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Stability and Kinetics of Generated Superoxide Ion in Trifluoromethanesulfonate Anion-Based Ionic Liquids

Maan Hayyan[1,*], *Farouq S. Mjalli*[2], *Inas M. AlNashef*[3], *Mohd Ali Hashim*[1]

[1] University of Malaya Centre for Ionic Liquids (UMCiL), Department of Chemical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
[2] Petroleum & Chemical Engineering Department, Sultan Qaboos University, Muscat 123, Oman
[3] Chemical Engineering Department, King Saud University, Riyadh11421, Saudi Arabia
[*]E-mail: maan_hayyan@yahoo.com

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The generation and long-term stability of superoxide ion ($O_2^{\bullet-}$) in two trifluoromethanesulfonate $[TfO]^-$ anion-based ionic liquids (ILs), with cations of 1-butyl-1-methylpyrrolidinium $[BMPyrr]^+$ and 1-butyl-2,3-dimethylimidazolium $[BDMIm]^+$ have been investigated. The electrochemical generation was carried out by reducing O_2 to $O_2^{\bullet-}$ in ILs and was analyzed using a cyclic voltammetry (CV) technique. The chemical generation of $O_2^{\bullet-}$ in ILs was carried out by the solvation of potassium superoxide (KO_2) in the aprotic solvent, dimethyl sulfoxide, in the presence of the corresponding IL. Long-term stability of generated $O_2^{\bullet-}$ in ILs was examined using UV-visible spectrophotometery at an absorbance range of 190–400 nm. It was found that the $[BMPyrr]^+$ based IL has a lower $O_2^{\bullet-}$ consumption rate than the $[BDMIm]^+$ based ILs indicating that [BMPyrr][TfO] offers a promising long-term stability of $O_2^{\bullet-}$ for various reactions and applications. This work represents the first attempt for using the $[TfO]^-$ based ILs as media for the chemical and electrochemical generation of $O_2^{\bullet-}$.

Keywords: ionic liquids; superoxide ion; pyrrolidinium cation; imidazolium cation; trifluoromethanesulfonate anion; cyclic voltammetry; long-term stability.

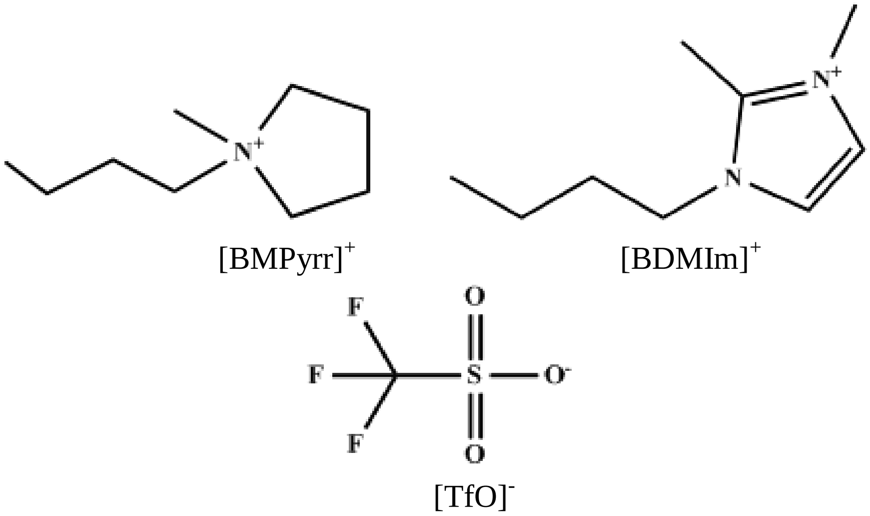
1. INTRODUCTION

Ionic liquids (ILs) have been investigated as media for radical ions [1]. Generation of $O_2^{\bullet-}$ has been studied in ILs as media. Carter *et al.* (1991) have shown that $O_2^{\bullet-}$ can be generated by O_2 reduction in imidazolium chloride-aluminum chloride. However, the resulting $O_2^{\bullet-}$ was unstable due to the subsequent irreversible reaction of $O_2^{\bullet-}$ with protic impurities present in the IL [2]. Hence, as was shown later, the presence of impurities have a dramatic effect on the stability of $O_2^{\bullet-}$ in ILs [3]. Ten years later, AlNashef *et al.* (2001) reported the first evidence for a stable generation of $O_2^{\bullet -}$ in 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][HFP] [3]. Subsequently, many studies have been carried out on ILs based on imidazolium, quaternary ammonium, quaternary phosphonium, pyridinium, morpholinium, sulfonium and pyrrolidinium cations [4-13].

However, most of previous studies conducted on ILs have utilized the short-term stability CV technique to test the feasibility of these ILs [4-10] as possible media for $O_2^{\bullet -}$ generation. However, this does not provide an indication for its real stability since a single CV run takes between a few seconds and up to a few minutes. Islam *et al.* (2009) and AlNashef *et al.* (2010) used the long-term stability to study the reaction of imidazolium based ILs with $O_2^{\bullet -}$ [12,14]. With the aim of utilizing $O_2^{\bullet -}$ in various applications, the long-term stability and kinetics of $O_2^{\bullet -}$ are necessary since most of industrial applications require continuous processes which require some particular period of time for utilizing the reaction ingredients [13,15].

2. MATERIALS AND METHODS

The ILs used in this work are 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPyrr][TfO] and 1-butyl-2,3-dimethylimidazolium [BDMIm][TfO]. The ILs were supplied by Merck and were of synthesis grade. Scheme 1 shows the structures of the cations and anion that make up the ILs used in this study. The chemical formulae, molecular weights and melting points of ILs are listed in Table 1. Dimethyl sulfoxide (DMSO) was purchased from Fisher with a purity of 99.98% and potassium superoxide (KO_2) from Sigma Aldrich with a purity of 99.9%.



Scheme 1. Structures of ions comprising the ILs.

Table 1. The chemical formulae, molecular weights and melting points of ILs.

IL	Formula	M.Wt. (g/mol)	Melting Point (°C)
[BMPyrr][TfO]	$C_{10}H_{20}F_3NO_3S$	291.34	3
[BDMIm][TfO]	$C_{10}H_{17}F_3N_2O_3S$	302.32	2

2.1 Electrochemical generation of $O_2^{\bullet-}$ (short-term stability)

CV tests were performed as the electrochemical analysis technique since this method is extremely powerful and is among the most widely practiced of all electrochemical methods [16]. The IL to be used was dried overnight in a vacuum oven at 50 °C. It should be noted that the ILs were acidic without pre-treatment, and the pH was 4-6. The pH of ILs was measured using pH strips supplied by Merck. A very small quantity of KO_2 was added to the acidic IL until its pH became 7 [15,17-18]. AlNashef *et al*. (2001) reported that $O_2^{\bullet-}$ was not stable in some ILs because of the acidity of these ILs [3]. Therefore, small additions of KO_2 can neutralize the acidic ILs without affecting the electrochemistry in these ILs [15,18].

The electrochemistry was performed using EG&G 263A potentiostat/galvanostat (PAR) controlled by computer and data acquisition software. CVs were conducted in a one compartment cell since the time of the experiment is relatively small to affect the ILs. The used electrochemical cell was a jacketed vessel (10 ml volume) with a Teflon cap including 4 holes for the three electrochemical electrodes and for the gas sparging tube.

Glassy carbon macro-electrode (BASi, 3 mm diam) was used as working electrode for CV analysis. A platinum electrode was used as a counter electrode. To avoid contaminating the target IL with water in the reference electrode, the content of the reference electrode was separated by a glass frit, a filtering material, and for this reason an Ag/AgCl electrode purchased from BASi [25-26] was used for this study. The macro-electrodes were polished using alumina solution (BASi) and sonicated in distilled water for 10 min prior to each experiment. This was done to ensure that there are no impurities on the surface of the working electrode.

All experiments were performed in a dry glove-box under either an argon or helium atmosphere. Prior to $O_2^{\bullet-}$ generation, a background voltammogram was obtained after the removal of O_2. The O_2 removal was achieved by purging the IL with dry N_2. This particular method is quite effective and also simple to be employed. Previous studies reported that 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 decreases according to Henry's law [19-20].

O_2 was then bubbled into the tested IL for at least 30 min to ensure that equilibrium was achieved [3-4,21-22]. In order to confirm that the tested IL is saturated with O_2, CVs at different time intervals were conducted and the final measurement was taken when the cathodic peak current of the CV is constant. Between consecutive CV runs, O_2 was bubbled briefly to refresh the system and to remove any concentration gradients. N_2 or O_2 sparging was discontinued during the CV runs.

2.2 Chemical generation of $O_2^{\bullet-}$ (long-term stability)

DMSO was dried overnight in a vacuum oven. KO_2 was kept in a sealed vial filled with molecular sieves. The chemical generation of $O_2^{\bullet-}$ was performed by dissolving KO_2 in DMSO while stirring with a magnetic stirrer [14,23]. Subsequently, a certain amount of IL was added to the generated $O_2^{\bullet-}$ in DMSO to investigate the dynamic stability of $O_2^{\bullet-}$. 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 hours. The reference solution of spectral measurements was DMSO or DMSO solution containing an appropriate amount of IL [15,18].

3. RESULTS AND DISCUSSION

3.1. Electrochemical generation of $O_2^{\bullet -}$ (short-term stability)

The CV for the reduction of O_2 to superoxide ion ($O_2^{\bullet -}$) was studied initially in ILs at a sweep rate of 100 mV/s, Figures 1 & 2. In order to complete the cycle of voltammetry, the potential was swept from a position of zero voltage down to a potential after the reduction peak (~ ±1 V *vs.* Ag/AgCl) and back to zero voltage. No prewave was observed prior to the onset of O_2 reduction, confirming that trace impurities in the IL were removed under vacuum conditions. An environment free of protons could enable the full reduction of O_2, and it is essential to realize the effect of IL without interference from protonated intermediates or products.

Most of the previously reported studies [3-4,8,24] utilized pure O_2 to generate $O_2^{\bullet -}$. Nonetheless, Randström *et al.* (2007) utilized air to generate $O_2^{\bullet -}$ as they observed a cathodic peak current density in air at 20 °C which was about one-tenth of that reported by Katayama *et al.* (2005) in pure O_2 at 25 °C. This ratio is reasonable, considering the lower concentration of O_2 in air and the lower diffusion coefficient of the species taking part in the reaction at a lower temperature [25-26].

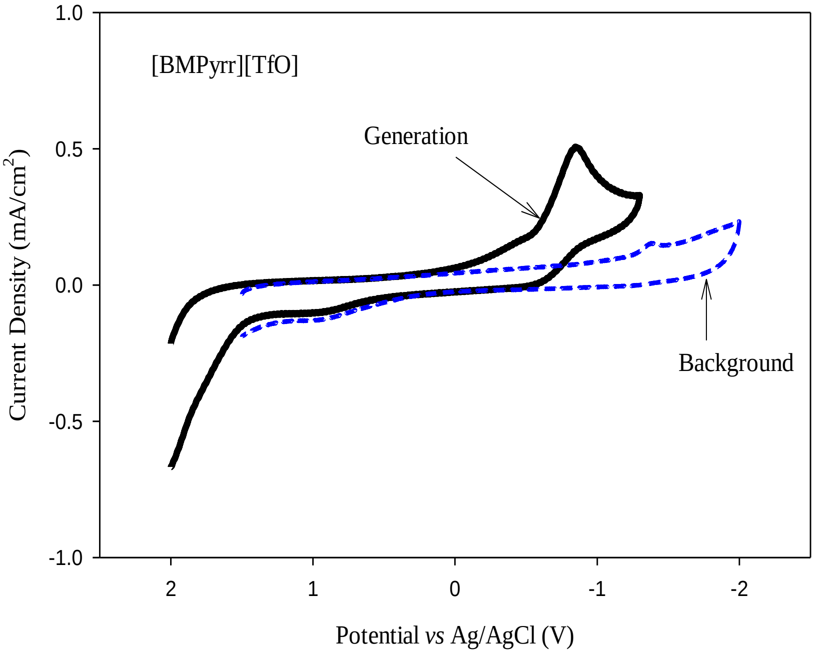


Figure 1. Cyclic voltammograms in [BMPyrr][TfO] after sparging with N_2 (Background) and O_2 at 25 °C using GC macro-electrode, sweep rate 100 mV/s.

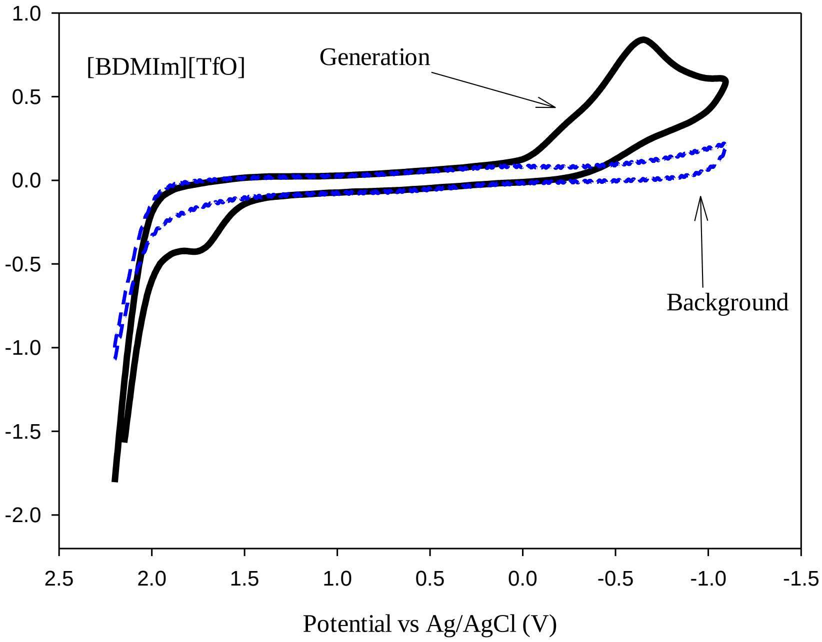


Figure 2. Cyclic voltammograms in [BDMIm][TfO] after sparging with N_2 (Background) and O_2 at 25 °C using GC macro-electrode, sweep rate 100 mV/s.

$O_2^{\bullet -}$ is successfully generated in ILs but CVs show that the generated $O_2^{\bullet -}$ is unstable, Figures 1 & 2. The absence of any peak after sparging of N_2 in the studied ILs confirms that there are no electrochemically active impurities in the ILs, and that the ILs are electrochemically stable within the screened range of potential. From Figures 1 & 2, it can be observed that there is a reduction peak, indicating the generation of $O_2^{\bullet -}$ at approximately ± -1.0 V *vs.* Ag/AgCl in ILs. However, the absence of any oxidation peak in the backward sweep indicates that the generated $O_2^{\bullet -}$ is not stable in these ILs. The instability may be due to the reaction of $O_2^{\bullet -}$ with the cation of the ILs or with products of the decomposition of the cations.

The presence of impurities can also have a dramatic effect on the stability of $O_2^{\bullet -}$ in the IL. For this reason, work is continuing on controlling the levels of impurities in the ILs in order to get a better purity. AlNashef *et al.* (2001) discussed the instability of $O_2^{\bullet -}$ in [BDMIm][HFP] and in [BMIm][HFP]. The only difference between these two ILs is the additional methyl group in position 2 for [BDMIm][HFP]. Both ILs have comparable proton acidity, therefore it is doubtful that the protons on [BDMIm][HFP] reacted with $O_2^{\bullet -}$. Rather, the instability of $O_2^{\bullet -}$ was believed to be due to the presence of impurities in the IL, even though the stated impurities of the two ILs were 3%.

It should be noted that the ILs without pre-treatment were acidic and the pH was 4-6. Hence, very small quantity of KO_2 was added to the studied IL until its pH became 7. The existence of a proton source leads to the spontaneously rapid disproportionation of the electrogenerated superoxide species [10,27-28]. Various studies have proven that reduction of O_2 is a complex process, the outcome of which is highly dependent on the solvent employed and, in particular, its acidity. The mechanism of O_2 reduction critically depends on the pH of the medium as well as the nature of the electrode material. For example, in an acidic medium, O_2 electro-reduction proceeds by a 2-electron reduction of O_2 to H_2O_2 on polycrystalline Au and single crystal Au electrode surfaces. Conversely, the reduction mechanism changes to a 4-electron process of O_2 to H_2O at pH > 6 on Au electrode. In non-aqueous media, polycrystalline Au electrode supports 1-electron reduction of O_2 to $O_2^{\bullet -}$ [13,29-31].

The imidazolium and pyrrolidinium based ILs were found to be unstable due to the combination of these cations with $[TfO]^-$. Previous studies showed, using short-term stability, that imidazolium and pyrrolidinium based ILs were stable [4,26].

3.2. Chemical generation of $O_2^{\bullet -}$ (long-term stability)

Despite the fact that all reported studies agree that $O_2^{\bullet -}$ can be generated chemically and electrochemically in ILs [5,7,12,14,24], the stability of this radical anion in the media under consideration is still being investigated [13,32].

In order to avoid the possibility of mass controlling process when investigating the long-term stability, KO_2 was dissolved in DMSO first, followed by the addition of IL to be investigated, and subsequently any consumption in the generated $O_2^{\bullet -}$ can be attributed to the reaction of $O_2^{\bullet -}$ [15].

Figures 3 & 4 show the time evolution of the maximum absorbance of $O_2^{\bullet -}$ generated in ILs. As reported in the literature [11,14], the absorbance band of $O_2^{\bullet -}$ can be observed within the range of 250-270 nm. Steady absorbance bands of $O_2^{\bullet -}$ at approximately 250 nm are obtained for the examined ILs.

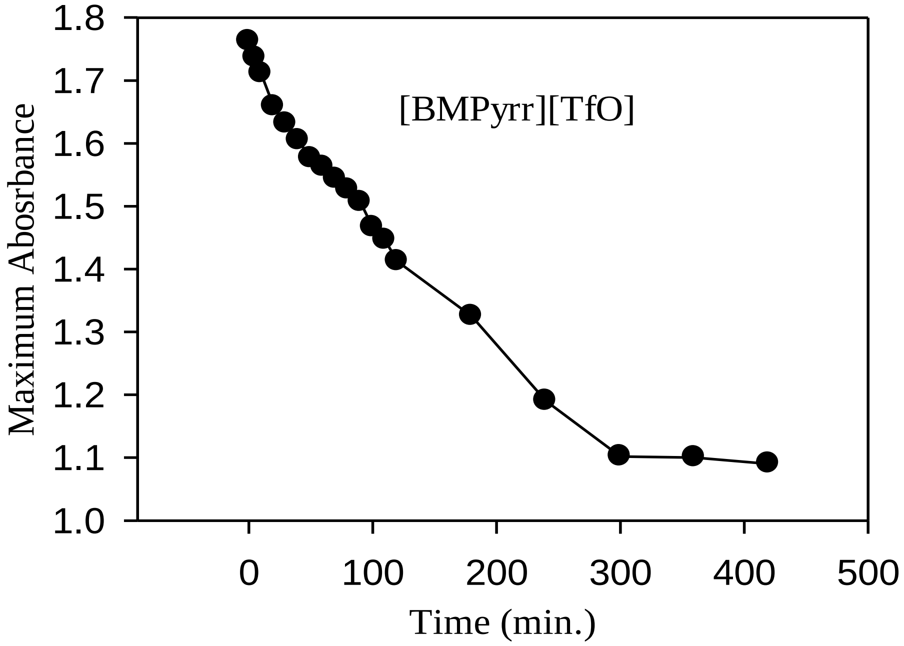


Figure 3. The change of $O_2^{\bullet -}$ absorbance peak with time for [BMPyrr][TfO] in DMSO.

Significant drop in absorbance is observed in Figure 4 for the stability of $O_2^{\bullet -}$ in [BDMIm][TfO]. This indicates that the generated $O_2^{\bullet -}$ is not stable in this IL. This can be attributed to the reaction of $O_2^{\bullet -}$ with the cation of IL producing 1-butyl-2,3-dimethylimidazolone. This is in accordance with AlNashef *et al.* (2010) who reported that $O_2^{\bullet-}$ has reacted with alkyl imidazolium based ILs to give the corresponding 2-imidazolones [12], Scheme 2.

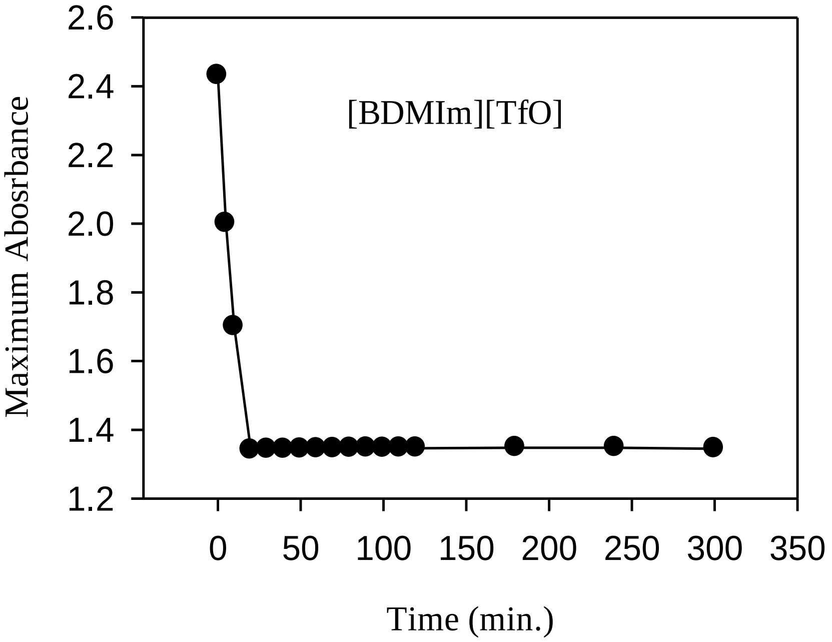
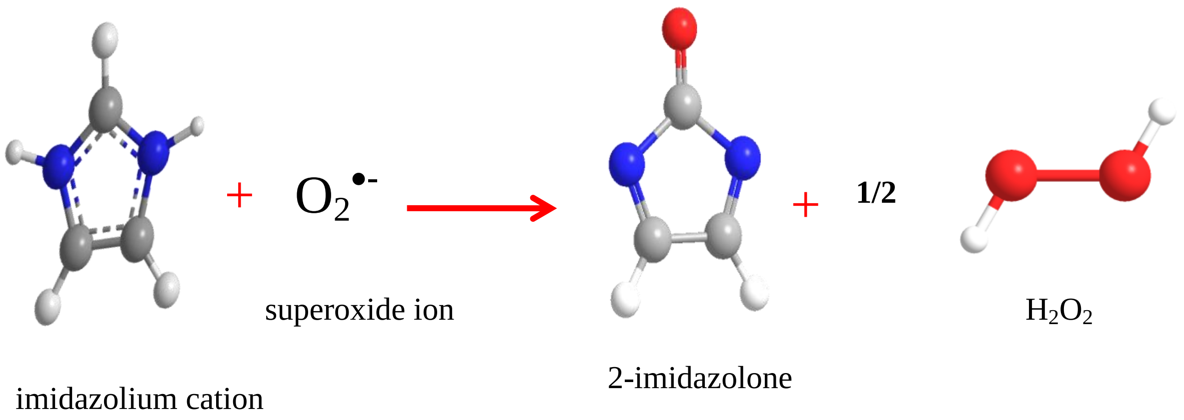


Figure 4. The change of $O_2^{\bullet-}$ absorbance peak with time for [BDMIm][TfO] in DMSO.



Scheme 2. Synthesis of 2-imidazolones by reaction of $O_2^{\bullet-}$ with the imidazolium cation of IL [12].

However, there is no significant development of any new band in the 150–450 nm range of the UV/Vis spectra in these ILs as reported in the literature for the reaction of $O_2^{\bullet-}$ and 1-n-butyl-2,3-dimethylimidazolium tetrafluoroborate, [BDMIm][BF_4] [14]. Marcinek *et al.* (2001) detected two absorption bands [λ_{max} = 320 (main) and 250 nm (weak)] for the neutral radical of imidazolium ring generated by pulse radiolysis. Hence, the UV/Vis spectrum observed by Islam *et al.* (2009) with two absorption bands can be attributed to the deprotonated $[Im]^+$ or other products [1,14].

On the contrary, a slight decrease in the absorbance peak of $O_2^{\bullet -}$ with time can be observed for the stability test of $O_2^{\bullet -}$ in [BMPyrr][TfO], as shown in Figure 3. This demonstrates that $O_2^{\bullet -}$ is very stable in this IL, and this confirms a high viability to serve as good medium for the generation of a stable $O_2^{\bullet -}$. This shows that the short-term stability was not indicative for this IL since the $O_2^{\bullet -}$ was unstable in the CV test. The instability in the electrochemical generation can be attributed to the adsorption of IL on the electrode or due to the reaction of $O_2^{\bullet -}$ with some electroactive impurities that were activated after O_2 sparging. Similar results were observed in triethylsulfonium bis(trifluoromethylsulfonyl)imide [S222][TFSI] but the effect was reversed since the short-term stability tests indicated that this IL was stable but the long-term stability test indicted that $O_2^{\bullet -}$ was unstable [13].

Table 2 shows the reaction rate constant, total consumption and consumption rate of $O_2^{\bullet -}$ in the studied ILs. The rate constants in Table 2 are calculated based on the assumption of pseudo first order reaction between the cation of the ILs and $O_2^{\bullet -}$. The rate constant of $O_2^{\bullet -}$ in [BMPyrr][TfO] and [BDMIm][TfO] were estimated to be 2.813×10^{-5} s^{-1} and 5.067×10^{-5} s^{-1}, respectively. These values are much lower than the reported value for $O_2^{\bullet -}$ in DMSO solution in the presence of [BDMIm][BF_4] which was estimated to be 2.5×10^{-3} s^{-1} [14] and similar in order of magnitude to those reported by AlNashef *et al.* (2010) and Hayyan *et al.* (2012) [12-13,15,33].

The total consumption of $O_2^{\bullet -}$ in ILs was calculated by comparing the initial concentration of $O_2^{\bullet -}$ with the concentration along 2 hours of measurements. Results show that only 19.88% of the initial $O_2^{\bullet -}$ in [BMPyrr][TfO] was consumed after 2 hours of reaction time. On the other hand, as much as 44.61% of the generated $O_2^{\bullet -}$ was consumed in [BDMIm][TfO]. This shows clearly that this IL is not an appropriate solvent to be used for generating a stable $O_2^{\bullet -}$. The consumption rate of $O_2^{\bullet -}$ was calculated by dividing the concentration of $O_2^{\bullet -}$ being consumed over the time period of the measurement [15]. The consumption rate of $O_2^{\bullet -}$ in [BMPyrr][TfO] was 3.693×10^{-3} mM/min which is comparable to the value of 3.334×10^{-3} mM/min reported by Hayyan *et al.* (2012) [15] for 1-hexyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide [HMPyrr][TFSI]. In contrast, the consumption rate of $O_2^{\bullet -}$ in [BDMIm][TfO] was 11.433×10^{-3} mM/min which is close to the value of 10.903×10^{-3} mM/min [33] reported in trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate [P14,666][TPTP].

Table 2. Rate constant, total consumption percentage and consumption rate of $O_2^{\bullet -}$ in ILs.

Abbreviation	Rate Constant $\times 10^5$ (s^{-1})	Total Consumption% of $O_2^{\bullet -}$ after120 min.	Consumption Rate of $O_2^{\bullet -}$ $\times10^3$ (mM/min)
[BMPyrr][TfO]	2.813	19.88	03.693
[BDMIm][TfO]	5.067	44.61	11.433

4. CONCLUSIONS

$O_2^{\bullet -}$ was generated electrochemically from O_2 dissolved in [BMPyrr][TfO] and [BDMIm][TfO] using the cyclic voltammetry (CV) technique. Furthermore, $O_2^{\bullet -}$ was generated chemically by the solvation of KO_2 in the studied ILs. A UV/Vis spectrophotometer was used for testing the long-term stability of generated $O_2^{\bullet -}$. The long-term stability of $O_2^{\bullet -}$ tests showed that $O_2^{\bullet -}$ was more stable in [BMPyrr][TfO] than in [BDMIm][TfO].

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