Autooxidation of Hydrocarbons with Oxygen in Ionic Liquids as Solvents

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ABSTRACT: The results of hydrocarbons autooxidation process carried out using several ionic liquids (IL) as solvents are demonstrated. Test studies to check the influence of ILs on this process showed that most ILs can accelerate the initiation rate of autooxidation. The results could be very useful for choosing an IL not only for autooxidation processes but also for catalytic oxidation systems. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 287–293, 2008

INTRODUCTION

A developing area of interest among industrial processes is the oxidation reactions; however, they are frequently disturbed by: low conversion and selectivity due to overoxidation, corrosive reaction media, lack of solvent and catalyst recycling, and the application of volatile organic solvents with high VOCs (volatile organic compounds) emission. In addition, the organic solvents used in these processes are very often undesirable because of their toxicity and flammability. In addition, their selection is further restricted due to the formation of explosive mixtures in a gas phase. The ideal system for "green" oxidation is the use of molecular oxygen or air as an oxidant without a solvent or together with a recyclable nontoxic and nonvolatile solvent or the solvent/catalyst system. The potential of ionic liquids (ILs) for catalytic oxidation reactions has not escaped the attention of the chemists [1]. ILs have been described as one of the most promising new reaction mediums—as a green alternative to volatile organic solvents. These substances dissolve many organic and inorganic substances and are readily recyclable and tunable to specific chemical tasks. Owing to their negligible vapor pressure, ILs could influence the safety of processes carried out in the presence of oxygen. Since the first application of IL as a reaction medium, there have been some reports of catalytic oxidation using various oxidants carried out in ILs as solvents [2].

To better understand oxidation processes with oxygen in ILs, it is necessary to learn about noncatalytic processes. In the case of free radical reactions, it is possible to run such a process in parallel to a catalytic one. Noncatalytic oxidation is known as autooxidation and is highly sensitive to various external factors, e.g., trace impurities. As such, we do not know what kind of influence to expect for ILs in this process. The main purpose of this study was to test the possibility of performing an oxidation process of model hydrocarbons with oxygen using select ILs as the reaction medium.

EXPERIMENTAL

Materials

The sources of the ILs used in this study are summarized in Table I. The residual halide contents of all ILs,

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ILs	at	90 ^c	'C
	ILs	ILs at	ILs at 90°

Ionic Liquids	Ionic Liquids Source	c_{cumene} (% v/v) ^a
1-Butyl-3-methylimidazolium <i>n</i> -octylsulfate ([bmim]OSO ₃ Oc)	Solvent Innovation GmbH,	50
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim]NTf ₂)	Synthesized in our laboratory [3a]	32
Butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([bmp]NTf ₂)	Solvent Innovation GmbH	31
Trimethylbytylammonium bis(trifluoromethylsulfonyl)imide ([tmba]NTf ₂)	Synthesized in our laboratory [3a]	14
1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF ₄)	Synthesized in our laboratory [3b]	12
1-Ethyl-3-methylpyridinium ethylsulfate ([empd]OSO ₃ Et)	Solvent Innovation GmbH	12
1-Butyl-3-methylimidazolium heksafluorophosphate ([bmim]PF ₆)	Synthesized in our laboratory [3c]	10
1-Butyl-3-methylimidazolium acetate ([bmim]OAc)	Solvent Innovation GmbH	10
1-Butyl-3-methylimidazolium hydrogensulfate ([bmim]HSO ₄)	Solvionic SA, Toulouse, France	5
1-Methyl-3-pentylimidazoliumtris (nonafluorobutyl)trisfluorophosphate ([pmim]PF ₃ (C ₄ F ₉) ₃)	Samples received as gift from Merck KGaA, Darmstadt, Germany	10
$\label{eq:linear} \begin{array}{l} 1 \mbox{-Hexyl-3-methylimidazoliumtris (pentafluoroethyl)trisfluorophosphate} \\ ([hmim]PF_3(C_2F_5)_3) \end{array}$	Samples received as gift from Merck KGaA	10

^a Determined by HPLC.

which were obtained from adequate halides, were less than 59 μ mol/g (determined by mixing the ILs with 1 M AgNO₃). Oxygen was purchased from BOC (Warsaw, Poland) (purity 99.99%). 1-Methyl-1-phenylethyl hydroperoxide was prepared according to standard procedures [4]. Isopropylbenzene and *n*-decane were purified by refining with concentrated sulfuric acid and by distillation over sodium in a nitrogen atmosphere.

Determining the Initial Rate of Oxidation

The experiments were carried out in a gasometric apparatus (Fig. 1).

The fundamental element of the gasometric apparatus was a 4-mL quartz flask (1), filled up with a solution of hydrocarbon in IL (2 mL) and ACHN



Figure 1 Gasometric apparatus.

(0.02 mol/dm³) placed in a thermostatic oil bath (2) at 100–130°C (temperature was kept with an accuracy of ± 0.01 °C). The flask was flushed with oxygen by successive connection to a vacuum pump and a container with oxygen (7). It was followed by filling a burette (3) with oxygen and establishing a constant pressure of 760 mmHg by means of a manometer (6). A precise stabilization of pressure (± 0.05 mmHg) in the apparatus was possible owing to the application of a manostat (5). Burette and manostat were kept at constant temperature of 25°C with ± 0.1 °C accuracy. During the experiment, the sample was effectively mixed with oxygen /stirrer (8). Each experiment was repeated five times.

The initial rate of oxidation r_{ox} was determined via the amount of chemisorbed oxygen, which can be expressed by the formula $r_{ox} = -d[O_2]/dt$. Using the definition of the molar concentration, the oxidation rate can be defined as $r_{ox} = n_{ox}/(V_t \cdot t)$, where n_{ox} is the amount of oxygen absorbed in 10 min, V_t is the total volume of the reaction mixture in process temperature, in mL, t = 600 (s) is the time to absorb n_{ox} mole of oxygen. The number of moles of chemisorbed oxygen can be expressed by using the formula $n_{\rm ox} = V_{\rm abs}/V_T$, where $V_{\rm abs}$ is the volume of chemisorbed oxygen in 10 min at 25°C and under a pressure of 1 atm, in mL, $V_T = 24467.6$ (mL) is the molar volume of oxygen at 25°C and under a pressure of 1 atm, which enables the easy calculation of oxidation rate $r_{\rm ox} = 1000 \cdot V_{\rm abs} / (600 \cdot V_{\rm pr} \cdot V_T) \, ({\rm mol/dm^3} \times$ s). V_{abs} was determined from the slope of dependence $V_{\text{abs}} = f(t)$ (example Fig. 2).



Figure 2 Cumene oxidation (10% v/v) in the presence of [bmim]OSO₃Oc gasometric apparatus with ACHN (0.02 mol/dm³) at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Long-Term Oxidations

Hydrocarbons were also oxidized in a reactor for longterm oxidations. The fundamental element of this reactor is a 25-mL round-bottom flask, placed into a thermostatic oil bath, filled up with the solution of hydrocarbon in IL (8 mL) and ACHN (0.02 mol/dm³) and placed in a thermostatic oil bath at 120–130°C and was effectively mixed with oxygen for 3 h under a constant pressure of 760 mmHg. The total volume of oxygen consumed during the reaction was measured. Each experiment was repeated five times. After the reaction, the composition of the reaction mixture was determined by HPLC.

Recycle of [bmim]OAc

IL was purified for recycle tests by extractions of postreaction mixture with diethyl ether (6 \times 5 mL), concentration and drying under vacuum. In the next experiments solution of cumene (10%v/v) in IL and a new batch of ACHN (0.02 mol/dm³) were used.

Stability of Ionic Liquids

Two milliliters of IL with ACHN (0.02 mol/dm³) was mixed with oxygen in gasometric apparatus at 120°C. The amount of absorbed oxygen was measured.

Solubility of Cumene in Ionic Liquids

One milliliter of IL and 1 mL of cumene were placed into a thermostatic oil bath at 90°C and were mixed for 1 min. A sample from the IL layer was taken with a syringe and was analyzed by HPLC. The amount of cumene in IL was recalculated.

Stability of Cumyl Hydroperoxide

A solution of 2 mL of cumyl hydroperoxide (CHP) in IL (10:90% v/v) was placed into a thermostatic oil bath at 100° C and mixed for 3 h. After this time the content of CHP was determined by iodometric titration.

Analysis

HPLC was performed by liquid chromatograph (Alliance, Waters 2690 system) with a Waters photodiode array detector and 3.9×150 mm cartridge column (Nova-Pak C18, 60A, 4 µm); the solvent system included methanol/water (70/30 v/v, flow rate 1 mL/min).

RESULTS AND DISCUSSION

We have chosen isopropylbenzene (cumene) as our model compound. Cumene is a typical compound used in this type of studies. All experiments concerning oxidation were carried out in the presence of 1,1'-azobis(cyclohexanecarbonitrile) (ACHN), a freeradical initiator. The ILs used in this study and their sources are listed in Table I.

We first checked the stability of ILs in the presence of molecular oxygen. ILs may potentially undergo an oxidation process because they possess alkyl chains (C2–C8) in their structure. The next step was to determine the solubility of hydrocarbons in ILs. Finally, we performed testing studies on the autooxidation process using two kinds of gasometric apparatus, one for initial rate determination and one for long-term oxidations.

Stability of Ionic Liquids under Free Radical Oxidation Conditions

All ILs used in this study were mixed with ACHN and shaken with oxygen using a gasometric apparatus at 120°C for 3 h. ACHN is soluble in all ILs. In every case, only the oxygen absorption resulting from oxygen solubility in a sample was noted. We compared these data to our previous results concerning oxygen solubility in ILs [5]. Together they demonstrate the stability of ILs in the presence of molecular oxygen in our experimental conditions.

Solubility of Cumene and *n*-Decane in Ionic Liquids

We determined the solubility of cumene in the ILs investigated. As it appears from Table I, cumene is the most soluble in [bmim]OSO₃Oc. This is probably due

to the long-alkyl chain (C_8) in the anion of the IL. In other ILs, the solubility of cumene varies from 5% to 32% v/v. The amount of cumene applied for oxidation processes in this study allowed for the preparation of homogeneous solutions with ILs at experimental temperatures.

Autooxidation Processes Carried Out in Ionic Liquids

The kinetic data of the autooxidation process of cumene (10% v/v solution in selected ILs) with molecular oxygen carried out in a gasometric apparatus with ACHN (0.02 mole/dm³) at 100°C are shown in Table II. The method of r_{ox} determination is described in the Experimental section. The advantage of this method is a short measuring time (10–15 min) and consequently low degree of conversion (0.03%). The influence of the oxidation products on the course of the reaction can be eliminated.

The rates of cumene oxidation in experiments carried out in some ILs (entries 2 and 3 in Table II) were equal to the rate obtained in the same reaction with *tert*-butylbenzene (*t*-BuPh) as a solvent ($r_{ox} = 7.15 \times 10^{-6} \text{ mol/(dm}^3 \text{s})$). This solvent is described in the literature as a classical representative of inert solvents. In the case of other ILs, the acceleration of the reaction rates ($r_{ox} = 8.89 \times 10^{-6}$ to $14.12 \times 10^{-6} \text{ mol/dm}^3 \text{s}$) was observed.

In addition, the oxidation of *n*-decane as a representative of *n*-alkyl linear hydrocarbons (15% v/v in

Table II Rate of Cumene Oxidation r_{ox} in the Presence of ACHN (0.02 mol/dm³) at 100°C

Entry	Solvent	$r_{\rm ox} \times 10^{-6}$ (mol/dm ³ s)
1	<i>t</i> -BuPh	7.06
2	[bmim]OSO ₃ Oc	7.05
3	[empd]OSO3Et	7.00
4	[bmp]NTf ₂	10.26
5	[bmim]NTf ₂	9.33
6	[tmba]NTf ₂	12.05
7	[bmim]BF ₄	12.72
8	[bmim]PF ₆	8.89
9	[bmim]OAc	14.12
10	[bmim]HSO4 ^a	14.30
11	$[hmim]PF_3(C_2F_5)_3$	13.23
12	<i>t</i> -BuPh ^b	13.02
13	[bmim]OSO ₃ Oc ^b	13.10

^a 5% v/v of cumene.

^b 15% v/v of *n*-decane at 130°C.

[bmim]OSO₃Oc) at 130°C was performed. In this process, [bmim]OSO₃Oc also does not influence the oxidation rate compared to similar process carried out in t-BuPh (entries 12 and 13 in Table I).

To confirm the thesis that some ILs do not influence the rate r_{ox} , the oxidation of cumene in [bmim]OSO₃Oc was examined by the method proposed by Russell [6]. The studies were performed for several solutions of different concentrations of cumene in ILs (25–100 v/v%) with constant ACHN molar concentration (0.002 mol/dm³). The linear dependence of the rate of oxidation on the cumene concentration confirmed the inert nature of ILs in this process (Fig. 3).

Exactly the same results were obtained for the same experiments with *t*-BuPh as solvent. For all experiments, good correlations (r = 0.9980.999) between the measured loss of oxygen and the time of oxidation were observed.

One of the reasons for the differing behavior of cumene in ILs than in t-BuPh could be the influence of ILs on the mechanism of the autooxidation process. As known from the reaction mechanism [7], hydroperoxides are the main intermediate products of the oxidation process in the liquid state with molecular oxygen. Under experimental conditions, they can be decomposed to free radicals that, in turn, generate new kinetic chains and thus the process becomes autocatalytic. That is why acceleration of CHP decomposition during the oxidation process can result in acceleration of the oxidation rate. A similar effect involving the influence of tetra-alkylammonium salts (used as phase-transfer catalysts) on oxidation reactions has been demonstrated in the literature [8]. It was shown that organic hydroperoxides were decomposed efficiently by these salts, accelerating the oxidation process.

For this reason, we have decided to perform some additional tests checking the stability of CHP in ILs at the reaction temperature. To begin, the mixture of CHP and IL (10:90 v/v) was stirred at 100° C for 3 h (Table III). After this time, the concentration of CHP was measured.

In the case of *t*-BuPh, 10% of the CHP was decomposed after 3 h in what can only be a result of thermal decomposition. Similar behavior of CHP at 100°C was observed in ILs based on alkylsulfate anions (entries 2 and 3 in Table III) and NTf₂⁻ anions (entries 4–6 in Table III). A different conclusion can be drawn from experiments with other ILs (entries 7–10 in Table III). These ILs influence the CHP decomposition process.

Taking into account data concerning the influence of ILs on the stability of CHP and r_{ox} values (Table II), an interesting dependence can be observed. ILs based on alkylsulfate anions do not influence the decomposition of CHP and do not accelerate r_{ox} in



Figure 3 Influence of cumene concentration (% v/v) on oxidation process in [bmim] OSO₃Oc as solvent and in the presence of ACHN (0.002 mol/dm³) at 110°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table III Decomposition of CHP in Selected ILs, Temperature 100°C, Time 3 h $\,$

Entry	Solvent	Decomposition of CHP $(\%)^a$	
1	t-BuPh	10	
2	[bmim]OSO ₃ Oc	10	
3	[empd]OSO3Et	10	
4	[bmim]NTf ₂	10	
5	[bmp]NTf ₂	10	
6	[tmba]NTf ₂	10	
7	[bmim]BF4	36	
8	[bmim]PF ₆	100	
9	[bmim]OAc	90	
10	[bmim]HSO ₄	90	

^a Concentration of CHP was determined by iodometric titration.

comparison to experiments with *t*-BuPh as solvent. ILs based on BF_4^- , PF_6^- , OAc^- , and HSO_4^- anions accelerate the rate of the oxidation process by decomposing CHP.

Exceptions to the rule are ILs based on bis(trifluoromethylsulfonyl)imide anions. Three ILs with different cation structures (1-butyl-3-methylimmidazolium, butylmethylpyrrolidinium, trimethylbytylammonium) did not have an influence on the CHP stability but did accelerate the oxidation process.

Long-Term Autooxidation Process Carried Out in Ionic Liquids

We also examined the extent of oxidation of the hydrocarbons in the reactions occurring over longer periods of time. This allowed us to draw the conclusions concerning the influence of the products on the reaction course. During the oxidation process, stable oxygen products, e.g., alcohols, ketones, or carboxylic acids occur as a result of consecutive reactions. These substances may influence the oxidation process by changing the reaction rate; they can accelerate or inhibit the process.

To investigate this, studies on the oxidation processes of cumene were typically carried out for 3 h at 120° C. The volume of absorbed oxygen was measured, and conversion of cumene (α) was recalculated. For comparison, Fig. 4 illustrates the similar course of the reaction carried out in *t*-BuPh (top line) and the reaction in [bmim]OSO₃Oc (bottom line).

In addition, the samples from the postreaction mixture were analyzed to determine the qualitative and quantitative composition of reaction products (Table IV). Then, as the medium of the reaction, *t*-BuPh, was applied, the concentration of CHP was about 12% and higher yields of dimethylphenyl carbinol (DMPC) than acetophenone (AcPh) were observed. In short-term oxidations with ILs based on alkylsulfate anions, we did not observe the influence of IL on the reaction rate. However, during the long-term processes, an influence on the product composition was observed.

In the case of other solvents, a lower concentration of CHP and different proportions of alcohol/ketone concentration were detected. When the reaction was carried out in [bmim]OAc, the highest selectivity of DMCP could be observed. This liquid was chosen as a representative for recycling studies. [bmim]OAc was purified after the process and was reused twice for other reactions without the loss of activity (entry 8 in Table IV).

Entry	Solvent		$lpha^a$	Yield ^{b} (%)		
		$c_{\text{cumene}}(\%)$		Cumyl Hydroperoxide	Dimethylphenyl carbinol	Acetophenone
1	t-BuPh	25	15.7	12.1	2.4	1.0
2	[bmim]OSO ₃ Oc	25	15.0	5.0	7.0	2.9
3	[bmim]NTf ₂	25	14.5	10.0	3.5	1.0
4	[bmp]NTf ₂	25	15.7	8.0	4.5	2.7
5	[bmim]BF ₄	25	11.4	4.1	5.1	2.1
6	[tmba]NTf ₂	15	10.0	3.0	3.6	3.1
7	[empd]OSO3Et	10	8.7	2.0	4.1	3.0
			14.7			
8	[bmim]OAc	10	14.1 ^c	2.0	10.2	2.3
			13.5 ^c			

Table IV Long-Term Oxidation of Cumene (10%–25% v/v) in the Presence of ACHN (0.02 mol/dm³), at 120°C, α = Conversion of Cumene, Reaction Time 3 h

^a Recalculated from amount of absorbed oxygen during the reaction time (3 h).

^b HPLC analysis.

^{*c*} α after first and second recycle of IL.



Figure 4 Long-term cumene oxidation (25% v/v) in the presence of [bmim]OSO₃Oc and *t*-BuPh with ACHN (0.02 mol/dm³) at 120°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

In conclusion, this study showed that the autooxidation process of the model hydrocarbon cumene can be carried out in the ILs studied. Two different tests with ILs as solvents were performed: short- and long-term oxidations. During the short-term oxidations, the initial rates of cumene oxidation were determined. Most ILs accelerate the oxidation rate, but ILs based on alkylsulfate anions acted similar to t-BuPh. The acceleration of the oxidation rate in the case of some ILs could be caused by the decomposition of CHP, which is formed during the process. The long-term oxidation test showed that all ILs tested influenced the product composition. Thus, by choosing different ILs we can control the composition of reaction products. Owing to the possibility of recycling, the solvent, processes with ILs provide a more environment friendly solution than conventionally used solvent systems. These results will be the basis for further studies concerning the possibility of catalytic oxidation processes in ILs.

BIBLIOGRAPHY

 (a) Welton, T. Chem Rev 1999, 99, 2071–2084;
(b) Wasserscheid, P.; Wilhelm, K. Angew Chem, Int Ed 2000, 39, 3772–3789;
(c) Olivier-Bourbigou, H.; Magna, L. J Mol Catal A: Chem 2002, 182, 419–437; (d) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Chem Rev 2002, 102, 3667–3692; (e) Wasserscheid, P.; Welton, T. Ionic Liquids in Synthesis; Wiley-VCH: Weinheim, 2003; (f) Binnemans, K. Chem Rev 2005, 105, 4148–4204; (g) Parvulescu, V.; Hardacre, C. Chem Rev 2007, 107, 2615–2665.

- 2. Muzart, J. Adv Synth Catal 2006, 348, 275-295.
- (a) Bonhote, P.; Dias, A.; Papageorgiou, N.; Kalyanasundaram, K.; Graetzel, M. Inorg Chem 1996, 35, 1168– 1178; (b) Shang, H.; Wu, J.; Zhou, Q.; Wang, L. J Chem Eng Data 2006, 51, 1286–1288; (c) Fuller, J.; Carlin,

R. T.; DeLong, H. C.; Haworth, D. Chem Commun 1994, 299–300.

- 4. Milchert, E. Pol J Appl Chem 1988, 32, 171–174.
- Chrobok, A.; Swadźba, M.; Baj, S. Pol J Chem 2007, 81, 337–344.
- (a) Russell, G. J Am Chem Soc 1956, 78, 1047–1054; (b) Russell, G. J Am Chem Soc 1957, 79, 3871–3877.
- Denisov, E.; Afanas'ev, I. Oxidation and Antioxidants in Organic Chemistry and Biology; Taylor & Francis: Boca Raton, FL, 2005.
- Csanyi, L.; Jaky, K.; Kota, Z.; Pali, T. J Mol.Catal A: Chem 2004, 209, 59–68.