_{17}$)$_3$NCH$_3$][NTf$_2$]	−		58.5[d]		−		
[BMIM][PF$_6$]	0.833	0.56	17[c]		5.8×10^{-8}		0.1−0.2
ACN (+ Et$_4$NPF$_6$)	0.869	0.55	19.5[e]	2−3[e]	−	$2-3 \times 10^{8e}$	0.3[e]

[a] Oxidation potential at 0.2 V s^{-1}, checked from ferrocene/ferricinium couple. [b] For $v = 0.1-200$ V s^{-1}. [c] For $v = 0.1-50$ V s^{-1}. [d] For $v = 0.1-5$ V s^{-1}. [e] From ref 50. [f] Estimation based on the variation $i_p = f(\sqrt{v})$. [g] For $v = 2-200$ V s^{-1}.

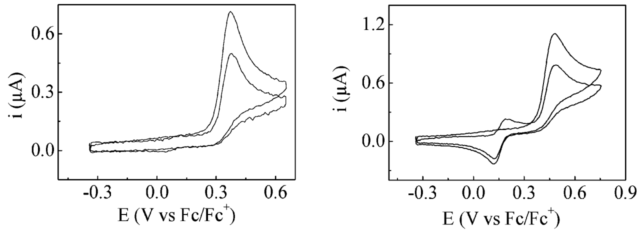


Figure 7. Cyclic voltammetry of 1×10^{-2} mol L^{-1} DTF−NO$_2$ in [EMIM][NTf$_2$] in the absence (left) and in the presence (right) of 1×10^{-1} mol L^{-1} 2,6-lutidine on a 0.3 mm diameter disk platinum electrode. Scan rate 2 V s^{-1}.

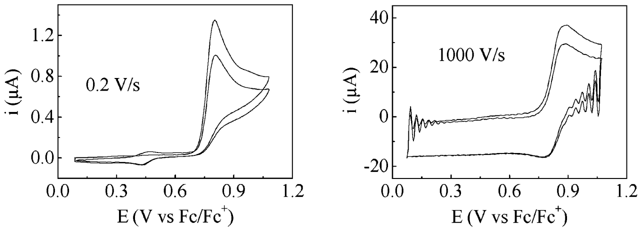


Figure 8. Cyclic voltammograms of 1×10^{-2} mol L^{-1} veratrole in [EMIM][NTf$_2$] at a platinum electrode (0.3 mm of diameter) recorded at different scan rates.

and in [BMIM][NTf$_2$]: $k_s = 0.2-0.3$ cm s^{-1} ($k_s/\sqrt{D} = 300$ s$^{-1/2}$) and $k_{\mathrm{dim}} = 2-3 \times 10^6$ L mol^{-1} s^{-1}. The same experiments performed in acetonitrile gave $k_s = 2-3$ cm s^{-1} ($k_s/\sqrt{D} = 800$ s$^{-1/2}$) and $k_{\mathrm{dim}} = 0.9-1 \times 10^7$ L mol^{-1} s^{-1},[56] showing (as for the other studied systems) a clear decrease of the electron-transfer rates in RTILs. Because of the lack of data, we did not try to go further into detailed investigations about the reaction sequence following the first electrodimerization step and leading to the formation of the trimer (intra and intermolecular bond formations). We may just notice that the height of the reversible redox system (veratrole trimer), relative to the veratrole oxidation peak, is smaller in [BMIM][NTf$_2$] than in [EMIM][NTf$_2$], suggesting that the follow-up reactions are slower in [BMIM][NTf$_2$] than in [EMIM][NTf$_2$].

A last point that is worth discussing is the difference in the values of the dimerization rate constant for both DTF−NO$_2$ and veratrole in the RTILs on one hand and in acetonitrile on the other hand. The dimerization kinetics rate constants in RTILs are between 5 and 10 times smaller than those measured in acetonitrile. Similar decreases are observed for bimolecular reactions in pulse radiolysis experiments.[17] Part of this effect can be due to a decrease of the diffusion limit rate constant related both to a higher viscosity of the ionic liquids and lower polarity of the media that affects the work term to bring together the two charged radical cations in the coupling step.[57] Estimates of the media polarity based on the solvatochromic effect on the spectra of some dyes indicate that the polarities of this type of RTILs are much lower than that of water and closer to that of ethanol.[1,2,5] As proposed to explain the pulse radiolysis investigations[17] and in another electrochemical study,[15] not only these latter effects in RTILs may explain the decrease of the dimerization kinetics. Indeed, it was suggested that solutes and solvent are highly ordered in the RTILs. Thus, a specific solvation between reactants may occur because of the ionic nature of the solvent, leading, for instance, to a high degree of ion-association. As a result, the activation energy for the reaction becomes important because it is necessary to break the order of the reaction medium to make all components react.

Conclusions

Three different 1-alkyl-3-methylimidazolium-based ionic liquids and the [(C$_8$H$_{17}$)$_3$NCH$_3$][NTf$_2$] ionic liquid were used as reaction media for several typical electrochemical reactions. [(C$_8$H$_{17}$)$_3$NCH$_3$][NTf$_2$] appears to be a highly resistive medium and consequently makes detailed electrochemical mechanistic studies that require a careful IR drop compensation more difficult. However, studies of the electrochemical oxidation of ferrocene, anthracene, durene, DTF−NO$_2$, and veratrole were readily achieved in [BMIM][PF$_6$], [EMIM][NTf$_2$], and [BMIM][NTF$_2$]. The processes of diffusion (semi-infinite linear diffusion) coupled with chemical reaction are similar that those known in more conventional media. These results make it possible to analyze the voltammetric current responses according to classical electrochemical methods that were developed in more conventional solvents. Thus, the extraction of thermodynamic and kinetics parameters were allowed from the variation of peak potential and reversibility ratio versus the scan rates. The most interesting result is that the use of ionic liquids does not modify the nature of the investigated mechanisms, as compared to conventional organic media, although the structure of molecular solvents and ionic liquids are expected to be quite different (formation of microdomains, ion pairing, and stronger solvation of cation radical by the anions of the RTILs). Concerning the physical properties and reaction kinetics, two other general observations can be made for all of the studied compounds. First, the diffusion coefficient of the organic compounds are about 100 times smaller than those in conventional media as expected from the lower viscosity of RTILs versus organic solvents and in agreement with previously obtained results. The second general behavior is the systematic decrease of all electron-transfer rates for reactions between aromatic molecules and the electrode (around 1 order of magnitude), whereas other reaction kinetics are not much affected, except for the bimolecular kinetics rate constants. In this latter case, the decrease of the bimolecular kinetics rate constants have been interpreted to be only partially due to the high viscosity of the RTILs, leading to a decrease of the limiting diffusion-controlled kinetics rate constant. It is also suggested that a high degree of ion-association in RTILs resulting in a specific solvation of the reactants may explain the decrease of the bimolecular reaction rates. To conclude, these preliminary electrochemical experiments show encouraging results for the use of room-temperature ionic liquids as new media for organic electrochemistry.

Acknowledgment. The authors are very grateful to Prof. D. Lorcy (University of Rennes 1) for the gift of a sample of DTF-NO_2.

References and Notes

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.

(2) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.

(3) (a) Fuller, J.; Carlin, R. T.; Osteryoung, R. A. *J. Electrochem. Soc.* **1997**, *144*, 3881. (b) Kosmulski, M.; Osteryoung, R. A.; Ciszkowska, M. *J. Electrochem. Soc.* **2000**, *147*, 1454.

(4) Papageorgiou, N.; Athanassov, Y.; Armand, M.; Bonhôte, P.; Pettersson, H.; Azam, A.; Grätzel, M. *J. Electrochem. Soc.* **1996**, *143*, 3099.

(5) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 11168.

(6) Xu, K; Ding, M. S.; Jow, R. R *J. Electrochem. Soc.* **2001**, *148*, A267.

(7) Koch, V. R.; Dominey, L. A.; Nanjundhia, C.; Ondrechen, M. J. *J. Electrochem. Soc.* **1996**, *143*, 798.

(8) Suarez, P. A. Z.; Selbach, V. M.; Dullius, J. E. L.; Einloft, S.; Piatnicki, C. M. S.; Azambuja, D. S.; de Souza, R. F.; Dupont, J. *Electrochim. Acta* **1997**, *42*, 2533.

(9) (a) Hurley, F. H.; U.S. Patent No. 2,445,331, Aug 3, 1948. (b) Wier, T. P.; Hurley, F. H. U.S. Patent No. 2,446,349, Aug 3, 1948. Wier, T. P. U.S. Patent No. 2,446,350, Aug 3, 1948.

(10) (a)Janiszewska, L; Osteryoung, R. A. *J. Electrochem. Soc.* **1987**, *134*, 2787. (b) Janiszewska, L; Osteryoung, R. A *J. Electrochem. Soc.* **1988**, *135*, 116. (c) Oudard, J. F.; Allendoerfer, R. D.; Osteryoung, R. A. *Synth. Met.* **1988**, *22*, 407.

(11) Arnautov, S. A. *Synth. Met.* **1997**, *84*, 295.

(12) Katayama, Y.; Dan, S.; Miura, T.; Kishi, T. *J. Electrochem. Soc.* **2001**, *148*, C102.

(13) Sweeny, B. K.; Peters, D. G. *Electrochem. Commun.* **2001**, *3*, 712.

(14) Schröder, U.; Wadhawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *New. J. Chem.* **2000**, *24*, 1009.

(15) Quinn, B.; Ding, Z.; Moulton, R.; Bard, A. J. *Langmuir* **2002**, *18*, 1734.

(16) Compton, D. L.; Lazlo, J. A. *J. Electroanal. Chem.* **2002**, *520*, 71.

(17) (a) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607. (b) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, *106*, 3139. (c) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 5468.

(18) Oxidation reactions were preferably investigated to reduction reactions because of the limitations due to the imidazolium cation in the electroactivity windows in the negative region. For example, in classical organic solvent (acetonitrile, dimethylformamide, etc.), the well-known reduction of anthracene exhibits a monoelectronic and reversible electrochemical process around −1.89 V/SCE. In alkylimidazolium-based ionic liquids ([BMIM][PF6], [BMIM][NTf2], and [EMIM][NTf2]), we were not able to see the reduction wave of anthracene because the cathodic window limit is narrowed by the reduction of alkylimidazolium ions at −1.8−2 V/SCE.

(19) Lozano, P.; de Diego, T.; Carrié, D.; Vaultier, M.; Iborra, J. L. *Biotechnol. Lett.* **2001**, *23*, 1529.

(20) Chen, P. Y.; Sun, I. W. *Electrochim. Acta* **1999**, *45*, 441.

(21) Sahami, S.; Osteryoung, R. A. *Anal. Chem.* **1983**, *55*, 1970.

(22) Wadhawan, J. D.; Schröder, U.; Neudeck, A.; Wilkins, S. J.; Compton, R. G.; Marken, F.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *J. Electroanal. Chem.* **2000**, *493*, 75.

(23) Lorcy, D.; Carlier, R.; Robert, A.; Tallec, A.; Le Maguerès, P.; Ouahab, L. *J. Org. Chem.* **1995**, *60*, 2443.

(24) Garreau, D.; Savéant, J.-M. *J. Electroanal. Chem.* **1972**, *35*, 309.

(25) Observed resistances were between 4.5 and 5.5 kΩ, 2.5−3.5 kΩ, 5−6 kΩ, and 24−28 kΩ for [BMIM][NTf2], [EMIM][NTf_2], [BMIM][PF_6], and [$(C_8H_{17})NCH_3$][NTf_2], respectively, under our experimental conditions. The exact values are strongly dependent on the amount of residual water present in the liquid ionic.

(26) Similar results were obtained in the other investigated ionic liquids.

(27) (a) Kuwana, T.; Bublitz, D. E.; Hom, G. J. *J. Am. Chem. Soc.* **1960**, *82*, 5811. (b) Ikeda, T.; Schmelh, R.; Denisevich, P.; Willman, K.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 2683.

(28) We must outline that the values of viscosities are susceptible to change with the presence of adsorbed moisture from the air as Schröder et al.[14] showed that the presence of water considerably decreases the viscosities in [BMIM][PF_6] and [BMIM][BF_4]. However, it remains that these media are much more viscous than other conventional media.

(29) For example, through the Stokes−Einstein equation for a spherical molecule $D = kT/6\pi\eta a$, where k is the Boltzmann constant, η the viscosity, and a is the solvodynamic radius of the diffusing species.

(30) Andrieux, C. P.; Savéant, J.-M. Electrochemical reactions. In *Investigations of rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, pp 305−390.

(31) Karpinski, Z. J.; Nanjundiah, C.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 3358.

(32) Safford, L. K.; Weaver, M. J. *J. Electroanal. Chem.* **1992**, *331*, 857.

(33) See, for example: *Organic Electrochemistry* 4th ed.; Lund, H., Hammerich, O., Eds.; Marcel Dekker Inc: New York, 2001.

(34) (a) Parker, V. D. *Acta Chem. Scan.* **1998**, 145. (b) Parker, V. D. *Acta Chem. Scan.* **1998**, 154. (c) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243. (d) Reitstöen, B.; Norrsell, F.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 8463. (e) Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1991**, *113*, 6954. (f) Parker, V. D.; Chao, Y. T.; Zheng, G. *J. Am. Chem. Soc.* **1997**, *119*, 11390.

(35) See, for example: Howell, J. O.; Wightman, R. M. *J. Phys. Chem.* **1984**, *88*, 3915.

(36) Wang, Y.; Tanko, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 8201

(37) However, to get similar current intensities taking into account the differences in diffusion coefficients, anthracene concentrations in acetonitrile were typically five times lower than that used in the ionic liquids.

(38) In [$(C_8H_{17})_3NCH_3$][NTf_2], the slope was higher (around 25 mV/log(v)) that may indicate a change in the mechanism but because of the higher resistivity of this media, we suspect the effect of some uncompensated IR drop.

(39) Fukuzumi, S.; Nakanishi, I.; Tanaka, K *J. Phys. Chem. A* **1999**, *103*, 11212.

(40) Mastragostino, M.; Nadjo, L.; Saveant, J. M. *Electrochim. Acta* **1968**, *13*, 721.

(41) Fry, A. J. *Synthetic Organic Electrochemistry*; Harper and Row: New York, 1972; p 72.

(42) Andrieux, C. P.; Garreau, D.; Hapiot, P.; Savéant, J.-M. *J. Electroanal. Chem.* **1988**, *248*, 447.

(43) As mentioned in the Experimental Section, a Pt wire coated with polypyrrole is used as a quasireference electrode. We checked this quasireference against the ferrocene/ferricinium couple ($E° = 0.405$ V/SCE).

(44) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98.

(45) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(46) Shlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.

(47) Shlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1986**, *90*, 3747.

(48) (a) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, J. H.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (b) Nalwa, H. S., Ed. *Handbook of organic conductive molecules and polymers*; John Wiley and Sons: New York, 1997; Vol. 2.

(49) (a) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 2439. (b) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Savéant, J.-M. *J. Phys. Chem.* **1991**, *95*, 10158.

(50) Hapiot, P.; Lorcy, D.; Tallec, A.; Carlier, R.; Robert A. *J. Phys. Chem.* **1996**, *100*, 14823.

(51) (a) Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, *94*, 4749. (b) Chapuzet, J.-M.; Simonet, J. *Tetrahedron* **1991**, *47*, 791.

(52) (a) Andrieux, C. P.; Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *42*, 223. (b) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113.

(53) We checked that the concentrations of water were almost the same in all the ionic liquids (less than a factor 2).

(54) Simonet, J. *Curr. Top. Electrochem.* **1994**, *3*, 227 and references therein.

(55) For a comparison between peak currents for the oxidation of the monomer and the reduction of the trimer radical cation, one should take into account that the first one corresponds to an exchange of 7 electron per mole against one for the trimer redox couple.

(56) We performed cyclic voltametry of 1×10^{-3} mol L^{-1} veratrole in acetonitrile (+ 0.1 mol L^{-1} Bu_4NPF_6) in the range of scan rates 0.1−500 V s^{-1}.

(57) (a) The value of the diffusion limit rate constant k_{diff} is given by $k_{diff} = 4\pi\bar{D}/\int_R^\infty e^{\omega(r)/kT}\, dr/r^2$ [56b,56c] where $\bar{D}$ is the sum of diffusion coefficients and $\omega(r)$ the work term to bring the reactant at the reaction distance R. A precise calculation of k_{diff} for a reaction involving two positively charged species $\omega(R) > 0$ requires the estimations of R and the potential surface. However, a stronger decrease of k_{diff} is expected in low polarity solvent because $\omega(R) > 0$ and has mainly an electrostatic origin. (b) Debye, P. *Trans. Am. Electrochem. Soc.* **1942**, *82*, 265. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.