Kinetics of Homogeneous Reactions in Ionic Liquids

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In this work, the double potential step chronoamperometry (DPSC) was used to determine the rate constants for the homogeneous reactions of alcohols with superoxide ion ($O_2^{\bullet-}$) at different temperatures in ionic liquids (ILs). The technique was first tested by determining the pseudo first order rate constant for reduction of azobenzene to hydroazobenzene that, in turn, undergoes the benzidine rearrangement. The results were in good agreement with values reported in the literature using DPSC and conventional kinetic methods. The pseudo first order rate constant for the homogeneous reaction of $O_2^{\bullet-}$ with different primary and secondary alcohols in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][HFP] and 1,2-dimethyl-3-*n*-butylimidazolium hexafluorophosphate [bdmim][HFP] at different temperatures was then determined. The Arrhenius plot was used to determine the activation energy and pre-exponential factor for the corresponding reactions.

1. INTRODUCTION

There is a paucity of reliable, quantitative information on reaction rates and rate constants in ILs despite the recent widespread interest in developing their use as alternative solvents for a wide range of applications including synthesis [1-2], biphasic catalysis [3-5], electrochemistry [6] and separations [7]. McLean *et al*. (2002) have determined the temperature dependence of the bimolecular rate constants for a diffusion controlled reaction involving neutral reactants in five commonly used imidazolium cation based ILs [8].

The use of ILs leads to significant improvements in rate and yield in many organic reactions [2]. Recently, a number of reports have described the use of ILs as media for radical polymerization [9-12]. These reports have commented on the large increases in both the rate of polymerization and the

molecular weights that are observed in polymerization of methyl methacrylate when ILs are used in place of conventional organic solvents. Harrison *et al.* (2002) measured the rate constants of propagation and termination of methyl methacrylate in [bmim][HFP] using the pulsed laser polymerization technique across a range of temperatures, and calculated Arrhenius parameters for the rate of propagation at different IL concentration [13]. Chiappe *et al.* (2002) studied the kinetic behavior and the product distributions of several arylalkynes with Br_2 in [bmim][HFP] and [bmim]Br at different temperatures. They compared the kinetic constants and the activation parameters for the reaction in [bmim]Br with those relating to the reaction of the same alkynes with tetrabutylammonium tribromide in 1,2-dichloroethane. On the basis of kinetic data, they found that a significant role for solvent viscosity in determining the reaction rate may be envisaged [14].

Mohammad *et al.* (2001) measured the rate constants for the reaction of $O_2^{\bullet-}$ with various substrates through stationary electrode polarography. In solvent acetonitrile (MeCN), the substrate and the rate constants of the reaction are AH = iso-propanol ($k_2 \leq 0.01$ M^{-1} s^{-1}); ethanol ($k_2 = 1.42 \times 10^2$ M^{-1} s^{-1}); methanol ($k_2 = 1.1 \times 10^7$ M^{-1} s^{-1}); H_2O ($k_2 = 1.0 \times 10^5$ M^{-1} s^{-1}). They also showed that $O_2^{\bullet-}$ is stable in pyridine as well as acetone and other aprotic solvents. The reaction rate was found to be first order with respect to both $O_2^{\bullet-}$ and the alcohol [15].

$$O_2^{\bullet-} + AH \xrightarrow{K_2} Products \qquad\qquad\qquad 1$$

$$O_2 + e^- \rightleftharpoons O_2^{\bullet-} \qquad\qquad\qquad\qquad 2$$

$$O_2^{\bullet-} + R1 - OH - R2 \longrightarrow Products \qquad\qquad 3$$

Andrieux *et al.* (1987) studied the electrochemical reduction of dimethyl sulfoxide (DMSO) as a function of the addition of acids by means of DPSC. Analysis of the kinetics as a function of dioxygen and acid concentrations and of the measurement time in a series of acids involving five phenols and nitromethane allowed them to determine the reaction mechanism and of the characteristic rate constants. The $HO_2^{\cdot}$ radical resulting from the neutralization of the initial $O_2^{\bullet-}$ undergoes an electron-transfer reduction by $O_2^{\bullet-}$ itself rather than abstracting a hydrogen atom from the solvent or exchanging an H atom with another $HO_2^{\cdot}$ radical, a commonly accepted mechanism. They found that this mechanism appears to be the same in dimethyl formamide (DMF); pointing to the conclusion that disproportionation of superoxide ions follows the same reaction pathway in aprotic organic solvents and in water. They determined the rate constant for the reaction of $O_2^{\bullet-}$ with halogenated aromatic alcohols and phenol [16].

Muldoon *et al.* (2001) found that the activation energy for hydrogen abstraction from imidazolium-based ILs is significantly higher than that observed in conventional solvents. As part of a continuing study of the influence of ILs on photochemical processes, they reported their initial results on hydrogen abstraction from these solvents by triplet excited state benzophenone [17]. Only a handful of photochemical systems have been studied in ILs to date, often with results that are quite different from those observed in conventional solvents [18-20]. The ILs used in their study were based on the

cations 1-butyl-3-methylimidazolium [bmim]$^+$, 1-methyl-3-octylimidazolium [moim]$^+$ and 1-butyl-2,3-dimethylimidazolium [bmmim]$^+$, combined with the anions [PF$_6$]$^-$ and [Tf$_2$N]$^-$ (Tf = CF$_3$SO$_2$), chosen to give a moderate degree of structural variation.

Conventional spectrophotometric techniques cannot be used when investigating reactions that occur at a sub-second rate, as in the case of the reaction between O$_2^{\bullet-}$ and alcohols. This is overcome by using a stopped-flow-apparatus. A stopped flow apparatus, which provides instantaneous mixing and recording of data on a tens-of-millisecond time scale, can be used. The stopped flow apparatus can be connected to a UV-vis spectrophotometer through a remote-send-cable that is attached to an accessory controller port on the instrument. Potassium superoxide (KO$_2$) can be dissolved in ILs at moderate temperatures ($\approx$ 40°C). The chemically generated O$_2^{\bullet-}$ in IL can be used to measure the rate constant of the homogeneous reaction using the stopped flow method.

Many electrochemical methods can also be used to measure the rate constant for fast homogeneous reactions, e.g. rotating ring disc electrode (RRDE) and DPSC. DPSC is a simple technique that does not require large volumes of the solution. The values of the diffusion coefficient and bulk concentration of the electrochemically active material are not needed, in contrast to RRDE. Briefly, DPSC involves producing O$_2^{\bullet-}$ at a stationary electrode under diffusion-controlled conditions by applying a constant potential for a timed interval,τ. During this interval, O$_2^{\bullet-}$ diffuses into the solution and simultaneously reacts. At $t = \tau$, the potential is switched to a value where O$_2^{\bullet-}$ is oxidized back to O$_2$. The anodic current is an indication of the amount of O$_2^{\bullet-}$ that has not reacted and can be related to the rate constant k. Schwarz and Shain (1965) developed this method and they gave an analytical solution for the boundary value problem for the combined diffusion-electron transfer-kinetic system for the case of planar electrode [21].

2. EXPERIMENTAL DETAILS

Before conducting DPSC experiments in the ILs [bmim][HFP] and [bdmim][HFP], cyclic voltammetry tests were performed to generate O$_2^{\bullet-}$ and to confirm its short-term stability. [bmim][HFP] and [bdmim][HFP] (SACHEM), both with a stated purity of 97%, were dried overnight in a vacuum oven at 50 °C. The electrochemistry was performed using an EG&G 263A potentiostat/galvanostat controlled by computer and data acquisition software. The electrode configuration was a glassy carbon, or Pt working (BASi, 3 mm dia.) and a platinum mesh counter (Aldrich). Ag/AgCl (Fisher Scientific) was used as a reference electrode. All [bmim][HFP] and [bdmim][HFP] experiments were performed in a dry glove box under an argon atmosphere. The systems were sparged prior to electrochemical experiments with UHP nitrogen or oxygen fitted through a Drierite gas purification column (W.A. Hammond).

Prior to O$_2^{\bullet-}$ generation, an argon sparge was used to obtain a background voltammogram. Oxygen was then bubbled through the system for 30 minutes to allow sufficient solubilization. Between consecutive CV runs, oxygen was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients. Nitrogen or oxygen sparging was discontinued during the CV data acquisition [6,22].

After confirming the short-term stability of $O_2^{\bullet-}$ a weighed amount of alcohol is added to the IL and the solution is stirred with a magnetic stirrer and sparged with argon. DPSC experiments at different values of switching time, τ, are then conducted and back ground currents are recorded. Oxygen is bubbled through the IL. After 15-20 min the sparging of oxygen is stopped and DPSC experiments are conducted in the O_2 saturated ILs. The background currents should be deducted from the corresponding values obtained after sparging with O_2.

The potential applied to the working electrode was a single square pulse with amplitude of –0.8 V. The initial potential value was set at –0.2 V vs. Ag/AgCl reference electrode. Under these conditions, the cathodic potential step was carried out at –1.0 V vs. Ag/AgCl; the subsequent anodic step, at –0.2 V. CVs in the ILs showed that the applied potential always fell in the diffusion controlled limiting current region. In addition, by running argon blanks it was verified that the initial potential used was sufficiently cathodic.

3. RESULTS AND DISCUSSION

DPSC involves producing $O_2^{\bullet-}$ at a stationary electrode under diffusion-controlled conditions by applying a constant potential for a timed interval, τ. During this interval, $O_2^{\bullet-}$ diffuses into the solution and simultaneously reacts, Eq 1.
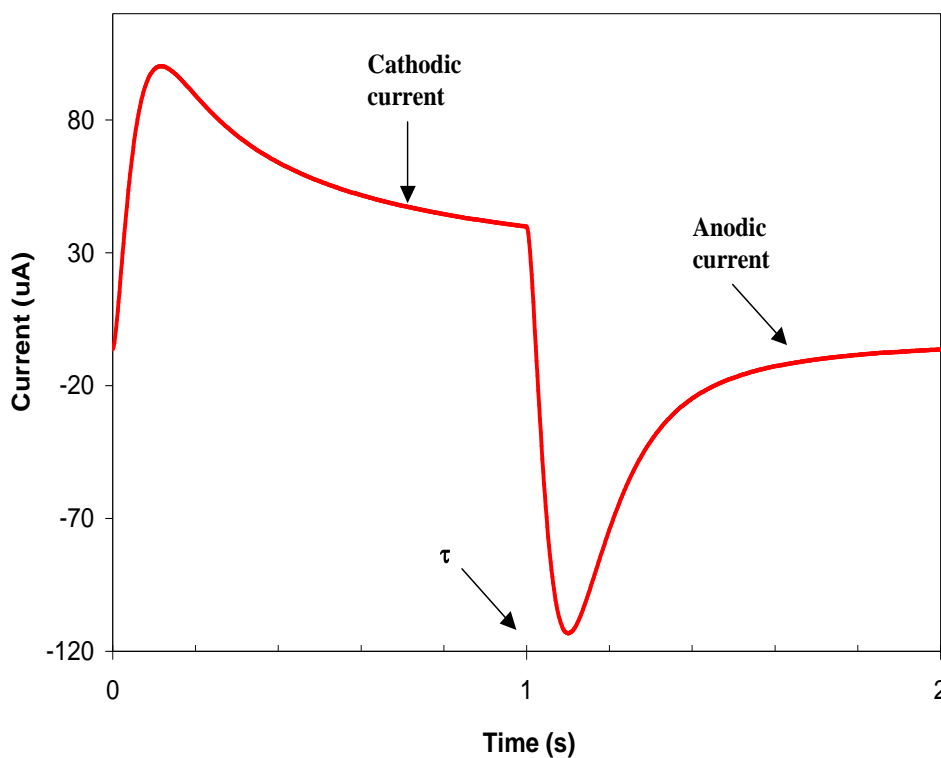

Figure1. Experimental cathodic-anodic current-time curves for 20 mM benzhydrol in [bmim][HFP] at 27 °C , τ=1s.

At $t = \tau$, the potential is switched to a value where $O_2^{\bullet -}$ is oxidized back to O_2 as shown by Eq 2. The rate expression for the homogeneous reaction can be written as shown in Eq 4.

$$r = k_2 C_{AH} C_{O_2^{\bullet -}} = k_1 C_{O_2^{\bullet -}} \qquad\qquad 4$$

Where C_{AH} is the concentration of the substrate that is in excess, $C_{O_2^{\bullet -}}$ is the concentration of the superoxide ion, k_2 is the second order rate constant, and k_1 is the pseudo first order rate constant.

The anodic current is an indication of the amount of $O_2^{\bullet -}$ that has not reacted and can be related to the rate constant k_1. Eqs 2 and 3 show the electrochemical reactions and the homogeneous reaction of $O_2^{\bullet -}$ with alcohol. Typical cathodic-anodic current-time curves are shown in Figure 1.

The theoretical relationship between the current, the time of electrolysis, and the rate constant, k_1, for a system following Eqs 5 and 6 can be derived by solving Fick's laws of diffusion to a plane (modified by the appropriate kinetic terms) [21].

$$\frac{\partial C_o}{\partial t} = D_o \left(\frac{\partial^2 C_o}{\partial x^2} \right) \qquad\qquad 5$$

$$\frac{\partial C_R}{\partial t} = D_R \left(\frac{\partial^2 C_R}{\partial x^2} \right) - k_1 C_R \qquad\qquad 6$$

Where C_O and C_R are concentrations of O_2 and $O_2^{\bullet -}$, t is the time, x is the distance from the electrode, and D_O and D_R are the diffusion coefficients of O_2 and $O_2^{\bullet -}$.

The electrolysis conditions resulting from the application of a single large amplitude square voltage pulse to the working electrode are expressed in the initial and boundary conditions

$$t = 0, x \geq 0 : C_0 = C_0^*, C_R = 0 \qquad\qquad 7$$

$$t \succ 0, x \to \infty : C_0 \to C_0^*, C_R \to 0 \qquad\qquad 8$$

$$\tau \succ t \succ 0, x = 0 : C_0 = 0, \quad D_0 \left(\frac{\partial C_0}{\partial x} \right) = - D_R \left(\frac{\partial C_R}{\partial x} \right) \qquad\qquad 9$$

$$t \succ \tau, x = 0 : C_R = 0, \quad D_o \left(\frac{\partial C_o}{\partial x} \right) = - D_R \left(\frac{\partial C_R}{\partial x} \right) \qquad\qquad 10$$

$$-i = nFAD_o \left(\frac{\partial C_o}{\partial x} \right)_{x=0} = -nFAD_R \left(\frac{\partial C_R}{\partial x} \right)_{x=0} \qquad\qquad 11$$

Here C_O^* is the bulk concentratism of O_2, τ is the switching time, n is the number of electrons involved in the charge transfer, F is the Faraday constant, and A is the area of the electrode. Schwarz and Shain (1965) gave an analytical solution to this problem and the results are shown in Eqs 12 and 13 [21].

for $t \prec \tau$

$$-\frac{i_c}{nFA} = -C_o^*\sqrt{D_o/\pi t} \qquad\qquad 12$$

for $t \succ \tau$

$$\frac{i_a}{nFA} = C_o^*\sqrt{D_0/\pi(t-\tau)} \times \left[\ e^{-kt}\,_1F_1(1/2,1,k\tau) + \sum_{n=1}^{\infty} \frac{e^{-kt}\left[(t-\tau)k\right]^n}{n!}\,_1F_1(n+1/2,n+1,k\tau)\ \right] - C_o^*\sqrt{D_o/\pi t} \qquad 13$$

Where $_1F_1(1/2,1,kt)$ is a confluent hypergeometric series [23] with the following properties

$$\frac{d}{dx}\left[\,_1F_1(\alpha,\gamma,x)\right] = (\alpha/\gamma)\,_1F_1(\alpha+1,\gamma+1,x) \qquad\qquad 14$$

and $\quad _1F_1(\alpha,\gamma,0) = 1 \qquad\qquad 15$

where

$$_1F_1(a,c,x) = 1 + \frac{a}{c}\frac{x}{1!} + \frac{a(a+1)}{c(c+1)}\frac{x^2}{2!} + \cdots \qquad\qquad 16$$

Dividing Eq 13 by Eq 12 gives

for $t \succ \tau$

$$\frac{i_a}{i_c} = \sqrt{t/(t-\tau)} \times \left[\ e^{-kt}\,_1F_1(1/2,1,k\tau) + \sum_{n=1}^{\infty} \frac{e^{-kt}\left[(t-\tau)k\right]^n}{n!}\,_1F_1(n+1/2,n+1,k\tau)\ \right] - 1 \qquad 17$$

It was found that if three terms of the infinite series in Eq 17 are used, approximately 0.4% accuracy in the anodic current is obtained. So in this study we used three terms of the infinite series. Eq 17 becomes:
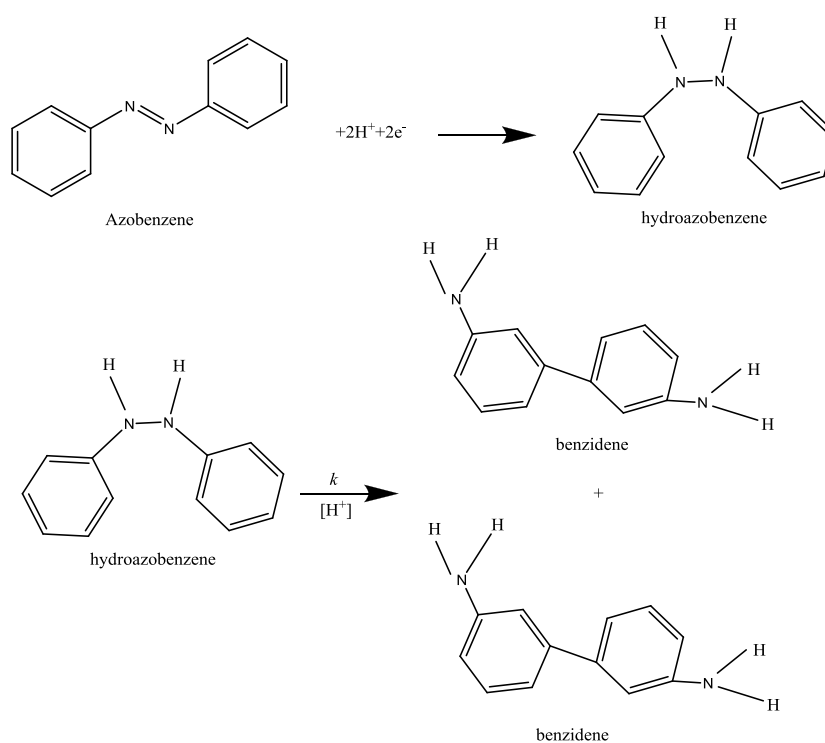
for $t \succ \tau$

$$\frac{i_a}{i_c} = \sqrt{t/(t-\tau)} \times e^{-k_1t}\left[\ 1 + \frac{k_1\tau}{2} + \frac{3(k_1\tau)^2}{8} + k_1(t-\tau) + \frac{3}{4}\frac{k_1^2\tau(t-\tau)}{1} + \right.$$

$$\frac{15}{8}\frac{k_1^3\tau^2(t-\tau)}{1}+k_1^2(t-\tau)^2+\frac{5}{24}\frac{k_1^3\tau(t-\tau)^2}{1}+\frac{35}{16}\frac{k_1^4\tau^2(t-\tau)^2}{1} \quad] \qquad 18$$

3.1 Azobenzene system

In order to test the theoretical calculations and the apparatus used, the reduction of azobenzene, Scheme 1, was investigated. The rearrangement of hydrazobenzene has been the subject of numerous investigations [21,24] in which spectrophotometric [25], potentiometric [26], or titration [27] techniques were used to follow the rate of the reaction. Schwarz and Shain (1965) used DPSC to determine the pseudo first order rate constant for the rearrangement of benzidine in 50% wt. ethanol-water at different perchloric acid concentrations [21].

Scheme 1. Electrochemical and homogeneous reactions for the azobenzene system.

We measured the pseudo first order rate constant for the rearrangement of benzidine in 50% wt. ethanol-water at one perchloric acid concentration. The potential applied to the working electrode was a single square pulse with amplitude of –0.6 V. The initial potential value was set at +0.3 V vs. Ag/AgCl reference electrode. Under these conditions, the cathodic potential step was carried out at – 0.3 V vs. Ag/AgCl; the subsequent anodic step, at +0.3 V. CVs in the solution showed that the applied potential always fell in the diffusion controlled limiting current region. In addition, by running argon blanks, in the absence of perchloric acid, it was verified that the initial potential used was sufficiently cathodic. The background current cannot be neglected because of adsorption on the surface of the solid

electrodes, glassy carbon or platinum in this case. Schwarz and Shain (1965) showed that the background currents can be neglected only when u mercury electrodes are employed, but mercury electrodes cannot be used due to hazards problems associated with the use of mercury [21]. Special attention should be given to polishing the working electrodes after each set of runs or whenever needed. Running CVs before DPSC experiments proved to be beneficial. The results, Table 1, are in good agreement with those reported by Shwarz and Shain (1965) [21].

Table 1. Kinetic data for the perchloric acid catalyzed rearrangement of hydrazobenzene in 50 wt% ethanol-water system.

Perchloric acid conc. (mol/L)	Azobenzene conc. (mol/L)	k_1 (s^{-1}) This work	k_1 (s^{-1}) Ref. [21]
0.641	0.6	0.61	0.57
0.641	1.0	0.59	0.56

3.2 Primary and secondary alcohols in ILs

A kinetic investigation was undertaken to obtain information on the kinetics of primary and secondary alcohols reaction with $O_2^{\bullet-}$ in ILs, and to compare these solvents with conventional organic solvents. The rates of the reaction of primary and secondary alcohols with $O_2^{\bullet-}$ in [bmim][HFP] and [bdmim][HFP] were measured with DPSC, under pseudo-first order conditions (in the presence of large excess of alcohol) at different temperatures and for different alcohol concentrations.

The potential applied to the working electrode was a single square pulse with amplitude of –0.8 V. The initial potential value was set at –0.2 V vs. Ag/AgCl reference electrode. Under these conditions, the cathodic potential step was carried out at –1.0 V vs. Ag/AgCl; the subsequent anodic step, at –0.2 V. CVs in the ILs showed that the applied potential always fell in the diffusion controlled limiting current region. In addition, argon blanks verified that the initial potential used was sufficiently cathodic.

Prior to kinetic measurements, a quantitative study was made of cathodic-anodic current time curves obtained after sparging with argon and oxygen in the absence of alcohol. These control experiments were used to evaluate the general procedures for the step functional method. Then under identical experimental conditions, a second cathodic-anodic current-time curves were obtained after sparging with O_2 and Ar in the presence of alcohol. Since the cathodic portion of these curves should be unaffected by the subsequent chemical reaction, they could be used for further evaluation of the techniques and for investigation of possible side reactions [21]. Then the anodic current-time curves were used along with respective cathodic portions for the determination of the rate constants.

For the experiments done in the absence of alcohol, the cathodic current time curves were analyzed according to Eq 10 and the results for different values of τ in ILs were essentially the same. Plots were made of i_c/C_o^* vs. $1/\sqrt{t}$ for each value of τ, see Figure 2 for example.

Straight lines were obtained for all experiments and the individual slopes showed a deviation less than 10% from the average. These results indicated that the generation of the superoxide ion was a simple diffusion-controlled process over the entire time scale of the experiments. Using Eq 10 gives:

$$\text{slope} = nFAC_0^* \sqrt{D_0/\pi} \qquad\qquad 19$$

$$\text{and} \qquad D_0 = \text{slope} \times \pi / (nFAC_0^*)^2 \qquad\qquad 20$$

The diffusion coefficient for O_2 calculated from the average slope was 2.4×10^{-6} cm^2/s, a value consistent with that calculated using cyclic voltammetry, 2.2×10^{-6} cm^2/s.
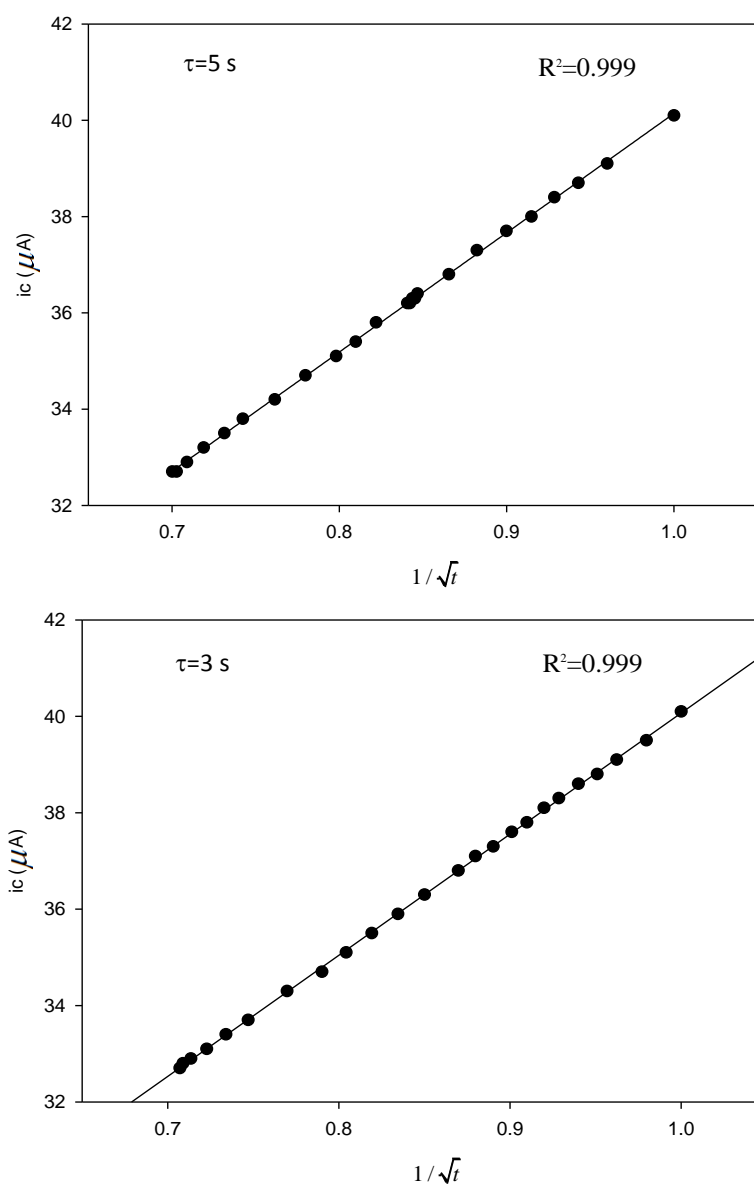

Figure 2. A plot of cathodic current vs. $1/\sqrt{t}$ for oxygen in [bmim][HFP] without the presence of any substrate for different values of τ.

The analysis of the anodic-current-time curves involved measuring the ratio of $-i_a/i_c$ for a series of time ratios $(t-\tau)/\tau$. Some typical results for $\tau = 1$ are shown in Figure 3. The results for different values of τ showed that the anodic currents were essentially controlled by the diffusion of oxygen to the electrode surface. The agreement between the experimental points and theory was reasonably good. In most cases, slight deviations of i_a/i_c from theory could be ascribed to deviation in i_a rather than i_c. The deviation is related, in part, to the adsorption of impurities in ILs on the surface of the electrode. We noticed that the experiments in IL with the same electrode that was used in azobenzene aqueous solution gave non-reproducible results even after the electrode was polished with 0.1 µM alumina. It is well known that the fundamental process in electrochemical reactions is the transfer of electrons between the electrode surface and the molecules in the interfacial region (either in solution or immobilized at the electrode surface). The kinetics of this heterogeneous process can be significantly affected by the microstructure and roughness of the electrode surface, the blocking of active sites on the electrode surface by adsorbed materials, and the nature of the functional groups (e.g. oxides) present on the surface. The most common method for surface preparation is mechanical polishing. The protocol chosen for polishing depends on the application for which the electrode is being used, and the state of the electrode surface.
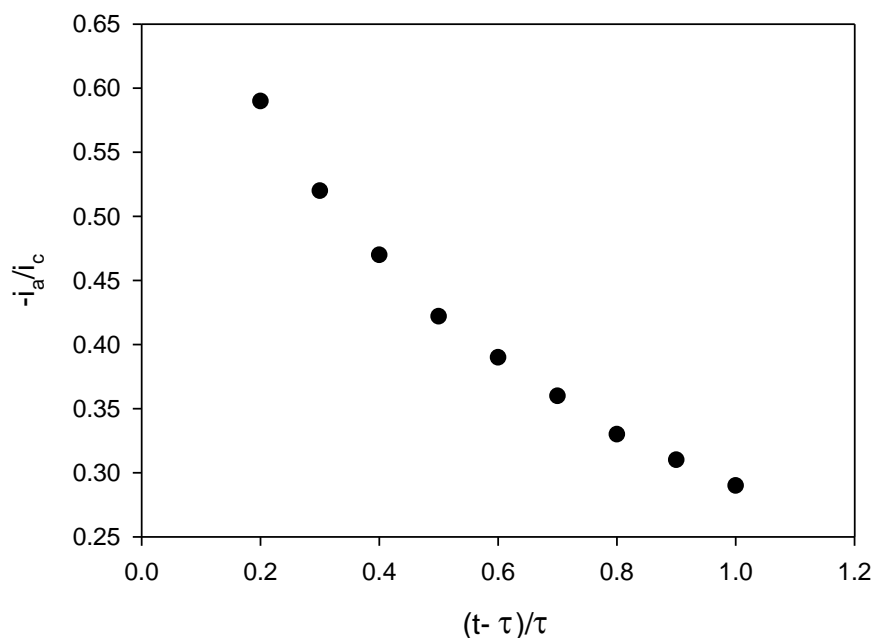

Figure 3. A plot of $-i_a/i_c$ vs. $(t-\tau)/\tau$ for oxygen in pure [bmim][HFP] for $\tau = 1$.

There are a variety of materials available (e.g., diamond, alumina, and silicon carbide), with different particle sizes suspended in solution. The pad chosen for polishing also depends on the material being used for polishing. Texmet pads are appropriate for alumina polish, and nylon pads for diamond polishing. Once polishing has been completed (this may require from 30 seconds to several minutes, depending upon the state the electrode) the electrode surface must be rinsed thoroughly with an appropriate solvent to remove all the traces of the polishing material, since its presence can affect the electron transfer kinetics [6,28]. We found that the working electrodes used in DPSC should be

polished with 1 μm diamond polish. The electrode was then thoroughly rinsed with water, de-ionized water, and methanol, respectively. This procedure should be repeated before any new set of experiments or when the CV run before DPSC gives unexpected results. So although DPSC is a simple and efficient technique, it is very sensitive to impurities that can adsorb on the surface of the electrode. This problem can be overcome easily by running CVs before conducting DPSC experiments.

We also noticed that the deviation between experimental and theoretical values is very small. We used UV-vis spectrophotometer to find an approximate value for the pseudo first order constant for the reaction of $O_2^{\bullet-}$ with [bmim][HFP]. The value was determined to be $\cong 2.1x~10^{-5}~s^{-1}$. This value is about 4 orders of magnitude less than the value of the pseudo first order constant for the reaction of aromatic alcohols with $O_2^{\bullet-}$ in IL and in a good agreement with earlier reported values by AlNashef *et al.* (2010) and Hayyan *et al.* (2012) [22,29]. So this side reaction can be neglected while conducting DPSC experiments. However, since the time needed for bulk electrolysis is much larger than the time needed to run DPSC and CV experiments and due to the high molar concentration of the solvent relative to the substrate, this side reaction cannot be neglected when running bulk electrolysis experiments. UV-vis analysis showed that $O_2^{\bullet-}$ does not react with [bdmim][HFP]. In the presence of alcohol, cathodic-anodic current-time curves were obtained at different temperatures and for different concentrations of primary and secondary alcohols in [bmim][HFP] and [bdmim][HFP]. As with the non-reactive system, τ values were in the range from 0.5 to 3 seconds.

In addition to their use in the analysis of the rate data, the cathodic current-time curves also serve as a method for detecting such side reactions as the reaction of $O_2^{\bullet-}$ with H^+, which is generated in ILs with PF_6 anion even if the solvent was kept inside a glove box. If such side reaction were present, the regeneration of oxygen by the chemical step would result in an enhancement of the cathodic current due to the catalytic effect.

Schwarz and Shain (1965) showed that the maximum accuracy in the kinetic measurements is achieved when the switching time, τ, is the same order of magnitude as the half-life of the chemical reaction [21]. Thus the switching times used here were selected to be approximately within 50% of the half-life of the chemical reaction. This permitted significant amount of reaction to take place, but at the same time enough superoxide ion remained so that the anodic currents could be measured with reasonable accuracy.

From any individual cathodic-anodic current-time curve, several estimates of the kinetic parameter were obtained. In principle, i_a and i_c could be measured at any arbitrarily selected value of t and (t-τ). However, we noticed that for small values of τ the currents take some time to reach reasonable values after switching the potential. The same phenomenon was observed while running experiments in aqueous solutions. This may be due to limitations in the potentiostat.

For each alcohol solution in IL, the values of k_1 were converted to $k_1(t-\tau)$ so that data obtained with different values of τ could be combined in a form to give weight to each value. Then plots were made of $k_1(t-\tau)$ versus (t-τ) and the rate constant was calculated directly from the slope. In each case, the experimental data determined a straight line that passed through the origin, as required by theory. One of these plots is shown in Figure 4. It worth mentioning here that if the concentration of the alcohol was not high enough so that pseudo-first-order conditions dominate, the plot of $k_1(t-\tau)$ versus (t-τ) will not give a straight line. The second order rate constant can be calculated from Eq 5.

The same procedure was repeated at least at three different temperatures and the natural logarithm of the rate constant was plotted versus the reciprocal of the absolute temperature to get the kinetic parameters as shown in Eq 20.

$$k_2 = A \exp(-E_a / RT) \qquad\qquad 20$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. Using Eq 20 the kinetic parameters for the reaction of the superoxide ion with benzhydrol in [bmim][HFP] and [bdmim][HFP] were determined. The results are summarized in Table 2 and Table 3.
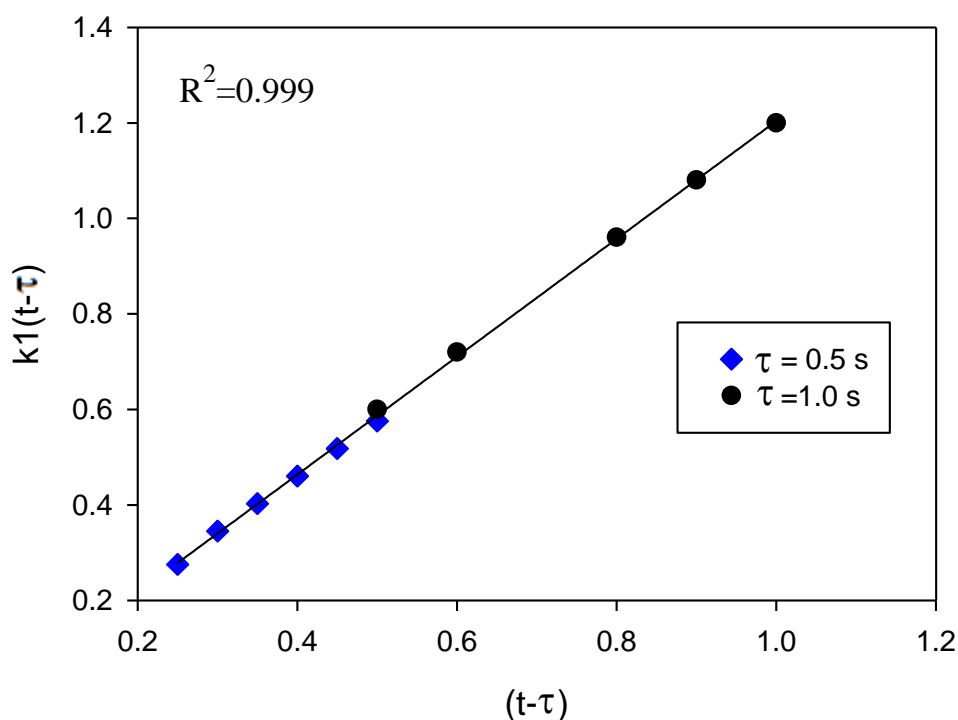

Figure 4. A plot of $(t-\tau)$ vs. $k_1(t-\tau)$ for the reaction of superoxide ion and 12.5 mM benzhydrol in [bdmim][HFP] at 65°C . Solid line is a linear fit to the experimental values.

Table 2. Kinetic parameters for the reaction of $O_2^{\bullet-}$ with benzhydrol in [bdmim][HFP].

Benzhydrol concentration (mM)	T (°C)	k_1 (s^{-1})	k_2 (L mol^{-1} s^{-1})
12.5	49	0.75	60
12.5	57	0.90	72
12.5	65	1.15	92
12.5	84	1.85	148
25	49	1.40	56
25	57	1.65	66
25	65	2.35	94

Table 3. Kinetic parameters for the reaction of $O_2^{\bullet-}$ with benzhydrol in [bmim][HFP].

Benzhydrol concentration (mM)	T (°C)	k_1 (s^{-1})	k_2 (L mol^{-1} s^{-1})
10	27	0.53	53
10	40	0.74	74
10	80	2.01	201

The values of k_2 in Table 2 and Table 3 were calculated by dividing k_1 by the concentration of the alcohol in IL. The values of k_1 and k_2 were determined for two different concentrations of benzhydrol in [bdmim][HFP]. It can be seen from Table 2 that doubling the concentration of benzhydrol doubles the value of the pseudo first order rate constant and does not, within the limits of the experimental error, affect the value of the second order rate constant. This indicates that the measured rate constant is an intrinsic rate constant. Muldoon *et al.* (2001) showed that there is a significant difference in E_a values for the hydrogen abstraction by benzophenone triplet excited states between the ionic liquids and those in conventional solvents (*ca.* 25 and 15 kJ mol^{-1}, respectively). They also indicated that the activation parameters for H abstraction in the ionic liquids are essentially independent of the anionic component and the availability of the hydrogen atom at the 2-position on the imidazolium ring [17].

McLean *et al.* (2002) reported the results of an investigation on the temperature dependence of diffusion-controlled rate constants and the solvent viscosity, η, of five structurally related ILs based on the 1-alkyl-3-methylimidazolium cation. They stated that the confirmation that measured rate constant values do reflect the diffusion controlled rate constant should come from the comparison of the temperature dependence of the measured rate constant values with the temperature dependence of viscous flow of the solvent [8]. Identical activation energies would indicate that both processes are driven by solvent viscous flow, and therefore that measured rate constant does indeed reflect the diffusion controlled rate constant. They determined the activation energy for viscous flow for [bmim][HFP] to be 37.6 kJ/mol. Using the results of DPSC in [bmim][HFP] at a series of temperatures we determined the diffusion coefficient of O_2 as a function of temperature. When the natural logarithm of the diffusion coefficient was plotted versus 1/T a straight line was obtained, Figure 5. The activation energy for the diffusion process was determined from the slope. This value, 36.9 kJ/mol is in good agreement with that reported by McLean *et al.* (2002) [8]. Comparing this value to the values of activation energy determined in our work for the reaction of superoxide ion with different alcohols in [bmim][HFP] (19-23 kJ/mol) and the fact that this value is different for different alcohols, Table 4 and Table 5, indicate that the measured kinetic parameters are those for the homogeneous reaction rather than for the diffusion-controlled process. The other kinetic parameters of the process can be calculated using the fundamental equation of the theory of the active complex [30]:

$$k = \frac{xek_BT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{E}{RT}\right) \qquad\qquad 21$$

where x is a transmission coefficient which is unity for monomolecular reactions, k_B the Boltzmann constant, h the corresponding Plank constant, $e=2.7183$ is the Neper number and $\Delta S^{\neq}$ is the change of entropy for the active complex formation from the reagent.
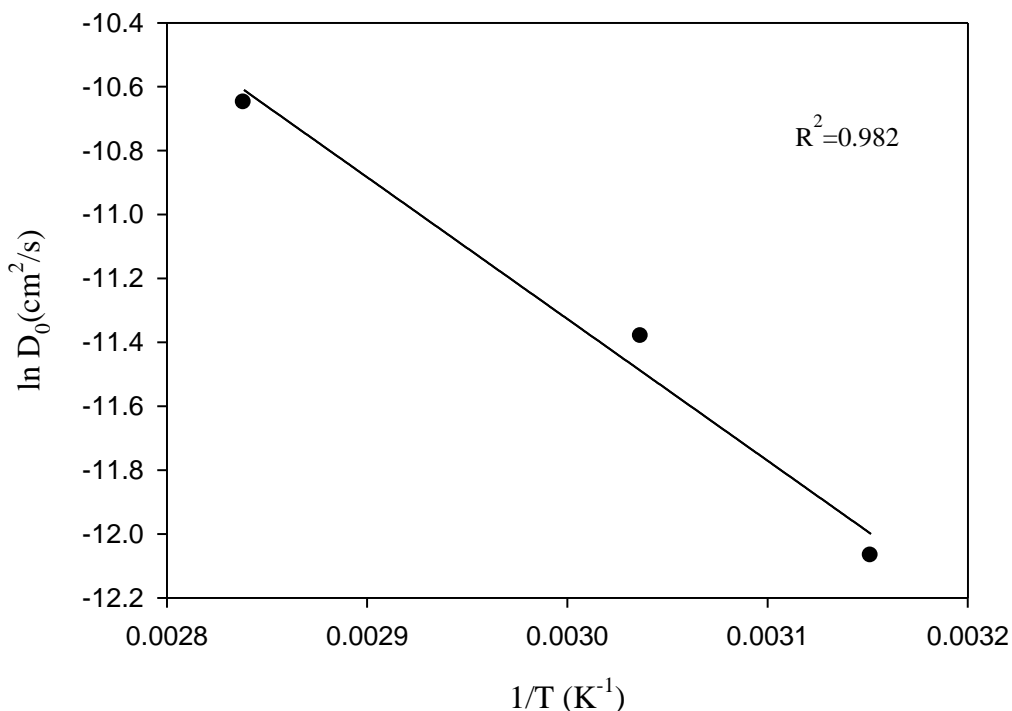

Figure 5. A plot of natural logarithm of the diffusion coefficient of O_2 in [bmim][HFP] versus 1/T in the presence of 2-hydroxymethyl pyridine.

Table 4. Arrhenius parameters for the reaction of $O_2^{\bullet-}$ with benzhydrol in ILs.

Solvent	Ea (kJ/mol)	ln(A)
[bmim][HFP]	22.3	12.9
[bdmim][HFP]	25.0	14.0
MeCN	29.1	14.5

Table 5. Arrhenius parameters for the reaction of $O_2^{\bullet-}$ with different alcohols in [bmim][HFP].

Substrate	Ea (kJ/mol)	ln(A)
Benzhydrol	22.3	12.9
Benzyl alcohol	19.1	8.8

Taking into account the pre-exponential constant A from the Arrhenius Eq, 20 and 21, the following expression is obtained:

$$A = \frac{xek_BT}{h}\exp(\frac{\Delta S^{\neq}}{R}) \qquad\qquad 22$$

and $\Delta S^{\neq}$ can be calculated:

$$\Delta S^{\neq} = R\left(\ln A - \ln\frac{xek_BT}{h}\right) \qquad\qquad 23$$

where A is the pre-exponential factor in the Arrhenius Eq with values presented in Tables 4 and 5. Since the changes of the enthalpy $\Delta H^{\neq}$ and Gibbs free energy $\Delta G^{\neq}$ for the active complex formation can be calculated using the well known thermodynamic equations:

$$E_a = \Delta H^{\neq} + RT \qquad\qquad 24$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad\qquad 25$$

The corresponding values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for the reaction of superoxide ion with benzhydrol in [bdmim][HFP] calculated at T = 45°C are –0.49 kJ/mole, 22.4 kJ/mole, and 177.9 kJ/mole, respectively. Unfortunately, no values are reported in the literature for the corresponding reaction.

McLean *et al*. (2002) stated that attention should be drawn to the correlation between pre-exponential factors and the activation energies for both the measured rate constant values and the temperature dependence of viscous flow of the solvent [8]. This correlation gives rise to isokinetic behavior in ILs and remains even when the conventional solvent data are included, Figure 6. Such correlations are relatively commonplace in organic chemistry.

McLean *et al*. (2002) reported that both E_a and A values show a significant, systematic dependence on the identity of the anion and the nature of the alkyl substituents on the cation constituting the ILs, Figure 6. For any particular cation, the E_a values are 12–15 kJ mol^{-1} higher for the [PF$_6$]$^-$ salts than the [Tf$_2$N]$^-$ salts, where Tf2 stands for CF$_3$SO$_2$. This is readily accounted for on the basis of the differences in charge distribution between these two anions. The more symmetrical distribution of the negative charge on [PF$_6$]$^-$ permits interaction with several of the surrounding cations whereas the more directional charge on [Tf$_2$N]$^-$ restricts the degree of interaction with the surrounding cations.

Consequently, the greater E_a values in the [PF$_6$]$^-$ salts may simply reflect the greater extent of ionic cross-linking possible in ILs with this anion compared to [Tf$_2$N]$^-$. The relative magnitudes of the pre-exponential factors may also reflect this, as enhanced ionic cross-linking would result in a greater effective diffusing mass. The movement of larger solvent masses requires the breaking of significant interionic bonding, whilst creating large cavities for solutes to jump into. This enhanced cross-linking may explain the apparent contradiction that the [PF$_6$]$^-$ salts display larger A factors than the [Tf$_2$N]$^-$ salts, despite the larger molar mass of the latter. They also found significant (*ca.* 10 kJ/ mol) increase in E_a values associated with octyl *vs.* butyl substitution on the cation. They attributed this to the

breakdown of van der Waals forces that play a significant part in facilitating diffusion processes in these liquids despite the presence of strong electrostatic interactions between ions. The apparent strength and significance of the van der Waals interactions is supported by the very large molar mass of ILs [8]. This is consistent with the values of E_a determined for the reaction of superoxide ion with benzhydrol in [bmim][HFP] and [bdmim][HFP] as can be seen from Table 4.
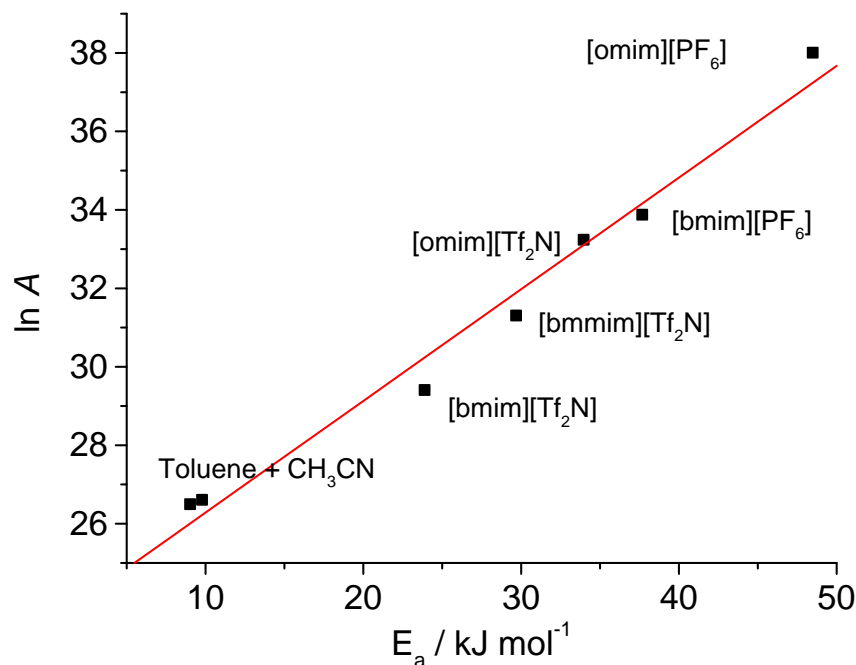

Figure 6. Isokinetic plot obtained for the energy transfer reaction of triplet benzophenone and naphthalene in five ionic liquids, toluene and acetonitrile reported by Mclean et *al.*[26] where [omim] = octyl methyl imidazolium; [bmmim] = [bdmim]; PF_6 = hexafluorophosphate; and [Tf] = CF_3SO_2.

Ganiev *et al*. (2002) studied the kinetics of the oxidation of a series of alcohols with the oxoammonium salt 2,2,6,6-tetramethypiperidine-1-oxyl chlorite in MeCN. They found that the activation energy for the oxidation of benzyl alcohol is 16.5 kJ/mol; this is in good agreement with the value reported here in [bmim][HFP], 19.1 kJ/mol. The second order rate constant for the oxidation of benzyl alcohol at 10°C was 0.037 L mol^{-1} s^{-1} [31]. This value is more than one order of magnitude lower than that for the same reaction utilizing the $O_2^{\bullet-}$ in the same IL determined by our group, $\cong$1.3 L mol^{-1} s^{-1}.

We also used DPSC to measure the rate constant for the reaction of the superoxide ion with benzhydrol in MeCN at different temperatures. The results are shown in Table 6 and plotted in Figure 7. All these experiments were done inside the glove box under argon atmosphere. It is clear from Table 6 that the values of the second order rate constant in ILs, Tables 2 and 3, are higher than those in MeCN although the viscosity of the IL is more than 3 orders of magnitude higher than that for MeCN. The activation energy in MeCN is also higher than that in ILs. This is an additional evidence that the measured parameters are the intrinsic kinetic parameters.

Table 6. Kinetic parameters for the reaction of $O_2^{\bullet-}$ with benzhydrol in MeCN.

T (°C)	k_2 (L mol^{-1} s^{-1})
18.5	7.7
27.0	10.9
33.0	13.6
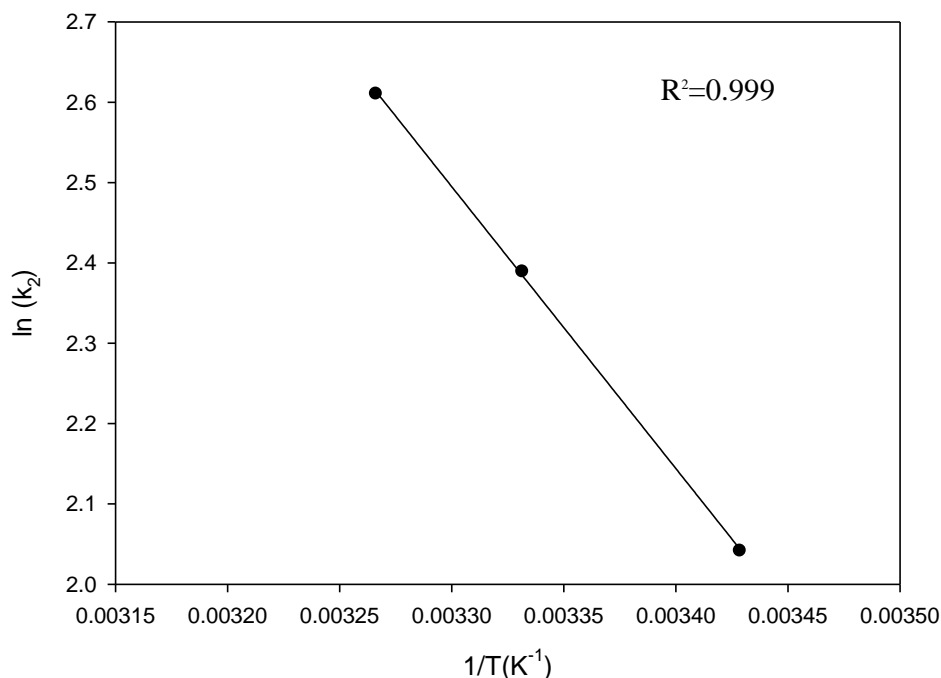
Figure 7. A plot of natural logarithm of k_2 versus 1/T for the reaction of $O_2^{\bullet-}$ with benzhydrol in MeCN.

4. CONCLUSIONS

It was shown that DPSC is an efficient and effective method for measuring the rate constants for the homogeneous reactions of alcohols with $O_2^{\bullet-}$ in [bmim][HFP] and [bdmim][HFP] ILs. It was also found that although DPSC is a simple method that does not need large quantities of the solvent. Careful attention should be given to polishing the working-electrode because this method is very sensitive to the adsorbed impurities on the surface of the working electrode. Activation energy values for different alcohols in [bmim][HFP] and [bdmim][HFP] were determined using Arrhenius plot for the kinetic data obtained at different temperatures. The values of the activation energy showed that the activation parameters determined in this work are the intrinsic kinetic parameters and not those associated with diffusion. It was found significant (*ca.* 5 kJ/mol) increase in E_a values associated with butyl *vs.* hydrogen substitution on the imidazolium cation. This can be attributed to the breakdown of van der Waals forces that play a significant part in facilitating diffusion processes in these liquids

despite the presence of strong electrostatic interactions between ions. The apparent strength and significance of the van der Waals interactions is supported by the very large molar mass of ILs.

References

1. J.D. Holbrey, K.R. Seddon, *Clean Prod. Processes* 1 (1999) 223.
2. T. Welton, *Chem. Rev.* 99 (1999) 2071.
3. C.M. Gordon, *Appl. Cat. A, General* 222 (2001) 101.
4. S.A. Stratton, K.L. Luska, A. Moores, *Catal. Today* 183 (2012) 96.
5. I.J. Villar-Garcia, A. Abebe, Y. Chebude, Inorg. *Chem. Commun.* 19 (2012) 1.
6. M. Hayyan, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, X.M. Tan, *J. Electroanal. Chem.* 657 (2011) 150.
7. M. Hayyan, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, *Fuel Process. Technol.* 91 (2010) 116.
8. A.J. McLean, M.J. Muldoon, C.M. Gordon, I.R. Dunkin, *Chem. Commun.* 17 (2002) 1880.
9. G. Schmidt-Naake, A. Schmalfuß, I. Woecht, *Chem. Eng. Res. Des.* 86 (2008) 765.
10. S. Perrier, T.P. Davis, A.J. Carmichael, D.M. Haddleton, *Eur. Polym. J.* 39 (2003) 417.
11. E. Andrzejewska, M. Podgorska-Golubska, I. Stepniak, M. Andrzejewski, *Polymer* 50 (2009) 2040.
12. S. Mallakpour, Z. Rafiee, *Prog. Polym. Sci.* 36 (2011) 1754.
13. S. Harrisson, S.R. Mackenzie, D.M. Haddleton, *Chem. Commun.* (2002) 2850.
14. C. Chiappe, V. Conte, D. Pieraccini, *Eur. J. Org. Chem.* (2002) 2831.
15. M. Mohammad, A.Y. Khan, M.S. Subhani, N. Bibi, S. Ahmad, S. Saleemi, *Res. Chem. Intermed.* 27 (2001) 259.
16. C.P. Andrieux, P. Hapiot, J.M. Saveant, *J. Am. Chem. Soc.* 109 (1987) 3768.
17. M.J. Muldoon, A.J. McLean, C.M. Gordon, I.R. Dunkin, *Chem. Commun.* 22 (2001) 2364.
18. C. Lee, T. Winston, A. Unni, R.M. Pagni, G. Mammantov, *J. Am. Chem. Soc.* 118 (1996) 4919.
19. M. Álvaro, B. Ferrer, H. García, M. Narayana, *Chem. Phys. Lett.* 362 (2002) 435.
20. M. Harada, C. Kawasaki, K. Saijo, M. Demizu, Y. Kimura, *J. Colloid Interface Sci.* 343 (2010) 537.
21. W.M. Schwarz, I. Shain, *J. Phys. Chem.* 69 (1965) 30.
22. M. Hayyan, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, S.M. Al-Zahrani, K.L. Chooi, *J. Electroanal. Chem.* 664 (2012) 26.
23. A. Erdelyi, Higher Transcendental Functions, McGraw-Hill, New York, 1953.
24. H. Zollinger, Azo and Diazo Chemistry, Interscience Publishers, New York, 1961.
25. R.B. Carlin, R.G. Nelb, R.C. Odioso, *J. Am. Chem. Soc.* 73 (1951) 1002.
26. E. Biilmann, J.H. Blom, *J. Am. Chem. Soc.* 125 (1924) 1719.
27. M.J.S. Dewar, *J. Chem. Soc.* (1946) 777.
28. M. Hayyan, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, S.M. Al-Zahrani, K.L. Chooi, *J. Mol. Liq.* 167 (2012) 28.
29. I.M. AlNashef, M.A. Hashim, F.S. Mjalli, M.Q.A.-h. Ali, M. Hayyan, *Tetrahedron Lett.* 51 (2010) 1976.
30. L.T. Vlaev, I.G. Markovska, L.A. Lyubchev, *Thermochim. Acta* 406 (2003) 1.

31. I.M. Ganiev, E.S. Suvorkina, A.V. Igoshina, N.N. Kabal nova, U.B. Imashev, G.A. Tolstikov, *Russ. Chem. Bull., Int. Ed.* 51 (2002) 982.