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Stability of Superoxide Ion in Imidazolium Cation-Based Room-Temperature Ionic Liquids

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The stability of superoxide ion ($O_2^{\bullet-}$) generated chemically by dissolving KO_2 in dried dimethyl sulfoxide solutions containing imidazolium cation [e.g., 1-ethyl-3-methylimidazolium (EMI^+) and 1-*n*-butyl-2,3-dimethylimidazolium ($BMMI^+$)] based ionic liquids (ILs) was investigated with UV−visible spectroscopic, NMR, and voltammetric techniques and an *ab initio* molecular orbital calculation. UV−visible spectroscopic and cyclic voltammetric measurements reveal that the $O_2^{\bullet-}$ species reacts with $BMMI^+$ and EMI^+ cations of ILs to form hydrogen peroxide. The pseudo first order rate constant for the reaction of $BMMI^+$ and $O_2^{\bullet-}$ species was found to be about 2.5×10^{-3} s^{-1}. With a molecular orbital calculation, the $O_2^{\bullet-}$ species is understood to attack the 2-position (C-2) of the imidazolium ring (i.e., $BMMI^+$) to form an ion pair complex in which one oxygen atom is bounded to C-2 and the other to the hydrogen atom of -CH_3 group attached to C-2. Eventually, the ion pair complex of $BMMI^+$ cation and $O_2^{\bullet-}$ species undergoes a ring opening reaction as evidenced with ^1H NMR measurement.

Introduction

Superoxide ($O_2^{\bullet-}$) is not “super” as an oxidant but behaves as a strong nucleophile in aprotic solutions.[1−4] Recently, a one-electron reduction of molecular oxygen (O_2) to $O_2^{\bullet-}$ (eq 1) in conventional aprotic solutions[1−6] and room-temperature ionic liquids (ILs)[7−19] including imidazolium cation based ILs (ImILs) (Scheme 1) has attracted a great deal of attention from the fundamental and practical viewpoints. AlNashef et al.[10,11] have first observed the electrochemical quasi-reversible behavior of the $O_2/O_2^{\bullet-}$ redox couple in ImILs and utilized the thus-generated $O_2^{\bullet-}$ as a reagent for the reduction of carbon dioxide. Besides ImILs, the redox reaction of the $O_2/O_2^{\bullet-}$ couple (eq 1) has also been extensively investigated in quaternary ammonium and pyrrolidinium cations-based ILs.[12−17]

$$O_2 + e^- \rightarrow O_2^{\bullet-} \qquad (1)$$

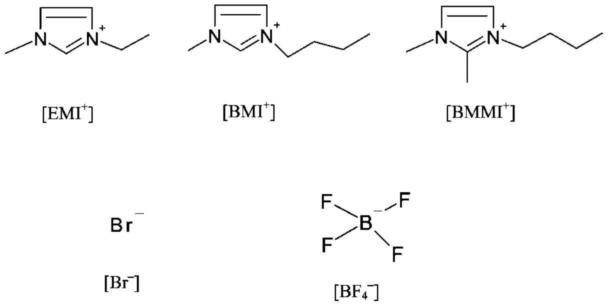
$$O_2^{\bullet-} + M \rightarrow O_2 + M^- \text{ (M: oxidant)} \qquad (2)$$

$$O_2^{\bullet-} + (\text{proton source}) \rightarrow HO_2^- \qquad (3)$$

$$O_2^{\bullet-} + RX \rightarrow RO_2^{\bullet} + X^- \text{ (RX: alkyl halide)} \qquad (4)$$

$$O_2^{\bullet-} + O_2^{\bullet-} \rightarrow O_2 + O_2^{2-} \qquad (5)$$

SCHEME 1: Structures of Imidazolium Cations and Anions of ILs



In addition to the redox reaction (eq 1), a variety of reactions of $O_2^{\bullet-}$ species, for example, one-electron transfer (eq 2), deprotonation (eq 3), nucleophilic substitution (eq 4), and disproportionation (eq 5), are also well-known. Due to the vital importance in biological system and electrochemical applications, namely fuel cells, the deprotonation reaction of the $O_2^{\bullet-}$ species has been widely investigated in various solutions containing a proton source.[3,6−8] On the other hand, in the imidazolium ring of ImILs (Scheme 1), the positive charge density on the carbon atom (C-2) at position 2 is greater than those on the other positions.[16] Very recently, we have observed that the electrogenerated $O_2^{\bullet-}$ undergoes ion pairing with the cation of ImILs (eq 6) and that the degree of association of $O_2^{\bullet-}$ with 1-ethyl-3-methylimidazolium cation ([EMI^+]) in dimethyl sulfoxide (DMSO) solution is very comparable to that of $O_2^{\bullet-}$ with H_2O.[8] Such ion pairing may ultimately lead to a nucleophilic attack on the C-2 of ImILs by $O_2^{\bullet-}$ to form some complex or new product.[20−22]

In the present study, the stability of $O_2^{\bullet-}$ (KO_2) dissolved[23] in dried DMSO solution in the presence of [$BMMI^+$] cation was typically examined using UV−visible spectroscopic and voltammetric techniques. The formation of an adduct of $O_2^{\bullet-}$ and the [$BMMI^+$] cation was also supported by an *ab initio*

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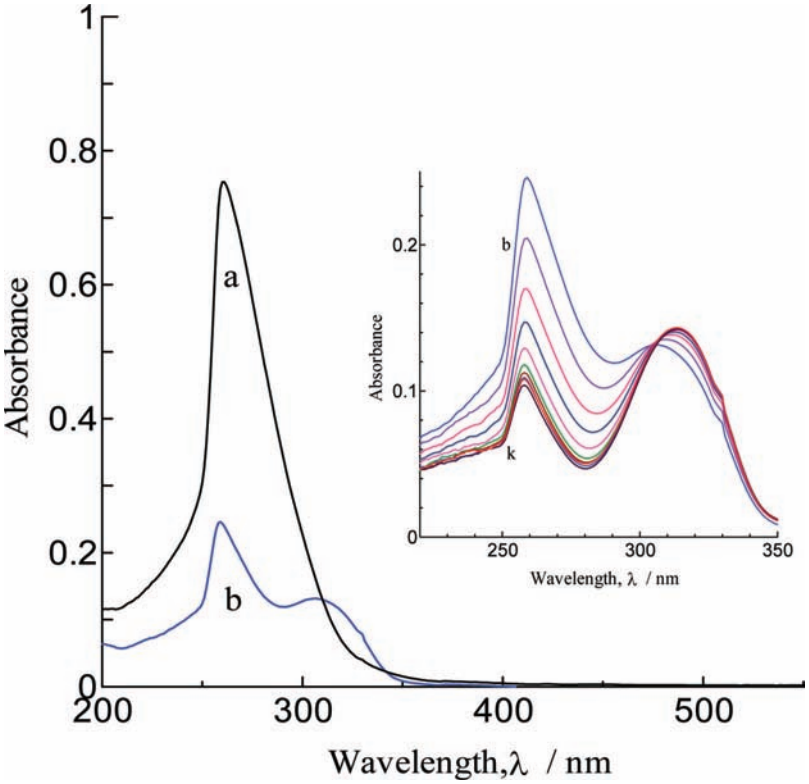


Figure 1. UV−visible spectra of 0.6 mM $O_2^{\bullet-}$ (KO_2) in DMSO solutions in the absence (a) and presence of 11.0 mM [$BMMI^+$][BF_4^-] (b). Inset shows the time course of the spectral changes. (Inset) Spectra (b−k) were measured after 4−90 min of the addition of [$BMMI^+$][BF_4^-] into the $O_2^{\bullet-}$ solution.

molecular orbital calculation. The knowledge of the reaction between $O_2^{\bullet-}$ and ImILs is very important especially when $O_2^{\bullet-}$, which can be generated via chemically (e.g., by dissolving KO_2) or electrochemical reduction of O_2 (eq 1), is used as an *in situ* reagent for the practical applications[5,11] in ILs. Finally, the bulk reaction of $O_2^{\bullet-}$ species with [$BMMI^+$] cation was carried out and the obtained reaction mixture was directly analyzed using UV−visible and ^{1}H NMR spectroscopic techniques.

Experimental Section

Reagents. DMSO of spectroscopic grade was purchased from Kanto Chemical Co. Inc., and dried over molecular sieves (4A 1/16, Wako Pure Chemicals Industries). The chemical generation of $O_2^{\bullet-}$ was performed by dissolving KO_2 in DMSO solution (described below).[23] 1-Ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) with a purity of more than 99% and less than 30 ppm (ca. 2.1 mM) H_2O was obtained from Stella Chemifa Co. (Japan). 1-*n*-Butyl-2,3-dimethylimidazolium tetrafluoroborate and bromide ([$BMMI^+$][BF_4^-] and [$BMMI^+$]-[Br^-]) were purchased from Acros Organics and used as received. Tetraethylammonium perchlorate (TEAP) (Kanto Chemical Co. Inc.) was used as a supporting electrolyte.

UV−Visible Spectroscopic Measurements. The absorption spectra were measured by using a computer-controlled UV/vis spectrophotometer (model V-550; JASCO, Japan). For the UV−visible studies, $O_2^{\bullet-}$ was generated by dissolving solid potassium superoxide (KO_2) in DMSO solution by its stirring with a magnetic stirrer. The saturated DMSO solution with $O_2^{\bullet-}$ was a pale yellow in color.[23] The obtained solution was diluted with DMSO. The reference solution of spectral measurements was DMSO or DMSO solution containing an appropriate amount of ILs or TEAP.

Cyclic Voltammetric Measurements. Electrochemical measurements were carried out using the computer-controlled electrochemical systems (model 50W, Bioanalytical Systems, Inc.). The electrochemical cell was a two-compartment Pyrex glass container with a glassy carbon (GC; diameter = 1 mm) working electrode, a spiral Pt-wire counter electrode and a sodium chloride saturated silver/silver chloride [Ag/AgCl/NaCl (sat.)] reference electrode. To minimize the IR drop yielded across the cell and the contamination of H_2O into the cell solution, the Ag/AgCl/NaCl (sat.) reference electrode was placed in a glass beaker containing NaCl-saturated aqueous solution and connected to the cell solution via a glass salt bridge filled with the solution of interest (i.e., DMSO containing TEAP). The working electrodes were polished with alumina powder and then washed with deionized water (Milli-Q, Milli-Pore, Japan) by sonication for 10 min. Prior to use, the electrode was washed well with deionized water and dried by blowing air. All measurements were carried out under N_2 atmosphere at 25 ± 2 °C.

Theoretical Calculations. All the calculations for $O_2^{\bullet-}$ and imidazolium ions were performed with the Beck's three parameter hybrid functional using the Lee−Yang−Parr correlation functional (B3LYP).[24] The geometry optimizations were carried out with 6−31G(d) basis sets. Calculations of analytical vibrational frequencies with B3LYP/6−31G(d) optimized structures were done to confirm the true minima.[25] All the quantum calculations were carried out on Gaussian03 program package.

Chemical Reaction of [BMM^+][Br^-] and KO_2. Appropriate amount of [BMM^+][Br^-] crystal (1 M) was dissolved in dried DMSO solution in a bottle. Then solid KO_2 (ca. 3 M) was added into the DMSO solution containing [BMM^+][Br^-] and the reaction mixture was continuously stirred with a bar magnet for several hours. To avoid the contamination of moisture, the bottle containing the reaction mixture was sealed with a Teflon stopper. The reaction progress was followed by monitoring the change of color of the solution. The initial yellow color, which

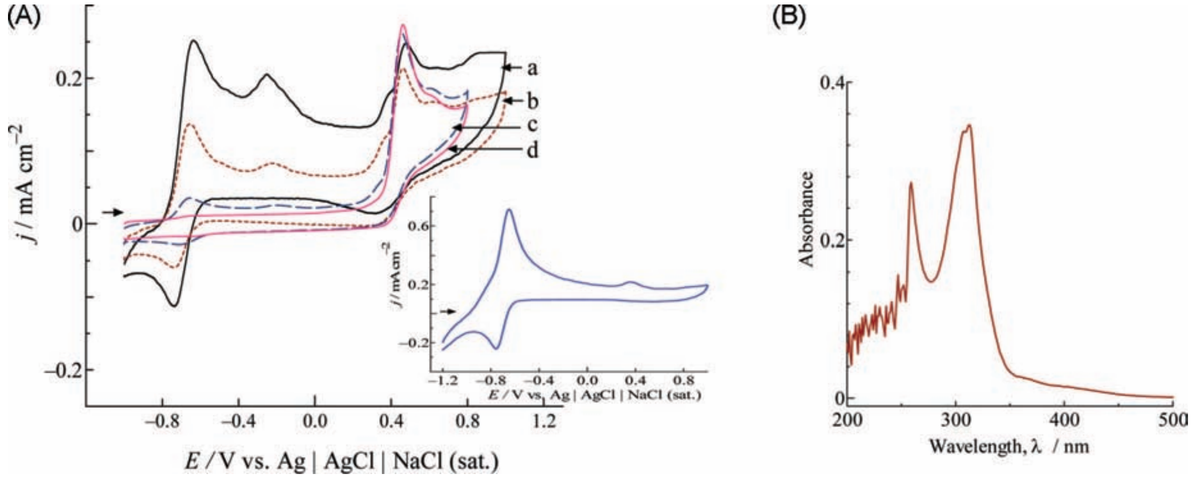


Figure 2. (A) CVs obtained at a GC electrode for 0.65 mM KO_2 in DMSO solutions containing 0.1 M TEAP: in the absence (inset) and presence (a-d) of 0.1 M $[BMMI^+][BF_4^-]$ at 0.1 V s^{-1}. The CVs (a), (b), (c), and (d) were measured after 5, 15, 40, and 60 min of the addition of $[BMMI^+][BF_4^-]$, respectively. (B) UV−visible spectrum was measured for the solution obtained after the measurement of the CV (d).

is due to KO_2, of the solution was found to become light brown after the elapse of about 5 min. The brown solution turned into magenta within 10 min. Ultimately, a white crystalline precipitate and a deep red solution were obtained. The obtained reaction mixture was directly (i.e., without separating the products) analyzed with UV−visible and ^1H NMR spectroscopic techniques.

NMR Measurements. The ^1H NMR measurements were carried out with JEOL-La-500 MHz instrument at 25 °C. The obtained results are noted as follows: For $[BMMI^+][Br^-]$ (in d6-DMSO): 7.77 (s, 1H), 7.74 (s, 1H), 4.15 (t, $NCH_2CH_2CH_2CH_3$), 3.79 (s, CCH_3), 2.63 (s, NCH_3), 1.67 (m, $NCH_2CH_2CH_2CH_3$), 1.28 (m, $NCH_2CH_2CH_2CH_3$) and 0.86 (t, $NCH_2CH_2CH_2CH_3$) ppm. For the reaction mixture of $[BMMI^+][Br^-]$ and KO_2 (in d6-DMSO): 8.55 (s), 2.98−2.39 (m), 1.76 (s), 1.25 (s) 0.85 (m) ppm.

Results and Discussion

UV−Visible Spectroscopic Observations. Figure 1 shows typical UV−visible spectra obtained for $O_2^{\bullet -}$ in DMSO solutions without and with $[BMMI^+][BF_4^-]$. In the absence of $[BMMI^+][BF_4^-]$, a characteristic absorption band was found with a maximum absorption (λ_{max}; $\epsilon = 1350$ mM^{-1} cm^{-1}) at 259 nm (spectrum a) as expected in DMSO solution for a $\pi \rightarrow \pi^*$ electronic transition.[23] When $[BMMI^+][BF_4^-]$ was added into the solution, a new band with $\lambda_{max} > 300$ nm grew at the cost of the band of $O_2^{\bullet -}$, resulting in an isosbestic point at 305 nm. Although the absorbance of $O_2^{\bullet -}$ decreased regularly, the increase in the absorbance of the new band was less significant with a red shift of λ_{max} with time and no change in the absorbances of both bands in spectrum k was measured even after two weeks. The observation of the isosbestic point clearly indicates a consumption of $O_2^{\bullet -}$ in forming a new product. In the presence of an excess of $[BMMI^+][BF_4^-]$ (85 mM), the consumption rate of $O_2^{\bullet -}$ (0.6 mM) (i.e., the pseudo first order rate constant of the reaction shown by eq 7) was roughly estimated to be 2.5×10^{-3} s^{-1} with a half-life of 4.6 min. Similar measurement with $[EMI^+][BF_4^-]$ was also performed and the observed result was less noteworthy: a small shoulder at ca. 290 nm with a steady absorbance was obtained, although the absorbance of $O_2^{\bullet -}$ gradually decreased with time (not shown).

Cyclic Voltammetric Observations. Figure 2A represents the cyclic voltammograms (CVs) measured for $O_2^{\bullet -}$ in N_2-saturated DMSO solution containing 0.1 M TEAP. In the absence of $[BMMI^+][BF_4^-]$ (inset), two anodic peaks at −0.64 (main) and 0.36 V (weak) were observed for the oxidation of $O_2^{\bullet -}$ and hydrogen peroxide (H_2O_2) to O_2, respectively.[1−4] In the reverse potential scan, a well-defined cathodic peak at −0.75 V was observed for the reduction of the thus-formed O_2 to $O_2^{\bullet -}$ (eq 1).[1−4] When $[BMMI^+][BF_4^-]$ was added, the current of the main anodic peak decreased regularly, and two new anodic peaks at −0.25 (an intermediate peak) and 0.46 V concurrently grew [compare the CVs (a−d) shown in Figure 2A]. Eventually, the currents of the anodic peak at −0.64 V (and hence the cathodic peak at −0.75 V) and the anodic peak at −0.25 V completely diminished after 60 min [i.e., the dissolved-$O_2^{\bullet -}$ was consumed totally; see CV (d) in Figure 2A], whereas that observed at 0.46 V increased.[26] The thus-obtained $O_2^{\bullet -}$-free solution was subjected to a spectral analysis and the UV−visible spectrum was observed to contain two bands with λ_{max} of 259 nm and >300 nm (and shoulders at >350 nm) (Figure 2B) as shown in Figure 1. The voltammetric results clearly support the spectroscopic observation that the $O_2^{\bullet -}$ species reacts with $[BMMI^+]$ cation to form some new product and at the same time that an irreversible oxidation of the product occurs at more positive potential than that of the oxidation of $O_2^{\bullet -}$ to O_2. The observed anodic peak at 0.46 V may be attributed to the two-electron oxidation of peroxide species, which is formed via the abstraction of proton from $[BMMI^+]$ by $O_2^{\bullet -}$ species (eqs 7 and 9), to O_2 (discussed later).

Theoretical Calculations. To support further the complexation between the cation of ImILs and $O_2^{\bullet -}$, an *ab initio* molecular orbital calculation was carried out and the obtained optimized structures are shown in Figure 3 in which for simplicity in the calculation, all the alkyl substitutents of imidazolium ring (**1**) were taken as -CH_3 groups. In the **1** cation, the partial charge density upon the C-2 is 0.578.[16] Thus, the positive center on the ring of the **1** cation may induce the $O_2^{\bullet -}$ species for a complexation via C-2. Practically this can be seen in the optimized structures, $\mathbf{1_a}$ and $\mathbf{1_b}$ (Figure 3). In $\mathbf{1_a}$, two oxygen atoms of $O_2^{\bullet -}$ species bind with C-2 and one hydrogen atom of -CH_3 group attached to C-2. In $\mathbf{1_b}$, on the other hand, the terminal oxygen atom of $O_2^{\bullet -}$ species attached to C-2 binds to one nitrogen atom of the imidazolium ring. Recently, Ohkubo et al. have investigated the binding mode of $O_2^{\bullet -}$ with ammonium ion (NH_4^+) using DFT calculation.[27] They have observed that the side-on binding of two hydrogen atoms of NH_4^+ with $O_2^{\bullet -}$ species is the most stabilized structure of NH_4^+-

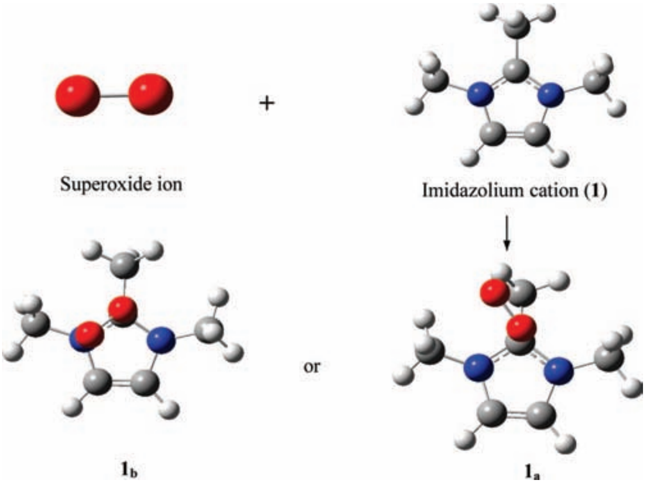
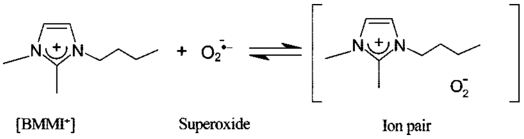


Figure 3. Structures of imidazolium-$O_2^{\bullet-}$ complex optimized by Gaussian03 program with B3LYP/6−31G(d). Among various initial structures, $\mathbf{1_a}$ and $\mathbf{1_b}$ are the optimized ones.

$O_2^{\bullet-}$ complex. Moreover, the binding of the $O_2^{\bullet-}$ species in $O_2^{\bullet-}$-Sc^{3+} complex has been revealed to take place in an end-on mode.[28] In our study, the calculation regarding the binding of $O_2^{\bullet-}$ species with [EMI^+] cation was also carried out. In this case, the partial positive charge on the C-2 of [EMI^+] cation was estimated to be 0.304. In addition, similarly to the case of $O_2^{\bullet-}$-Sc^{3+} complex,[28] the $O_2^{\bullet-}$ species was found to bind in an end-on mode in which one oxygen atom of $O_2^{\bullet-}$ species is bounded to the C-2 of the imidazolium ring and the other is directed toward the hydrogen atom attached to C-2 of [EMI^+] cation. On the basis of our observations, the structure $\mathbf{1_a}$, which possibly breaks to form peroxide species as evidenced with voltammetric (Figure 2A) and spectroscopic measurements (discussed below), may be reasonably considered to be the most stabilized one.

Reaction of $O_2^{\bullet-}$ with [$BMMI^+$] Cation. Thus far, it is obvious that the $O_2^{\bullet-}$ species react with imidazolium cation. Based on the present observations and reported reactions,[1−4,7,8,20−22,29−34] it is thought that various steps are involved in this reaction (eqs 6–10). Recently, we have studied the ion paring (adduct formation) of $O_2^{\bullet-}$ with imidazolium (e.g., [EMI^+]) cation (eq 6).[8] In the ion pair, the $O_2^{\bullet-}$ species may eventually abstract the proton from C-2 of [EMI^+] cation and the -CH_3 group attached to the C-2 of [$BMMI^+$] cation to form carbene[7,20−22,30,33] and a new compound, respectively, and $HO_2^{\bullet}$ (eq 7). It has been well accepted that $O_2^{\bullet-}$ species can abstract the proton from phenol with effective pK_a's of 9.2 and 20.8 in H_2O and DMSO, respectively,[31] to form $HO_2^{\bullet}$ species, although pK_a values of the $HO_2^{\bullet}/O_2^{\bullet-}$ couple are 4.75 and 11.7 in H_2O and DMSO, respectively,[32] because the $HO_2^{\bullet}$ radicals formed undergo predominantly a further electron-transfer reaction with $O_2^{\bullet-}$ to form HO_2^-.[1−4,31,32] In the present case, the pK_a value of [EMI^+] cation has been reported to be 24 in DMSO solution.[21] The pK_a of -CH_3 in [$BMMI^+$] cation is unknown, but would be smaller than that of [EMI^+] since the calculated positive charge density on C-2 of [$BMMI^+$] is significantly larger than that of [EMI^+] (described above). Thus, the reaction shown by eq 7 is considered as an uphill[32] reaction as in the above-mentioned proton abstraction by $O_2^{\bullet-}$ from phenol, but this reaction is followed by a downhill electron-transfer reaction of $HO_2^{\bullet}$ with $O_2^{\bullet-}$ (eq 9) and consequently HO_2^- is formed.[29,31,32] The formed HO_2^- can be electrochemically oxidized at 0.46 V (Figure 2).[1,3,7,8]



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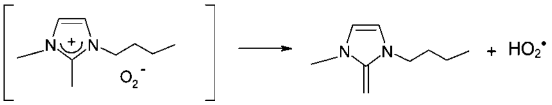

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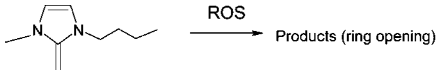

(8)

$$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^- + O_2 \qquad (9)$$

$$HO_2^- + 2\,Br^- + 3\,H^+(IL) \rightarrow Br_2 + 2\,H_2O \qquad (10)$$

In this study, the reaction of $O_2^{\bullet-}$ and [$BMMI^+$][Br^-] in DMSO solution was found to form a deep red solution (see Experimental Section). The UV−visible spectrum measured for the reaction mixture showed an intense band at wavelength shorter than 300 nm and a broad band consisting of several small bands at the wavelength range of 350−420 nm (not shown). Marcinek et al.[33] have observed two absorption bands [λ_{max} 320 (main) and 250 nm (weak)] for the neutral radical of imidazolium ring generated by pulse radiolysis. Therefore, the observed UV−visible spectrum with two absorption bands would be ascribed to the deprotonated imidazolium cation (eq 7) or other products (mentioned below). In the ^{1}H NMR spectrum measured for the reaction mixture, the peak corresponding to the proton attached to an unsaturated carbon, which is found at 7.77 and 7.74 ppm for [$BMMI^+$], is absent (see Experimental Section), suggesting that the deprotonated form of [$BMMI^+$] cation may further react with reactive oxygen species (ROS) (e.g., $O_2^{\bullet-}$, $HO_2^{\bullet}$ and HO_2^-) to form ring opening (colored) product (eq 8). On the other hand, it has been known that peroxide species oxidize halide ion to form dihalide molecule.[34] In this case, the oxidation of Br^- by HO_2^- species to form Br_2, which is brown in color and shows the absorption band at 350−420 nm, may be presumed to take place in the presence of IL in DMSO solution (eq 10).

Conclusions

The stability of the $O_2^{\bullet-}$ species generated chemically in DMSO solution containing ImILs was investigated with UV−visible spectroscopic, cyclic voltammetric and NMR measurements and theoretical calculation. With a molecular orbital calculation, it was suggested with that the $O_2^{\bullet-}$ species initially attacks the C-2 of the imidazolium ring to form an ion pair complex.[8] Then, the $O_2^{\bullet-}$ species is considered to abstract the proton attached to the C-2 or one proton of -CH_3 group attached to the C-2 of the imidazolium ring to form $HO_2^{\bullet}$ and the deprotonated imidazolium ring. This uphill reaction is followed by a downhill electron-transfer reaction of $HO_2^{\bullet}$ with $O_2^{\bullet-}$ and consequently HO_2^- is formed. Moreover, ^{1}H NMR results suggest that the deprotonated imidazolium ring eventually breaks down to form some ring opening products. Thus, it can be reasonably concluded that the $O_2^{\bullet-}$ species is not practically stable in ImILs, although the reversible cyclic voltammetric redox reaction of the $O_2/O_2^{\bullet-}$ couple could be often observed.[7−19]

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