

Heterogeneous electron-transfer kinetics of nitro compounds in room-temperature ionic liquids

Corinne Lagrost^a, Loredana Preda^b, Elena Volanschi^b, Philippe Hapiot^{a,*}

^a *Laboratoire d'Electrochimie Moléculaire/Synthèse et Electrosynthèse Organiques, UMR CNRS-University of Rennes 1, No. 6510, Bat 10C Campus de Beaulieu, F-35042 Rennes, France*

^b *Department of Physical Chemistry, University of Bucharest, Blvd Elisabeta 4-12, RO-70346 Romania*

Received 24 May 2005; received in revised form 18 June 2005; accepted 24 June 2005

Available online 19 August 2005

Abstract

The influence of using room temperature ionic liquids on the heterogeneous electron transfer kinetics has been investigated with the example of the reduction of a series of nitro aromatic and aliphatic compounds. The standard electron transfer kinetic rate constants, k_s , were measured in two ionic liquids (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and triethylbutylammonium bis(trifluoromethylsulfonyl)imide) and compared with the same data determined in acetonitrile. For the fastest redox couples (nitrobenzene derivatives) for which the outer sphere contribution to the activation energy is the major factor controlling the electron transfer, the values of k_s considerably decrease in the ionic liquids (at least 2 orders of magnitude). On the contrary, when the inner sphere contribution is large, for example for the reduction of the 2-methyl-2-nitropropane, the k_s shows negligible variations when passing in the ionic liquid. For aromatic molecules, the amplitude of the kinetics slowness is inversely proportional to the steric hindrance introduced around the NO_2 group.

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Keywords: Ionic liquid; Reduction of nitro compounds; Cyclic voltammetry; Electron transfer kinetics

1. Introduction

Room-temperature ionic liquids (RTILs) are salts that are liquids at room temperature. Classical non-haloaluminate RTILs result from the combination of a non-symmetrical bulky organic cation (*N,N*-dialkylimidazolium, quaternary ammonium, phosphonium, pyridinium, etc.) with a weakly coordinating anion ($\text{N}(\text{SO}_2\text{CF}_3)_2^-$, PF_6^- , etc.). Due to their interest in numerous fields of chemistry, the literature about non-haloaluminate RTILs is rapidly growing and several reviews [1–6] and two recent books are available [7,8] about their general chemistry and physical–chemical properties. RTILs exhibit

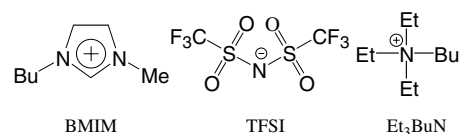
several desirable properties including negligible volatility, thermal and chemical stabilities, ability to dissolve a wide range of organic or inorganic compounds, wide electrochemical window and good intrinsic conductivity [6]. Although they were originally developed as versatile electrolytes in electrochemical devices [9–11], applications of RTILs as reaction media in electrochemistry are currently in widespread use [5,6]. They present particular and interesting prospects in electrochemical organic synthesis because they can be used as electrolyte without the need of adding any extraneous supporting salts [12–17]. This intrinsic property renders them a superior reaction media for preparative-scale electrosynthesis as compared with conventional electrolytes for which product recovery and solvent recycle are not very easy [18].

* Corresponding author.

E-mail address: philippe.hapiot@univ-rennes1.fr (P. Hapiot).

However, the transfer of electrochemical processes from conventional electrolytic media to the ionic liquids is not necessarily straightforward. Indeed, ionic liquids exhibit rich physicochemical properties (i.e., hydrogen-bonding ability, π - π interactions, ion pair-like solvation effect due to their pure ionic nature, Lewis/Brønsted acidity/basicity) that are likely to affect the chemical reactivity, especially in the case of charged reactants [6–8,19–22]. Thus, while a number of recent works have highlighted the advantages of conducting electrochemical analyses in RTILs by contrasting the results to those obtained in classical electrolytes [6,12–17], little has been focused on the kinetics of electrochemical processes in these complex media. It is becoming apparent that the nature of ionic liquids does influence the heterogeneous electron-transfer processes [23–29]. In previous works, we observed that the kinetics of the heterogeneous electron-transfer were slower by at least 1 order of magnitude in imidazolium or quaternary ammonium bis(triflimide) (or bis(trifluoromethylsulfonyl)imide) ionic liquids as compared with conventional solvent containing a supporting electrolyte [21,30]. This slowdown was attributed to larger solvent-reorganization in the highly organized and viscous RTILs media. A closely related rationale based on viscosity considerations was also used by Compton et al. [31] in their study of the electrochemical oxidation of *N,N,N',N'*-tetraalkyl-*para*-phenylenediamine in ammonium or imidazolium bis(triflimide) salts. Nevertheless, this question remains open because our previous work [21] and others evidenced intriguing features regarding the heterogeneous electron-transfer kinetics that could not be accounted for the former explanations [32]. First, we found that the solvation free energy did not seem to correlate the variations of the apparent standard kinetic constant, k_s , regarding two compounds under study (4-chlorobenzophenone and 9-chloroanthracene). Both of them displays similar values of k_s , whilst a strong decrease of electron-transfer kinetics would be expected for the more stabilized 4-chlorobenzophenone radical anion as observed in conventional electrolyte [33–36]. In that relation in a recent report, the electrochemical reduction of benzaldehyde in pyrrolidinium- and imidazolium-based bis(triflimide) ionic liquids was investigated [32]. Although both media exhibit similar bulk viscosities, large discrepancies were found when comparing the two media. The two-electron reduction was shown to be essentially unaffected in pyrrolidinium-based ionic liquids as compared to inert classical electrolyte, whereas a dramatic positive shift in the formal potentials together with a 1 order of magnitude decrease of the electron-transfer kinetics was observed in the imidazolium-based ionic medium.

In light of this, the purpose of the present investigation is to make a more systematic study of the effects of the ionic liquids on the kinetics of electron transfer.



Scheme 1. Cations and anions used in the investigated RTILs.

As reactants, a series of nitro aromatic and aliphatic compounds was chosen to be investigated in two different classical ionic liquids, [BMIM][TFSI] and [Et₃BuN][TFSI]. The reduction of nitro compounds to form a stable radical anion has been widely studied in non-aqueous media [33,34,37–42] providing accurate thermodynamic and kinetic descriptions of this process in organic solvent. In these media, the heterogeneous electron-transfer rate constants, k_s , were found to vary markedly among the series of nitro compounds and to be sensitive to the nature of the cation electrolyte in solution [37,38,40] (see Scheme 1).

2. Experimental section

2.1. Room-temperature ionic liquids

RTILs ([BMIM][TFSI], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and [Et₃BuN][TFSI], triethylbutylammonium bis(trifluoromethylsulfonyl)imide) were prepared from LiN(CF₃SO₂)₂ (Aldrich) and BMIMCl or Et₃BuNBr aqueous solutions according to previously published procedures [43,44]. The product was purified by repeated washing with H₂O, filtered over neutral alumina. Prior to each experiment, vacuum pumping carefully dried RTILs overnight and the amount of residual water was measured with Karl Fischer titration (Karl Fischer 652 Metrohm). The amount of water measured in our samples ranged from 100 to 300 ppm.

2.2. Chemicals

2-Nitromesitylene (**3**) was from Lancaster. The other nitro aromatic and aliphatic compounds (4-nitrotoluene (**1**), 2-nitro-*m*-xylene (**2**), 2,4,6-tri-*tert*-butyl-nitrobenzene (**5**) and 2-methyl-2-nitropropane (**6**)) were from Aldrich. Ferrocene was from Acros Organics. All commercially available compounds (highest available quality) were used without further purification. Acetonitrile was from Merck and was distilled over CaH₂ before use. *N*-tetrabutylammonium hexafluorophosphate was purchased from Fluka (puriss electrochemical grade). The nitro-pentamethylbenzene (**4**) was synthesized according to published procedure [45,46]. Pentamethylbenzene and nitrosonium tetrafluoroborate (NOBF₄) were purchased from Aldrich and used as received. 0.946 mmol of pentamethylbenzene and 0.726 mmol of NOBF₄ were dissolved in 50 mL of distilled acetonitrile

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