

Full Paper

Kinetics of Alcohol Oxidation by Electrochemically Generated Superoxide Ions in Ionic Liquids Using Double Potential Step Chronoamperometry

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Abstract- Double Potential Step Chronoamperometry (DPSC) was used to determine the rate constants for the homogeneous reactions of alcohols with the superoxide ion ($O_2^{\bullet-}$) at different temperatures in two room temperature ionic liquids (RTILs). 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. Our results were in good agreement with values reported in the literature using DPSC and conventional kinetic methods. The activation energy for the oxidation of benzyl alcohol is 19.1 kJ/mol in [bmim][HFP]; which is in good agreement with the value reported in the literature. The corresponding values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger 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. The second order rate constant for the oxidation of benzyl alcohol at 10°C in RTIL in [bmim][HFP] was determined to be $\cong 1.3 \text{ L mol}^{-1} \text{ s}^{-1}$. 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-butyl-2,3-dimethylimidazolium hexafluorophosphate [bdmim][HFP] at different temperatures was measured. The pseudo first order rate constant for the reaction of $O_2^{\bullet-}$ with benzhydrol in [bdmim][HFP] at T= 49, 57, 65, 84 C were found to be 60, 72, 92, 148 $L mol^{-1} s^{-1}$. The pseudo first order rate constant for the reaction of $O_2^{\bullet-}$ with benzhydrol in [bmim][HFP] at T=27, 40 and 80 °C were found to be 53,74, 201 $L mol^{-1} s^{-1}$. The Arrhenius plot was then used to determine the activation energy and pre-exponential factor for the corresponding reactions.

Keywords- Superoxide, Kinetics, Alcohol oxidation, Double potential chronoamperometry

1. INTRODUCTION

There is a scarcity of reliable, quantitative information on reaction rates and rate constants in RTILs 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.* 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 RTILs [8]. The use of RTILs leads to significant improvements in rate and yield in many organic reactions [2]. Recently, a number of reports have described the use of RTILs 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 ionic liquids are used in place of conventional organic solvents [13]. 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 RTIL concentration [14]. 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.

Found that the activation energy for hydrogen abstraction from imidazolium-based ionic liquids is significantly higher than that observed in conventional solvents [15]. As part of a continuing study of the influence of ionic liquids on photochemical processes, they reported their initial results on hydrogen abstraction from these solvents by triplet excited state benzophenone.

We previously showed that a stable superoxide ion can be electrochemically generated in some RTILs [16]. We then used the superoxide ion to synthesize carboxylic acids and ketones from primary and secondary alcohols, respectively [17]. The results of the synthesis showed that the ionic liquid plays an important role in the reaction. In some cases it increased the yield from 50%, in dimethylformamide, to 98%, while in other cases it reduced the yield to zero. A kinetic study is needed to understand the role of RTILs in these reactions.

Mohammad *et al.* measured the rate constants for the reaction of $O_2^{\bullet-}$ with various substrates through stationary electrode polarography [18]. In solvent MeCN, the rate constants of the reaction



Where AH is a primary alcohol, were determined. The reaction rate was found to be first order with respect to both $O_2^{\bullet-}$ and the alcohol.

Studied the electrochemical reduction of O_2 in DMS as a function of the addition of acids by means of DPSC [19]. 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. They also determined the rate constant for the reaction of $O_2^{\bullet-}$ with halogenated aromatic alcohols and phenol.

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 although the high viscosity of RTILs may cause problems.

Many electrochemical methods can also be used to measure the rate constant for fast homogeneous reactions, e.g., Cyclic voltammetry (CV), rotating ring disc electrode (RRDE), and double potential step chronoamperometry (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. For a quantitative investigation of the kinetics, DPSC is preferred to CV because the heterogeneous electron transfer to dioxygen in aprotic solvents is not very rapid. The kinetics of electron transfer would thus interfere besides that of the follow up reactions in the characteristics of the CVs, rendering the extraction of the kinetics of the follow up reactions difficult and inaccurate [19].

2. EXPERIMENTAL

The RTILs of [bmim][HFP] and [bdmim][HFP] were obtained from SACHEM (USA), both with a stated purity of 97%. [bmim][HFP] was dried under vacuum for at least 24 h. For

[bdmim][HFP], with a melting point of ca. 30 °C, the ionic liquid was dissolved in ethyl acetate at room temperature and then mixed with molecular sieves. The slurry was stirred for several hours. The molecular sieves were then decanted and ethyl acetate was removed under vacuum. This procedure was done to remove the water without heating the ionic liquid in order to avoid the formation of HF.

Before conducting DPSC experiments in the ionic liquids [bmim][HFP], and [bdmim][HFP], cyclic voltammetry (CVs) tests were performed to generate $O_2^{\bullet-}$ and to confirm its short-term stability. 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 working (BAS, 3 mm dia.) and a platinum mesh counter (Aldrich). Ag/AgCl (Fisher Scientific) was used as a reference electrode. All [bmim][HFP] and [dmbim][HFP] experiments were performed in a dry glove box under an argon atmosphere. The systems were sparged prior to electrochemical experiments with UHP argon or oxygen, supplied by National Welders (USA), fitted through a Drierite gas purification column provided by W.A. Hammond (USA).

Prior to superoxide ion 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. Argon or oxygen sparging was discontinued during the CV data acquisition.

After confirming the short-term stability of $O_2^{\bullet-}$ a weighed amount of alcohol is added to the RTIL 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. Oxygen is bubbled through the RTIL. After 15-20 min the sparging of oxygen is stopped and DPSC experiments are conducted in the O_2 saturated RTILs. 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 RTILs showed that the applied potential always fell in the diffusion controlled limiting current region.

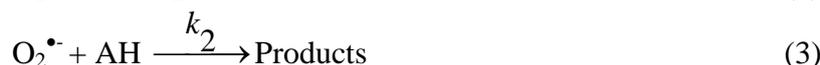
We noticed that the experiments in RTIL with the same electrode that was used in azobenzene aqueous solution gave non-reproducible results even after the electrode was polished with $0.1 \mu\text{M}$ alumina. It is well known that the fundamental process in electrochemical reactions is the transfer of 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 [25]. 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.

3. RESULTS AND DISCUSSION

3.1. Theory

Briefly, DPSC involves producing $\text{O}_2^{\bullet-}$ at a stationary electrode under diffusion-controlled conditions by applying a constant potential for a timed interval, τ . During this interval, $\text{O}_2^{\bullet-}$ diffuses into the solution and simultaneously reacts. At $t = \tau$, the potential is switched to a value where $\text{O}_2^{\bullet-}$ is oxidized back to O_2 , Equations 2 and 3. The anodic current is an indication of the amount of $\text{O}_2^{\bullet-}$ that has not reacted and can be related to the rate constant k .



Schwarz and Shain [20] 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.

At $t = \tau$, the potential is switched to a value where $\text{O}_2^{\bullet-}$ is oxidized back to O_2 as shown by Equation 2. The rate expression for the homogeneous reaction can be written as shown in Equation 4.

$$r = k_2 C_{\text{AH}} C_{\text{O}_2^{\bullet-}} = k_1 C_{\text{O}_2^{\bullet-}} \quad (4)$$

Where C_{AH} is the concentration of the substrate that is in excess, $C_{\text{O}_2^{\bullet-}}$ 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 $\text{O}_2^{\bullet-}$ that has not reacted and can be related to the rate constant k_1 . Equations 2 and 3 show the electrochemical reactions and the homogeneous reaction of $\text{O}_2^{\bullet-}$ with alcohol. Typical cathodic-anodic current-time curves are shown in Fig. 1.

The theoretical relationship between the current, the time of electrolysis, and the rate constant, k_1 , for a system following equation 2 and 3 can be derived by solving Fick's laws of diffusion to a plane (modified by the appropriate kinetic terms) [20].

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

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

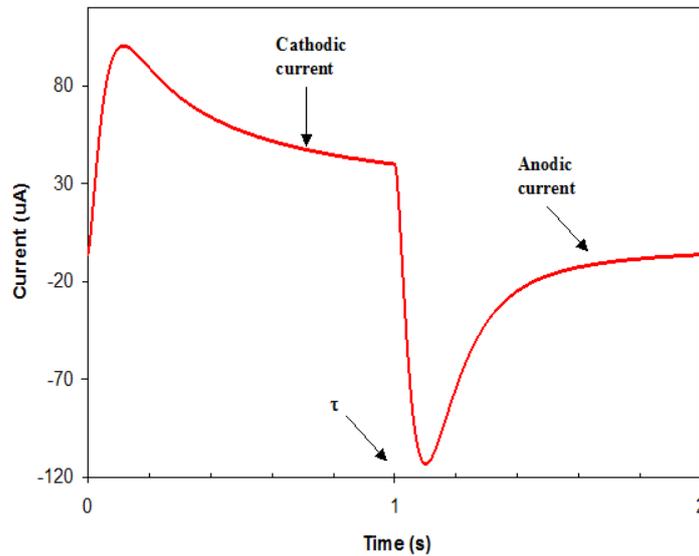


Fig.1. Experimental cathodic-anodic current-time curve for 20 mM Benzhydrol in [bmim][HFP] at 27° C, $\tau=1$ s

Where C_O and C_R are concentrations of O_2 and $O_2^{\bullet-}$, t is the time [6], x is the distance from the electrode, and D_O and D_R are the diffusion coefficients of O_2 and $O_2^{\bullet-}$, respectively.

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.

$$t = 0, x \geq 0 : C_o = C_o^*, C_R = 0 \quad (7)$$

$$t \gg 0, x \rightarrow \infty : C_o \rightarrow C_o^*, C_R \rightarrow 0 \quad (8)$$

$$\tau \gg t \gg 0, x = 0 : C_o = 0, \quad D_o \left(\frac{\partial C_o}{\partial x} \right) = -D_R \left(\frac{\partial C_R}{\partial x} \right) \quad (9)$$

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

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

Here $C_{O_2}^*$ is the bulk concentration 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 [19] gave an analytical solution to this problem and the results are shown in Equations 12 and 13.

For $t < \tau$

$$-\frac{i_c}{nFA} = -C_{O_2}^* \sqrt{D_{O_2} / \pi t} \quad (12)$$

For $t > \tau$

$$\frac{i_a}{nFA} = C_{O_2}^* \sqrt{D_{O_2} / \pi (t - \tau)} \times [e^{-kt} {}_1F_1(1/2, 1, k\tau) + \quad (13)$$

$$\sum_{n=1}^{\infty} \frac{e^{-kt} [(t - \tau)k]^n}{n!} {}_1F_1(n + 1/2, n + 1, k\tau)] - C_{O_2}^* \sqrt{D_{O_2} / \pi t}$$

Where ${}_1F_1(1/2, 1, kt)$ is a confluent hypergeometric series [20] with the following properties

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

$$\text{and } {}_1F_1(\alpha, \gamma, 0) = 1 \quad (15)$$

Where

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

Dividing Equation 13 by Equation 12 gives

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

We found that if three terms of the infinite series in Equation 18 are used, approximately 0.4% accuracy in the anodic current is obtained. So in this work the first three terms of the infinite series were used. Equation 17 becomes.

$$\text{for } t > \tau$$

$$\frac{i_a}{i_c} = \sqrt{t/(t-\tau)} \times e^{-k_1 t} \left[1 + \frac{k_1 \tau}{2} + \frac{3(k_1 \tau)^2}{8} + k_1(t-\tau) + \frac{3}{4} \frac{k_1^2 \tau(t-\tau)}{1} + \right. \\ \left. \frac{15}{8} \frac{k_1^3 \tau^2(t-\tau)}{1} + k_1^2(t-\tau)^2 + \frac{5}{24} \frac{k_1^3 \tau(t-\tau)^2}{1} + \frac{35}{16} \frac{k_1^4 \tau^2(t-\tau)^2}{1} \right] \quad (18)$$

3.1.1. Azobenzene system

In order to test the theoretical calculations and the apparatus used, the reduction of azobenzene was investigated. The rearrangement of hydrazobenzene has been the subject of numerous investigations [19,21] in which spectrophotometric [22], potentiometric [23], or titration [24] techniques were used to follow the rate of the reaction. Schwarz and Shain [20] 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.

We measured the pseudo first order rate constant for the rearrangement of benzidine in 50% wt. ethanol-water. 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. 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 [20] showed that the background currents can be neglected only when mercury electrodes are employed, but mercury electrodes cannot be used due to hazards problems associated with the use of mercury. The results, see Table 1, were in good agreement with those reported by Schwarz and Shain [19] and others.

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

S. No	Perchloric acid conc.	Azobenzene conc.	k_1 (s ⁻¹)	k_1 (s ⁻¹)
	(mol/L)	(mol/L)	This work	Ref. 20
1	0.641	0.6	0.61	0.57
2	0.641	1.0	0.59	0.56

3.1.2. Primary and secondary alcohols in RTILs

A kinetic investigation was undertaken to obtain information on the kinetics of primary and secondary alcohols reaction with the superoxide ion in RTILs, and to compare these

solvents with molecular ones. 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.

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 [19]. 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 equation 11 and the results for different values of τ in RTILs were essentially the same. Plots were made of i_c vs. $1/\sqrt{t}$ for each value of τ , see Fig. 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 Equation 11 gives.

$$\text{slope} = nFAC_0^* \sqrt{D_0 / \pi} \quad (19)$$

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

The diffusion coefficient for O_2 calculated from the average slope was $2.4 \times 10^{-6} \frac{cm^2}{s}$, a value consistent with that calculated using cyclic voltammetry, $2.2 \times 10^{-6} \frac{cm^2}{s}$ [21].

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 $\tau=0.5$ s are shown in Fig. 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 very good. In some 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 RTILs on the surface of the electrode. So although DPSC is a simple and efficient technique, it is very sensitive to impurities that can adsorb on the surface of the electrode.

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] [21]. The value was determined to be $\cong 2.1 \times 10^{-5} \text{ s}^{-1}$. 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 RTIL. So this side reaction can be neglected while conducting DPSC experiments in [bmim][HFP]. 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].

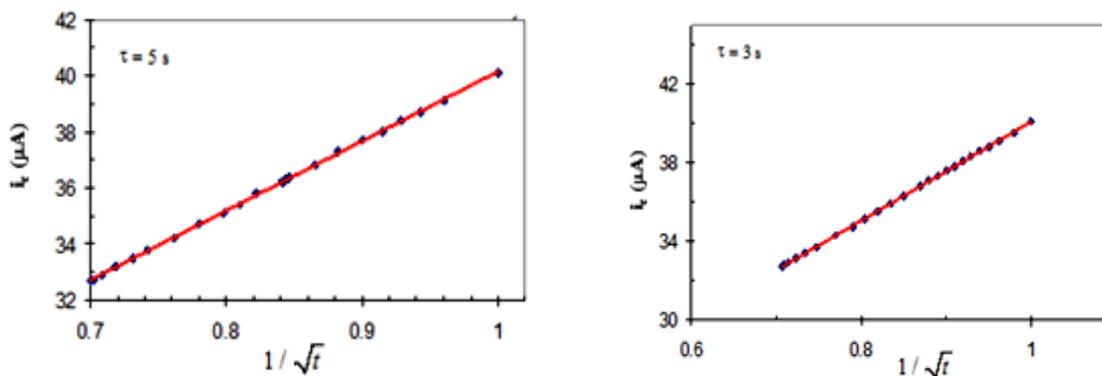


Fig. 2. A plot of cathodic current vs. $1/\sqrt{t}$ for oxygen in [bmim][HFP] without the presence of any substrate for different values of τ

Schwarz and Shain [19] 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. 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.

For each alcohol solution in RTIL, 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 $(t-\tau)$ 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 Fig. 4. The second order rate constant can be calculated from Equation 5. 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 $(t-\tau)$ will not give a straight line.

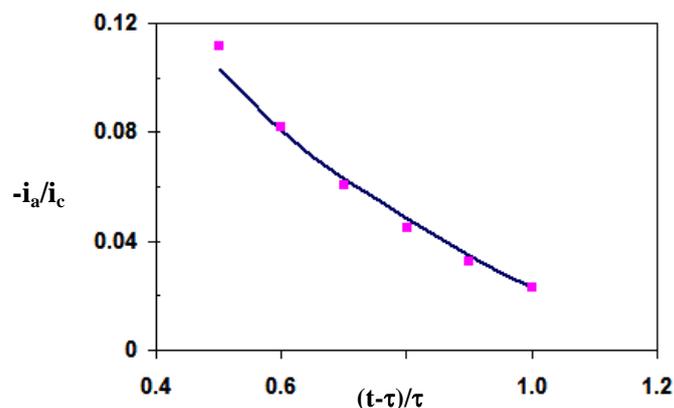


Fig. 3. A plot of $-i_a/i_c$ vs. $(t-\tau)/\tau$ for oxygen in 12.5 mM benzhydrol in [bdmim][HFP] $\tau=0.5$ s

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 Equation 21.

$$k_2 = A \exp(-E_a / RT) \quad (21)$$

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 Equation 21 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. The values of k_2 in Table 2 and Table 3 were calculated by dividing k_1 by the concentration of the alcohol in RTIL. 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.

McLean *et al.* reported the results of an investigation on the temperature dependence of diffusion-controlled rate constants and the solvent viscosity [26], μ , of five structurally

related RTILs 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. 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 temperature we determined the diffusion coefficient of O₂ as a function of temperature. When the natural logarithm of the diffusion coefficient was plotted versus 1/T a straight line was obtained, see Fig. 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 [26] 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 [27]:

$$k = \frac{xek_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E}{RT}\right) \quad (22)$$

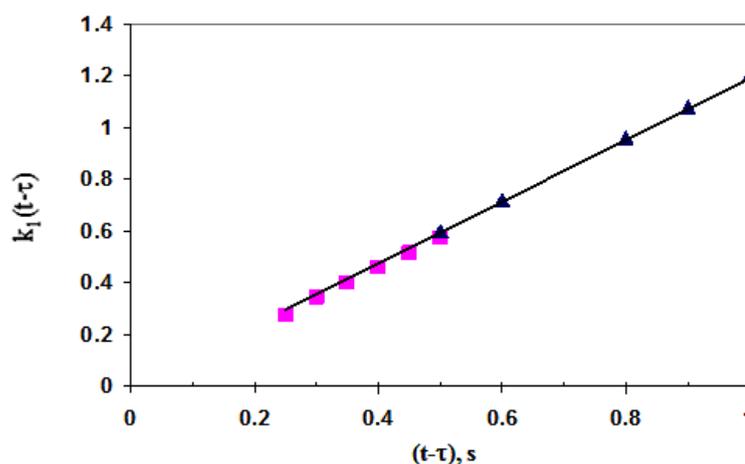


Fig. 4. A plot of $k_1(t-\tau)$ vs. $(t-\tau)$ for the reaction of superoxide ion and 12.5 mM benzhydrol in [bdmim][HFP] at 65°C . ■ $\tau = 0.5$ s, ▲ $\tau = 1.0$ s. Solid line is a linear fit to the experimental values

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

S.No	Benzhydrol concentration (mM)	T (°C)	k_1 (s^{-1})	k_2 ($L mol^{-1} s^{-1}$)
1	12.5	49	0.75	60
2	12.5	57	0.90	72
3	12.5	65	1.15	92
4	12.5	84	1.85	148
5	25	49	1.40	56
6	25	57	1.65	66
7	25	65	2.35	94

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

S.No	Benzhydrol concentration (mM)	T (°C)	k_1 (s^{-1})	k_2 ($L mol^{-1} s^{-1}$)
1	10	27	0.53	53
2	10	40	0.74	74
3	10	80	2.01	201

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

S.No	Solvent	E_a (kJ/mol)	$\ln(A)$
1	[bmim][HFP]	22.3	12.9
2	[bdmim][HFP]	25.0	14.0
3	MeCN	29.1	14.5

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

S. No	Substrate	E_a (kJ/mol)	$\ln(A)$
1	Benzhydrol	22.3	12.9
2	Benzyl alcohol	19.1	8.8

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 ΔS^\ddagger is the change of entropy for the active complex formation from the reagent. Taking into account the pre-exponential constant A from the Arrhenius equation, 20 and 21, the following expression is obtained:

$$A = \frac{xek_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (23)$$

and ΔS^\ddagger can be calculated:

$$\Delta S^\ddagger = R \left(\ln A - \ln \frac{xek_B T}{h} \right) \quad (24)$$

Where A is the pre-exponential factor in the Arrhenius equation with values presented in Table 4. Since

$$E_a = \Delta H^\ddagger + RT \quad (25)$$

The changes of the enthalpy ΔH^\ddagger and Gibbs free energy ΔG^\ddagger for the active complex formation can be calculated using the well known thermodynamic equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (26)$$

The corresponding values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger for the reaction of superoxide ion with benzhydrol in [bdmim][HFP] calculated at $T=45^\circ\text{C}$ 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.* reported that both E_a and A values show a significant [26], systematic dependence on the identity of the anion and the nature of the alkyl substituents on the cation constituting the RTILs. They found significant (*ca.* 10 kJ/ mol) increase in E_a values associated with octyl *vs.* butyl substitution on the cation. This is consistent with the values of E_a we determined for the reaction of superoxide ion with benzhydrol in [bmim][HFP] and [bdmim][HFP] as can be seen from Table 3.

Ganiev *et al.* studied the kinetics of the oxidation of a series of alcohols with the oxoammonium salt 2,2,6,6-tetramethylpiperidine-1-oxyl chlorite in MeCN [28]. 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 $0.037 \text{ L mol}^{-1} \text{ s}^{-1}$. This value is

more than one order of magnitude lower than that for the same reaction utilizing the superoxide ion in RTIL determined by our group, $\cong 1.3 \text{ L mol}^{-1} \text{ s}^{-1}$.

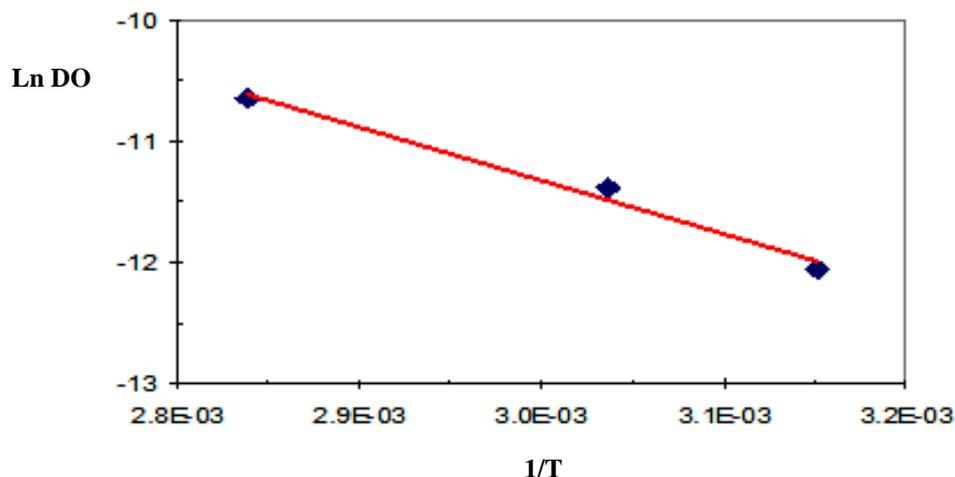


Fig. 5. A plot of natural logarithm of the diffusion coefficient of O_2 in [bmim][HFP] versus $1/T$ in the presence of 2-hydroxymethyl pyridine

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. It is clear from Table 6 that the values of the second order rate constant in RTIL is higher than those in MeCN although the viscosity of the RTIL is more than 3 orders of magnitude higher than that for MeCN. The activation energy in MeCN is also higher than that in RTILs. This is additional evidence that the measured parameters are the intrinsic kinetic parameters.

Table 6. Kinetic parameters for the reaction of $\text{O}_2^{\bullet-}$ with benzhydrol in MeCN

S.No	T (°C)	k_2 ($\text{L mol}^{-1} \text{ s}^{-1}$)
1	18.5	7.7
2	27.0	10.9
3	33.0	13.6

4. CONCLUSION

We showed that DPSC is an efficient and effective method for measuring the rate constants for the homogeneous reactions of alcohols with the superoxide ion in [bmim][HFP]

and [bdmim][HFP] RTILs. We 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 we found that 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], [bdmim][HFP], and MeCN 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.

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