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Generation of superoxide ion in 1-butyl-1-methylpyrrolidinium trifluoroacetate and its application in the destruction of chloroethanes

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ABSTRACT

Ionic liquids (ILs) have attracted the curiosity of researchers due to their unique properties in different applications such as separation, extraction, purification, catalysis and electrochemical applications. The generation of superoxide ion ($O_2^{\bullet-}$) in ILs is one of these interesting areas. In this work $O_2^{\bullet-}$ was generated and analyzed electrochemically using cyclic voltammetry and chronoamperometry techniques from O_2 dissolved in 1-butyl-1-methylpyrrolidinium trifluoroacetate, [BMPyrr][TFA]. Moreover, $O_2^{\bullet-}$ was generated chemically by the addition of potassium superoxide (KO_2) into the same IL. UV/Vis spectrophotometer was used for testing the stability of the generated $O_2^{\bullet-}$ and GC/MS was used to investigate any possible reaction between [BMPyrr][TFA] and $O_2^{\bullet-}$. For our best knowledge this is the first time that trifluoroacetate based IL was used for the generation of $O_2^{\bullet-}$. The results showed that $O_2^{\bullet-}$ was very stable in this IL. This encourages further investigation on the use of this particular class of ILs in diverse applications involving the $O_2^{\bullet-}$. The chemically generated $O_2^{\bullet-}$ by dissolving KO_2 was then used for the destruction of hexachloroethane in [BMPyrr][TFA] under ambient conditions. The destruction percentage was higher than 98%. This work presents the first attempt to utilize KO_2 for destruction of chloroethanes in ILs.

1. Introduction

Ionic liquids (ILs) have been widely regarded as 'green solvents' owing to their potential as a recyclable alternative to the traditional organic solvents [1–4].

ILs have unique properties as compared with conventional solvents; they are nonvolatile, nonflammable, and have high ionic conductivity, high thermal stability, and large electrochemical windows. Moreover, their physicochemical properties can be modulated by changing the anion or the cation. Nowadays, these properties of ILs make them highly desirable in many industrial applications [4,5]. On the other hand, ILs have high viscosity, generally 1–2 orders of magnitude more than traditional solvents, e.g., acetonitrile. This results in lower diffusion coefficients of the electroactive species than would be observed in conventional solvents [6].

Research involving ILs has been directed towards the various properties of this new class of materials. Especially, much attention have been directed to nonchloride-containing imidazolium or pyrrolidinium cation-based ILs. It was reported that imidazolium/pyrrolidinium cations-based ILs have many unique characteristics especially those related to their electrochemical properties. Therefore, these ILs meet exactly the requirements of electrochemical devices, capacitors, and can be utilized in many electrochemical applications [7–11]. One of these important applications is the reduction of oxygen in IL mediums [12].

The electroreduction of O_2 is a key reaction in various applications, including metal–air batteries; fuel cells; and electrosynthesis of reactive oxygen species, such as superoxide ($O_2^{\bullet-}$) and hydrogen peroxide [13,14].

Carter et al. (1991) showed that $O_2^{\bullet-}$ can be generated by the reduction of O_2 in imidazolium chloride–aluminum chloride IL. However, the generated $O_2^{\bullet-}$ was unstable [15]. Ten years later, AlNashef et al. (2001–2002) reported the first evidence for generation of a stable $O_2^{\bullet-}$ in imidazolium based IL 1-methyl-3-*n*-butylimidazolium hexafluorophosphate [12,16]. Subsequently, many studies have been carried out on the generation of $O_2^{\bullet-}$ in different ILs based on imidazolium, quaternary ammonium, quaternary phosphonium, and pyrrolidinium cations [17–24], as listed in Table 1.

It was reported that the cation in the IL structure has a significant effect on the stability of the generaterd $O_2^{\bullet-}$, and since the superoxide is a radical anion, it was found that $O_2^{\bullet-}$ reacts with some cations of ILs

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Table 1
Some published ILs as media for $O_2{\bullet}^-$ generation.

IL	Reference
1,2-dimethyl-3-*n*-butylimidazolium hexafluorophosphate	[12]
1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl) imide	[18]
1,3-dimethylimidazolium diphosphate	[27]
1,3-dimethylimidazolium trifluoromethanesulfonate	[27]
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide	[14,18,21,25]
1-butyl-2,3- dimethylimidazolium bis (trifluoromethanesulfonyl) imide	[20,21]
1-butyl-2,3-methylimidazolium bis(trifluoromethanesulfonyl) imide	[23]
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	[21,22]
1-butyl-3-methylimidazolium hexafluorophosphate	[12,16,21,27]
1-butyl-3-methylimidazolium tetrafluoroborate	[21]
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	[17,18,27,29]
1-ethyl-3-methylimidazolium chloride mixed with $AlCl_3$	[15]
1-ethyl-3-methylimidazolium ethylsulfate	[27]
1-ethyl-3-methylimidazolium tetrafluoroborate	[13,19]
1-hexyl-3-methylimidazolium chloride	[27]
1-*n*-butyl-3- methylimidazolium tetrafluoroborate	[13]
1-*n*-propyl-3-methylimidazolium tetrafluoroborate	[13]
1-octyl-3-methylimidazolium chloride	[27]
n-hexyltriethylammonium bis(trifluoromethylsulfonyl) imide	[17,21,23,25,29]
trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl) imide	[18]
tris(*n*-hexyl)tetradecylphosphonium trifluorotris (pentafluoroethyl) phosphate	[25]
tris(*n*-hexyl)tetradecylphosphonium bis (trifluoromethylsulfonyl) imide	[25,26]

such as the quaternary phosphonium cation [25c,26], and the imidazolium cation [18,27,28].

On the other hand, many anions have also been studied such as chloroaluminate [15], hexafluorophosphate [12,16,21], tetrafluoroborate [13,21], and bis (trifluoromethylsulfonyl) imide, $[N(Tf)_2]^-$, [14,17,18,21–25,29–31].

There are different applications of $O_2{\bullet}^-$; one of these important applications is the destruction of chlorinated hydrocarbons (CHCs) in conventional aprotic solvents [32–41]. The CHCs are used and involved in various applications such as pesticides, herbicides, degreasing, dry cleaning, transformer oils, and heat exchanger fluids. However, these materials and their wastes are classified as hazardous and represent a major environmental problem. There are several standard methods used for the degradation of CHCs such as incineration, biological, electrochemical, photochemical and chemical oxidation [42–51]. Though, there are many disadvantages for using these methods such as production of toxic by-products (free halogen gases (Cl_2, F_2, or Br_2) and/or acid gases (HCl, HF, or HBr)), high energy consumption, economical viability and high degree of complexity.

In contrast, it was found that $O_2{\bullet}^-$ was able to destroy CHCs by nucleophilic substitution reaction to halide ions and carbonates without toxic by-products [37,39]. However, the volatility of the used conventional aprotic solvents in addition to the limited solubility of superoxide salts in these organic solvents inhibited the use of $O_2{\bullet}^-$ industrially.

In this work we investigated the electrochemical and chemical generation as well as the stability of $O_2{\bullet}^-$ in 1-butyl-1-methylpyrrolidinium trifluoroacetate, [BMPyrr][TFA] which was not reported in previous studies. The tested IL was then utilized as medium for the destruction of hexachloroethane which was selected as a model compound of the hazardous CHCs, in particular chloroethanes. Hexachloroethane is a colorless solid that gradually evaporates when it is exposed to air. It is used in the manufacture of aluminum and by the military for smoke-producing devices [52].

2. Experimental and materials

The IL used in this study, i.e. 1-Butyl-1-methylpyrrolidinium trifluoroacetate, [BMPyrr][TFA], was of synthesis grade from Merck. Scheme 1 and Table 2 show the chemical structure of the used IL. Dimethyl sulfoxide, DMSO, (Fisher, 99.98%), potassium superoxide, KO_2, (Sigma Aldrich, 99.9%), acetonitrile, AcN, (UNICHROM, HPLC grade 99.9%), diethyl ether, DEE, (UNIVAR, 99.9%), and hexachloroethane, HCE, (Aldrich 99%) were used without any further purification.

2.1. Experimental methodology

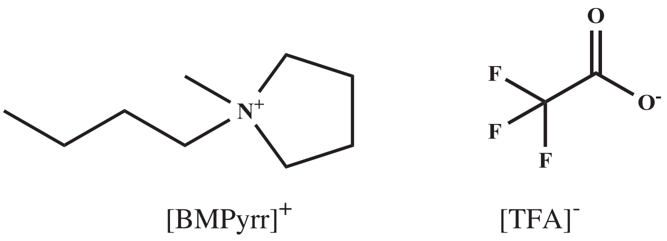
2.1.1. Electrochemical generation

Cyclic voltammetry (CV) tests were performed in the IL. The IL samples of were dried overnight in a vacuum oven at 50 °C. The electrochemistry was performed using PAR EG&G 263A potentiostat/galvanostat controlled by computer and data acquisition software. CVs were conducted in a one compartment cell since the time of the experiment was relatively small to affect the ILs.

Glassy carbon (GC) macro-electrode (BASi, 3 mm diam) was used as a working electrode for CV while a carbon fiber (CF) ultramicroelectrode (BASi, 11 μm diam) for chronoamperometry (CA), platinum electrode was used as a counter electrode while Ag/AgCl electrode (BASi) was used as a reference electrode. All experiments were performed in a dry glove box under either an argon or helium atmosphere. Prior to $O_2{\bullet}^-$ generation, a nitrogen sparge was used for obtaining a background voltammogram. Oxygen was then bubbled through the system for at least 30 min to allow sufficient solubilization [12,17,53,54]. This is to ascertain that saturation with O_2 has taken place and stable maximum peak current of CV has been achieved as evidence. Between consecutive CV runs, O_2 was bubbled briefly to refresh the system and to remove any concentration gradients. Nitrogen or oxygen sparging was discontinued during the CV data acquisition. CA measurements were conducted inside a Faraday cage to avoid any interference. The O_2 removal could be achieved by purging the IL with dry N_2 as it is considered the most common used method. This particular method was quite effective and also simple to be employed. Previous studies reported that by purging a solution with an inert gas can reduce the partial pressure of O_2 above the solution, and as a consequence the solubility of dissolved O_2 in the solution is decreased according to Henry's law.

2.1.2. Stability of superoxide ion

Dimethyl sulfoxide (DMSO) (Fisher, 99.98%) was dried overnight in a vacuum oven. The chemical generation of $O_2{\bullet}^-$ was performed by dissolving potassium superoxide (KO_2) in DMSO while stirring with a magnetic stirrer. Subsequently, a certain amount of IL was added to the DMSO containing generated $O_2{\bullet}^-$ to investigate the stability of $O_2{\bullet}^-$ with time. A computer-controlled UV/Vis spectrophotometer (PerkinElmer-Lambda 35) was used to measure the absorption spectra of $O_2{\bullet}^-$ every 10 min for 2 h. The reference solution of spectral measurements was DMSO or DMSO solution containing an appropriate amount of IL.



Scheme 1. Structure of the ions comprising the IL.