

Benign Degradation of Chlorinated Benzene in Ionic Liquids

Inas M. AlNashef, Mohd Ali Hashim, Farouq S. Mjalli, Maan Hayyan

Abstract— Chlorinated hydrocarbons (CHCs), which include materials such as polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB), represent a major environmental problem. These materials contain components that are animal carcinogens and can cause birth defects, and their continual release into the ecosystem has a deleterious effect on animal life. Thermal incineration (oxidation) is the standard method of destroying chlorinated hydrocarbons, and is currently the only legal method of destruction of PCBs. Destructive oxidation is done in high-efficiency thermal incinerators or in cement kilns, but the potential for emission of dioxins makes regulations on these operations very strict. Installing and operating direct thermal incineration plants incurs significant public resistance.

In this study we demonstrated that low-temperature oxidation of chlorinated benzenes can be done using the superoxide ion generated in ionic liquids (ILs). The products of the destruction were the chloride and the bicarbonate ions.

The stability of the superoxide ion in selected ILs was also studied using UV-vis analysis. It was found that the superoxide ion is not stable in some used ILs.

We also showed that the temperature does not have any effect on the conversion of the CHCs. However, raising the temperature to about 50°C reduced the viscosity of the IL dramatically and hence increased mixing. In addition, it was found that the solubility of chlorinated hydrocarbons in ILs increased with the increase of temperature.

Low-temperature oxidation of waste solvents can provide a much-needed alternative to high temperature waste incinerators, whose use is greatly complicated by regulatory requirements and site selection.

Keywords— Chlorinated hydrocarbons, Destruction, Ionic liquids, Superoxide ion.

I. INTRODUCTION

THE handling, storage, and destruction of hazardous wastes (which includes polychlorinated biphenyls, hexachlorohexane, and most chlorinated organics) is regulated by law in most of countries. Although industry is making strides in reducing the usage of chlorinated solvents, a survey done in 1999 shows that approximately 341,000 kg of trichloroethylene, perchloroethylene, trichloroacetylene, and

other chlorinated solvents being used in part by dry cleaning, critical cleaning, paint stripping, and similar operations [1]. Significant volumes of chlorinated hazardous wastes exist in landfills, brownfields, and other contaminated sites. Polyhalogenated aromatic hydrocarbons, which include materials such as PCBs and HCB, represent a major environmental problem. These materials contain components that are animal carcinogens and can cause birth defects, and their continual release into the ecosystem has a deleterious effect on animal life [2]. Hexachlorobenzene, which is a byproduct of the poly(chloroethylene) solvent industry, is as environmentally persistent as PCBs and is a human carcinogen [3].

Thermal incineration (oxidation) is the standard method of destroying chlorinated hydrocarbons, and is currently the only legal method of destruction of PCBs. Noyes [4] reviewed commercial and near commercial of hazardous waste incineration. Destructive oxidation is done in high-efficiency thermal incinerators or in cement kilns, but the potential for emission of dioxins makes regulations on these operations very strict. Installing and operating direct thermal incineration plants incurs significant public resistance. Another high temperature destruction methods include injection of the waste into a moving bed of molten sodium carbonate salt. Supercritical water oxidation (SCWO), Savage [1] and Anitescu & Tavlarides [2] employed high temperature and pressure (>300 °C, 20 MPa typically), at which state both oxygen and hydrocarbons become very soluble and destruction rates high. The severe process conditions require high-pressure vessels, and corrosion is a significant limitation. However, commercial installations of SCWO are appearing, and sufficient information for economic evaluation is being generated. Photochemical oxidation is also at the research stage. In this process, photocatalysts such as TiO₂ are used to generate active hydroxyl or superoxide radicals in aqueous media. Biological destruction of chlorinated pollutants is receiving much attention, especially for in situ remediation; at present the kinetics are very slow [5].

Superoxide ion can be formed directly from solvation of KO₂ in aprotic solvents, or electrochemically via direct cathodic reduction of dioxygen (typically E=-1.0V vs SCE) as shown in Eq. 1:



O₂^{•-} is a strong nucleophile and disproportionates in water to O₂ and hydroperoxide:



To avoid this reaction, generation and utilization of O₂^{•-}

Inas M. AlNashef is with King Saud University, Riyadh, Saudi Arabia (Phone: +966-1-4676865; Fax: +966-1-4677787; e-mail: alnashef@ksu.edu.sa)

Mohd Ali Hashim is with University of Malaya, Kuala Lumpur, Malaysia (email: alihashim@um.edu.my)

Farouq S. Mjalli is with Sultan Qaboos University, Muscat, Oman (e-mail: farouqsm@yahoo.com)

Maan Hayyan is with University of Malaya, Kuala Lumpur, Malaysia (e-mail: maan_hayyan@yahoo.com)

must be done in aprotic solvents. Acetonitrile (MeCN), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) are commonly used.

Sawyer discussed in detail the reactions of the superoxide ion with halogenated hydrocarbons [6]. Sugimoto *et al* [7] reported that polyhalogenated aromatic hydrocarbons (e.g., PCB's and hexachlorobenzene) are rapidly degraded by superoxide ion in dimethylformamide to carbonate and halide ions. The efficient destruction of such materials is accomplished via the in situ electrolytic reduction of dioxygen to generate the superoxide ion, which reacts with poly aromatics by nucleophilic substitution.

The electro-generation of $O_2^{\bullet-}$ from dissolved air represents a much more practical approach for an effective system to destroy PCB's and other halogenated aromatic hydrocarbons.

Kalu and White [8] studied the effects of current, electrolyte flow, and aprotic media on the extent of degradation of HCB by the electrochemically generated superoxide ion in a flow cell system equipped with a gas fed, porous electrode. The authors found that the degradation efficiency reported by Sugimoto *et al.* [7] almost 100% for a batch system was not duplicated for a once-through flow reactor. The disagreement between the results of this work and the batch results indicated the complexity introduced into the system performance due to the flow effects. The authors found that the flow rates or residence time of the electrolyte in the reactor and the applied current density affected the level of substrate destruction achievable. They found that the type of solvent in use also influenced the degradation efficiency. Their experimental results demonstrated that, under the same operating conditions, the percentage degradation achievable was highest in dimethylformamide /dimethylsulfoxide solvent.

ILs have been proposed as "green" solvents for organic synthesis due to the ease with which they can be recycled, whilst offering an inert, dipolar media compatible with much conventional chemistry [9]. These properties have been reflected in their use in a range of reactions [10]. ILs are organic salts whose cations, substituents, and anions can be varied virtually at will to change their chemical and physical properties. In principle, the ILs solvent can be tailored for a given application. The most important feature of these compounds is that, while they are liquid in their pure state at or near room temperature, they have essentially no vapor pressure [11]. ILs have a number of favorable properties that make them attractive for electrochemistry, including a wide electrochemical window, high conductivity, a wide operating temperature range, and a low dielectric constant. In addition, their low flammability and non-volatile nature would seem to promote process safety. The wide and readily accessible range of ILs with corresponding variation in physical properties offers the opportunity to design an ionic liquid-solvent system optimized for a particular process. Early work on ILs in electrochemistry focused on their use as an electrolyte for advanced battery systems. Certain ILs are electrically stable over a range of 2-4V and higher, are thermally stable, and are

resistant to oxidation.

It was shown that the superoxide ion could be generated by the reduction of dioxygen in imidazolium chloride-aluminum chloride molten salt [12]. However, the resulting superoxide ion was unstable and thus cannot be used as a reagent in subsequent reactions. AlNashef *et al.* showed that a stable superoxide ion can be generated by the electrochemical reduction of dioxygen in ILs [12] and [13]. Buzzeo *et al.* studied the electrochemical reduction of oxygen in two different room-temperature ionic liquids, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [emim][N(Tf)₂], and hexyltriethylammonium bis((trifluoromethyl)sulfonyl)imide [15]. They used chronoamperometric measurements to determine the diffusion coefficient and concentration of the electroactive oxygen dissolved in the ionic liquid by fitting experimental transients to the Aoki model. They also determined the diffusion coefficient of the electrogenerated superoxide species.

In this work we used the chemically and electrochemically generated superoxide ion for the destruction of chlorinated hydrocarbons at ambient conditions. The solubility of selected chlorinated hydrocarbons in ILs was also measured as a function of temperature.

II. EXPERIMENTAL

A. Materials and Equipment

The following ILs (Solvent Innovation, Germany) were studied in this work: ECOENG 500 (Cocosalkyl pentaethoxy methyl ammonium methosulfate); 1-ethyl-3-methylimidazolium ethylsulfate; AMMOENG 110 (quaternary ammonium chloride); and AMMOENG 111 (Poly[oxy(methyl-1,2-ethanediyel)]-alpha-[2-diethylhydroethylammonio)ethyl]-acetate. The ILs were dried under vacuum until the water content is constant. All other chemicals were of >99% purity and were used without further purification.

B. Experimental Procedure

The solubility of CHCs was measured at different temperatures and in different ILs using two methods: gravimetric method and using UV-vis spectrophotometer.

It is well known that the superoxide ion reacts instantaneously with water. In addition, it was found that the superoxide ion reacts with organic cations of some ILs. In order to conduct the destruction of CHCs in ILs the superoxide ion should be stable in the used IL. To determine the stability of the superoxide in ILs pre-weighed amount of potassium superoxide was added to the IL in a vial. The solution was then stirred for several hours. About 0.3 g of the solution was then taken and dissolved in 5 ml of ethanol or iso-butanol. UV-vis spectrum was then taken and the height of the peak corresponding to the superoxide ion was noted. The solution was kept at the same temperature for a certain time and then another sample from the solution was taken and analyzed the same way described before. The effect of time on the height of the superoxide peak was monitored. If the peak

does not change considerably with time, this shows that the superoxide ion is stable in that IL.

For the destruction of CHCs a pre-weighed amount of a CHC was added to the ionic liquid and kept at a certain temperature and stirred using a hot plate/magnetic stirrer device. After reaching equilibrium a sample is withdrawn from the solution and added to a 5 ml ethanol or iso-butanol. The UV-vis spectrum is conducted for the sample and the height of the peak corresponding to CHC is noted. A small weighed amount of KO₂ is added to the solution of CHC in IL. The solution is stirred for several hours and a sample of the solution is taken and dissolved in 5 mL of ethanol or iso-butanol. The UV-vis for the sample is then taken. The height of the peak corresponding to the CHC is compared to that before the addition of KO₂. More KO₂ is added and the procedure is repeated until the peak of the CHC did not change. The sample is then analyzed using GC/MS for the detection of the remaining reactants and any possible product.

III. RESULTS AND DISCUSSION

A. Stability of Superoxide Ion in ILs

The superoxide ion can be generated in aprotic solvents and ILs by the electrochemical reduction of dissolved oxygen, Eq. 1, or by dissolving potassium superoxide in the aprotic solvent. The solubility of KO₂ in most aprotic solvents is very small. It was found that the addition of crown ethers enhances the solubility of KO₂ in aprotic solvent. AlNashef *et al.* reported that KO₂ is soluble in some ILs without the need to add crown ethers [14]. Some research groups found that the superoxide ion reacts with cation of some of the ILs [16-19]. This is why it was necessary to test the stability of superoxide ion in IL before conducting the destruction of CHCs in ILs.

1-Ethyl-3-methyl-Imidazolium ethyl sulfate is characterized by a relatively low viscosity, 109 cP at 25°C. It is liquid at room temperature with a yellowish color. The UV-vis spectra of KO₂ in 1-ethyl-3-methyl-imidazolium ethylsulfate are shown in Fig. 1. The peak at 234 nm shows that the superoxide ion is generated as a result of dissolving KO₂ in 1-ethyl-3-methyl-imidazolium ethylsulfate. As the concentration of KO₂ increased from 0.4 wt % to 1.2 wt % the height of the peak corresponding to the superoxide ion increased from 0.25 to 0.99. In order to confirm that this peak is the peak corresponding to the superoxide ion, small quantities of water were added to the solution. The corresponding UV-vis spectra are shown in Fig.2. The superoxide ion reacts instantaneously with water as shown in Eq. 2. This explains the decrease of the superoxide peak as more water is added to KO₂/1-ethyl-3-methyl-imidazolium ethylsulfate solution. It should be emphasized that the solution is always kept in a closed vial away from the moisture of the atmosphere.

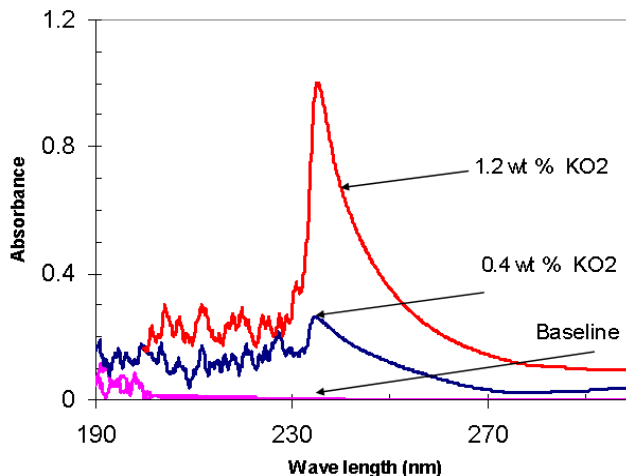


Fig. 1 UV-vis spectra for KO₂ in 1-ethyl-3-methyl-imidazolium ethylsulfate: Effect of concentration of KO₂.

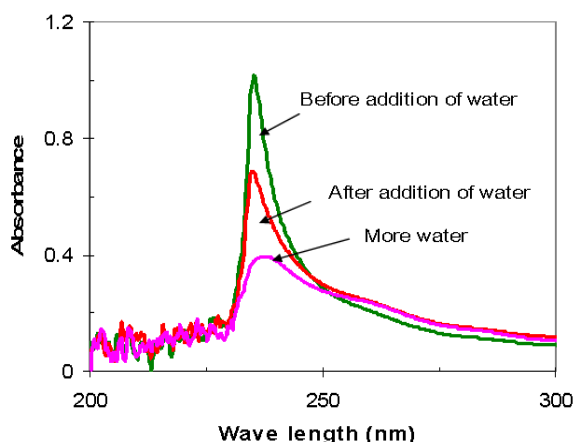


Fig. 2 Effect of water on the UV-vis spectra of KO₂ in 1-ethyl-3-methyl-imidazolium ethylsulfate.

In order to study the stability of the superoxide ion in 1-ethyl-3-methyl-imidazolium ethylsulfate, different samples were taken at different time intervals and their spectra were taken using UV-vis spectrophotometer. The results are shown in Fig.3. The height of the peak corresponding to the superoxide ion decreased from 1.3 to 1.0 in about 5.5 hours. The pseudo first order reaction rate constant can be calculated to be $1.2 \times 10^{-5} \text{ s}^{-1}$. This is close enough to the value reported in the literature for the electrochemically generated superoxide ion in 1-butyl-3-methyl-imidazolium hexafluorophosphate ($2.1 \times 10^{-5} \text{ s}^{-1}$) [16].

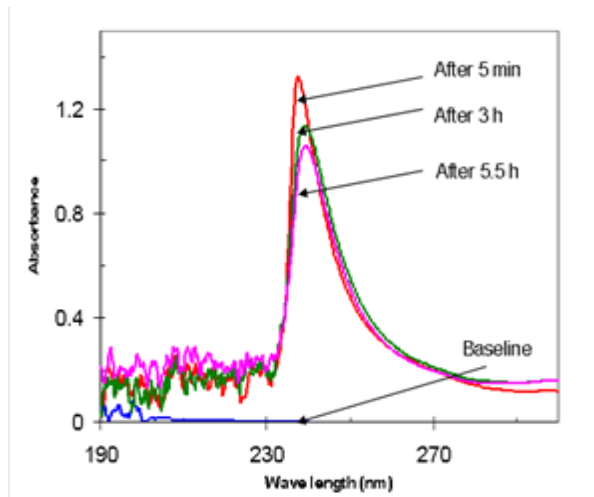


Fig. 3 Stability of the superoxide ion in 1-ethyl-3-methyl-imidazolium ethylsulfate.

We also determined the stability of superoxide ion in AMMOENG 110. AMMOENG 110 is a quaternary ammonium cation based ionic liquid. Its viscosity at 25°C is 109 cP. It is liquid at room temperature with a yellowish color. The UV-vis spectra of KO_2 in AMMOENG 110 are shown in Fig. 4. The peak at 242 nm shows that the superoxide ion is generated as a result of dissolving KO_2 in AMMOENG 110. As the concentration of KO_2 increased from 0.49 wt % to 1.2 wt % the height of the peak corresponding to the superoxide ion increased from 0.3 to 1.3. In order to study the stability of the superoxide ion in AMMOENG 110, different samples were taken at different time intervals and their spectra were taken using UV-vis spectrophotometer. The results are shown in Fig.5. The height of the peak corresponding to the superoxide ion decreased from 1.3 to 1.1 in about 23.5 hours. The pseudo first order reaction rate constant can be calculated to be $2.0 \times 10^{-6} \text{ s}^{-1}$. This is one order of magnitude less than that in 1-ethyl-3-methyl-imidazolium ethylsulfate. This clearly shows that the structure of the ionic liquid is very important for the stability of the superoxide ion.

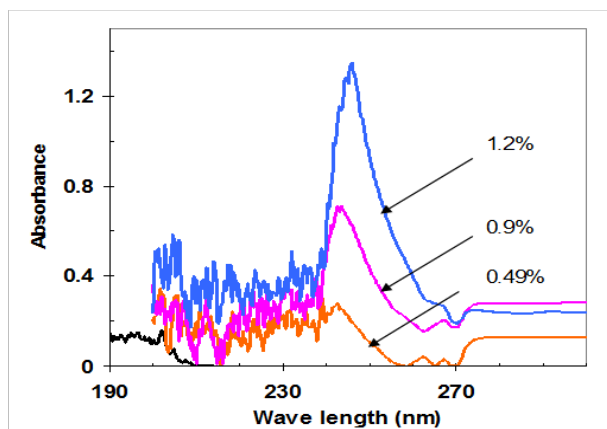


Fig. 4 UV-vis spectra of KO_2 in AMMOENG 110: Effect of concentration of KO_2 .

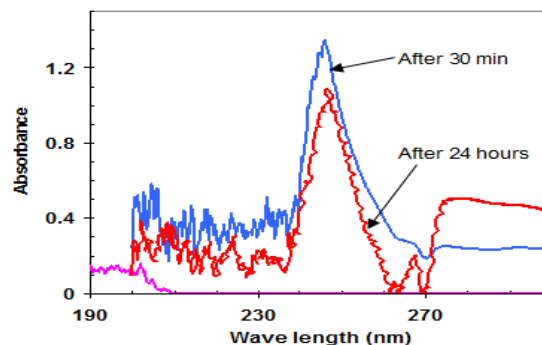


Fig. 5 Stability of superoxide ion in AMMOENG 110

In addition, we measured the solubility of three different chlorinated hydrocarbons, hexachlorobenzene (HCB); 1,2-dichlorobenzene (12DCB); and 1,3-dichlorobenzene (13DCB) in two different ionic liquids, ECOENG 500 and 1-ethyl-3-methyl-imidazolium ethylsulfate. The solubility was measured using gravimetric methods and using UV-vis spectrophotometer as explained in the procedure section. The solubility data are shown in Tables 1 and 2 for HCB, 12DCB, and 13DCB.

TABLE I
SOLUBILITY OF POLYCHLORINATED HYDROCARBONS IN ECOENG 500 AND 1-ETHYL-3-METHYL-IMIDAZOLIUM ETHYLSULFATE AT 65 °C.

Material	Solubility (g/100g)	
	ECOENG 500	1-ETHYL-3-METHYL-IMIDAZOLIUM ETHYLSULFATE
Hexachlorobenzene	42	0.0030
1,2-dichlorobenzene	miscible	0.0041
1,3-dichlorobenzene	miscible	0.0071

The solubility of HCB in 1-ethyl-3-methyl-imidazolium ethylsulfate is close enough to the value reported in the literature in 1-butyl-3-methyl-imidazolium hexafluorophosphate [12]. We notice that there is a four order of magnitude difference between the solubility of HCB in ECOENG 500 and 1-ethyl-3-methyl-imidazolium ethylsulfate. 12DCB and 13DCB are miscible with IL1 in all proportions. This dramatic change in the solubility emphasizes the effect of the structure of ILs on their physical properties. We also note that as the number of chlorine atoms increases in the CHC the solubility decreases.

It was shown before that the polyhalogenated aromatic hydrocarbons (e.g., PCB's and HCB) are rapidly degraded by superoxide ion in dimethylformamide to carbonate and halide ions [6]. The efficient destruction of such materials is accomplished via the in situ electrolytic reduction of dioxygen to generate the superoxide ion, which reacts with poly

aromatics by nucleophilic substitution. However, the used solvents are flammable, very volatile, and some of them are poisonous. On the contrary, ILs are non-flammable, non-volatile, and much less toxic than the classical organic solvents.

HCB was taken as a model compound for poly chlorinated hydrocarbons. Fig. 6 shows the UV-vis spectrum of HCB in IL3 before the addition of KO_2 . The characteristic peaks of HCB are clearly seen. After the addition of about 0.02 g of KO_2 to the solution of HCB in AMMOENG 110 we noticed that the height of the peaks corresponding to HCB decreased, Fig. 6. When about 0.1 g of KO_2 was added, the peaks approximately disappeared. It is clear that the superoxide ion generated by dissolving KO_2 in AMMOENG 110 reacted with HCB. Fig. 7 shows the UV-vis spectrum of HCB in AMMOENG 111 before and after the addition of KO_2 . The characteristic peaks of HCB are clearly seen. After the addition of about 0.1 g of KO_2 to the solution of HCB in IL4 the height of the peaks corresponding to HCB decreased dramatically.

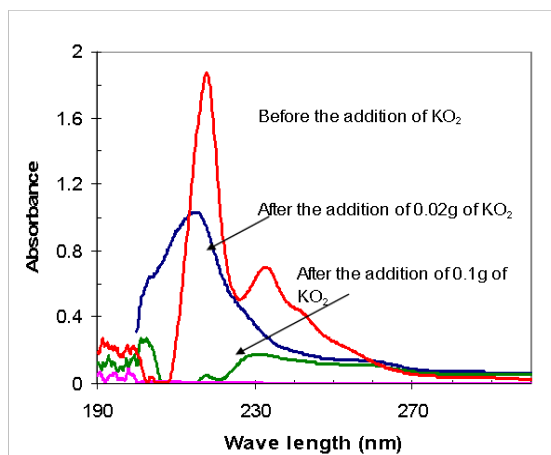


Fig. 6 UV-vis spectrum of HCB in IL3 before and after the addition of KO_2 .

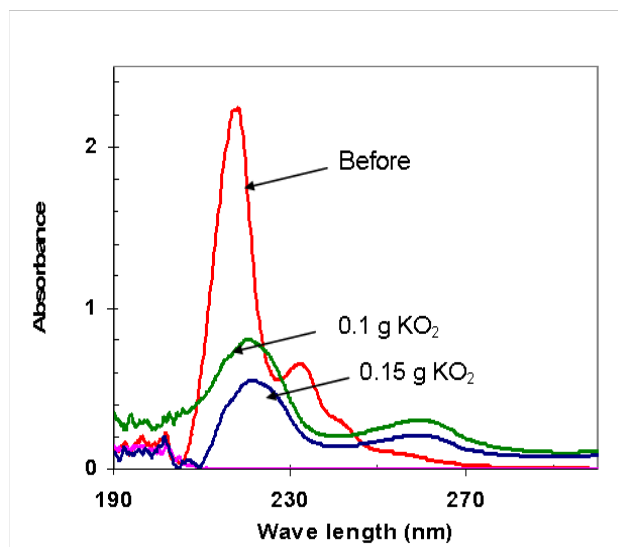


Fig. 7 UV-vis spectrum of HCB in IL4 before and after the addition of KO_2 .

To investigate the effect of the temperature on the conversion of PCH, experiments were conducted at three temperatures, 25, 50 and 70°C. The results showed that the temperature does not have any effect on the conversion of the PCH. However, raising the temperature to about 50°C reduced the viscosity of the IL dramatically and hence increased mixing. In addition, it was found that the solubility of KO_2 in ILs increases with the increase of temperature.

The optimum value for the mole ratio of the superoxide ion to PCH was estimated to be ten. This is close enough to the value nine that is reported in the literature.

IV. CONCLUSIONS

The solubility of different types of chlorinated hydrocarbons was measured in different ionic liquids at different temperature. It was found that the structure of the ionic liquid has a dramatic effect on the solubility of CHCs in ILs.

In addition, we demonstrated that low-temperature oxidation of polychlorinated hydrocarbons can be done using potassium superoxide dissolved in ionic liquids (ILs). It was found that the superoxide ion is not stable in some used ILS. UV-vis spectrophotometer was used for analysis of the samples. Low temperature oxidation of CHC is an important alternative for the thermal incineration (oxidation) that is the standard method of destroying chlorinated hydrocarbons, and is currently the only legal method of destruction of PCBs. The potential for emission of dioxins makes regulations on these operations very strict. Installing and operating direct thermal incineration plants incurs significant public resistance.

This study showed that the temperature does not have any effect on the conversion of the PCH. However, raising the temperature to about 50°C reduced the viscosity of the IL dramatically and hence increased mixing. In addition, it was found that the solubility of KO_2 in ILs increases with the increase of temperature.

The optimum value for the mole ratio of the superoxide ion to PCH was estimated to be ten. This is close enough to the value nine that is reported in the literature.

ACKNOWLEDGMENT

The authors thank the National Plan for Science, Technology, and Innovation at King Saud University for their financial assistance through project no. 10-ENV1010-02, University of Malaya Centre for Ionic Liquids (UMCiL), and Department of Petroleum and Chemical Engineering at Sultan Qaboos University for their support to this research.

REFERENCES

- [1] Savage, P. E. Organic Chemical Reactions in Supercritical Water, *Chem. Rev.*, 1999, 99, 603.
- [2] Anitescu, G. and Tavlariades, L.L., Oxidation of Aroclor 1248 in Supercritical Water: A Global Kinetic Study. *Ind. Eng. Chem. Res.* 2000, 39, 583.
- [3] DOE/EM-0459 Direct Chemical Oxidation. Innovative Technology Summary Report, prepared for the U.S. Department of Energy, December 1998.

- [4] Noyes, R. Ed. Handbook of pollution control processes. Noyes Publications: Park Ridge, NJ. 1991.
- [5] Jones, A.P.; Watts, R.J. Dry phases titanium dioxide-mediated photocatalysis: basis for in situ surface destruction of hazardous chemicals. *J. Env. Eng.* 1997, 974.
- [6] Sawyer, D. T., Oxygen Chemistry; Oxford University Press: New York, 1991.
- [7] Sugimoto, H., Matsumoto, S., Sawyer, D. T. Peroxy radicals and singlet oxygen (1O_2) from the addition of superoxide ion ($O_2^{\cdot-}$) to CCl_4 , CF_3CCl_3 , $PhCCl_3$, $N-BuBr$ and $N-BuCl$ in acetonitrile. *Environ. Sci. Technol.* 1988, 22, 1182.
- [8] Kalu, E. E. and White, R. E. *J. Electrochem. Soc.* 1990, 138, 3656.
- [9] Holbrey, J. D. and Rogers, R. D. Green Chemistry and Ionic Liquids: Synergies and Ironies, in *Ionic Liquids: Industrial Applications to Green Chemistry*. R. D. Rogers and K. Seddon, (Editors) Oxford University Press, New York, 2002.
- [10] Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis, *Chem. Rev.*, 1999, 99, 2017.
- [11] Brennecke, J. F. and Maginn, E. J. Ionic liquids: Innovative fluids for chemical processing, *AIChEJ*, 2001, 47 (11), 2384.
- [12] Carter, M. T. Hussey, C. L., Strubinger, S. K. D. and Osteryoung, R. A. Electrochemical Reduction of Dioxygen in Room-Temperature Imidazolium Chloride-Aluminum Chloride Molten Salts. *Inorg. Chem.* 1991, 30, 5, 1149.
- [13] AlNashef, I. M. Leonard, M. L. Kittle, L. M. Matthews, M. A. and Weidner, J. W. Electrochemical Generation of Superoxide in Room-Temperature Ionic Liquids. *Solid-State Letters*, 2001, 4, D16.
- [14] AlNashef, I. M. Leonard, M. L. Kittle, L. M. Matthews, M. A. and Weidner, J. W., in "Ionic Liquids as Green Solvents: Progress and Prospects", R. Rogers and K. Seddon, Editors, Oxford University Press, New York, 2003.
- [15] Buzzeo, M. C., Klymenko, O. V., Wadhawan, J. D., Hardacre, C., Seddon, K. R., and Compton, C. R. Voltammetry of oxygen in the room-temperature ionic liquids 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide and hexyltriethylammonium bis((trifluoromethyl)sulfonyl)imide: One-electron reduction to form superoxide. Steady-state and transient behavior in the same cyclic voltammogram resulting from widely different diffusion coefficients of oxygen and superoxide *J. Phys. Chem. A*, 2003, 107, 8872.
- [16] AlNashef, I. M. Ph.D. Thesis, University of South Carolina, 2004.
- [17] AlNashef, I.M., Hashim, M.A., Mjalli, F.S., Ali, Q.A., Hayyan, M., A novel method for the synthesis of 2-imidazolones, *Tetrahedron Letters*, 2010, 51, 1976.
- [18] Islam, M. M.; Ohsaka, T. *J. Phys. Chem. C* 2008, 112, 1269.
- [19] Islam, M.; Imase, T.; Okajima, T.; Takahashi, M.; Niikura, Y.; Kawashima, N.; Nakamura, Y.; Ohsaka, T., *J. Phys. Chem. A* 2009, 113, 912.