

Synthesis and Characterization of Task-Specific Ionic Liquids Based on Peroxydisulfate and Their Application in Oxidation Reactions

Shenyi Shi,^[a] Aiguo Kong,^[a] Xinhua Zhao,^[a] Qiyang Zhang,^[a] and Yongkui Shan*^[a]

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Four new task-specific ionic liquids based on the peroxydisulfate ion were synthesized by the ion exchange method and characterized by FTIR and ¹H NMR spectroscopy and elemental analysis. The physicochemical characteristics of these ionic liquids such as density, thermal stability, conduc-

tivity, viscosity, and solubility in common solvents have been investigated in detail. The experimental results testify that the ionic liquids prepared show excellent performance as both oxidant and medium in given oxidation reactions of alcohols and thiols under mild reaction conditions.

Introduction

Task-specific ionic liquids (TSILs) attract enormous interest due to the potential to modulate their physicochemical properties through appropriate structure modification or component change and to tailor the best ionic liquid for each specific application.^[1] Intelligent choice of the anion and cation or the introduction of functional groups on the components of ionic liquids can create a TSIL that has wide anodic or cathodic limits (or both), more or less hydrophobic behavior, chiral character, acidic and/or basic properties, etc. A large number of TSILs have been created in recent years because of this flexibility in their design. In general, hydrophilic properties will be tuned by anion exchange of the ionic liquid moiety. For example, 1-butyl-3-methylimidazolium ([bmim]) tetrafluoroborate ([BF₄]) is a hydrophilic ionic liquid, whereas its hexafluorophosphate ([PF₆]) analogue is hydrophobic.^[2] The basic ionic liquid [bmim]OH can be obtained by the reaction of 1-butyl-3-methylimidazolium bromide with potassium hydroxide,^[3] whereas an imidazole cation that bears an alkane sulfonic acid group can behave as a Brønsted acid.^[4] In an ionic liquid designed for CO₂ capture, 1-butyl-3-aminopropylimidazolium tetrafluoroborate, the cation core is assembled by the reaction of 1-butylimidazole with 3-bromopropylamine hydrobromide in ethanol.^[5] Ionic liquids bearing thiol groups on the imidazolium cation can stabilize nanomaterials in homogeneous fluids.^[6] Although TSILs have been investigated since their first introduction in 2001,^[7] little work has concentrated on their intrinsic redox behavior.^[8]

Oxidation reactions are key steps in the industrial synthesis of chemicals. The catalytic oxidation of hydrocarbons accounts for approximately one quarter of the catalytic processes worldwide.^[9] Although environmentally benign processes to prepare chemicals by using molecular oxygen or hydrogen peroxide as the oxidant have been presented,^[10] inorganic oxidants (such as permanganate, peroxydisulfate, and high-valent oxochromium species) and conventional volatile organic solvents are still widely utilized in the manufacture of fine chemicals and pharmaceuticals. Ecological and economic concerns associated with chemical synthesis have posed stringent and compelling demands for greener, more sustainable technologies. Obviously, in the development of various oxidation processes, fine-tuning the reactivity of common oxidants, expanding the application of “new” oxidants, avoiding the use of conventional solvents, applying solvent-free reactions, and recycling reaction media are of prime importance to dramatically reduce energy consumption, material cost, waste, and risk.

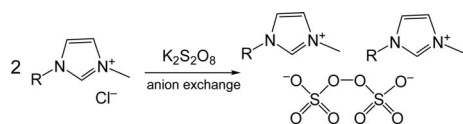
In this paper, we describe the synthesis and characterization of a new series of TSILs with high oxidizing abilities based on peroxydisulfate, 1-alkyl-3-methylimidazolium peroxydisulfate, denoted as [C_nmim]₂[S₂O₈] {*n* = 4 (TSIL-1), 6 (TSIL-2), 8 (TSIL-3), 10 (TSIL-4)} (in which alkyl = butyl, hexyl, octyl, decyl, respectively), and their performance as both reactant and reaction medium in oxidation reactions of alcohols and thiols.

Results and Discussion

Preparation

Four task-specific ionic liquids were prepared by the metathesis reaction of 1-alkyl-3-methylimidazolium chloride with potassium peroxysulfate, as shown in Scheme 1. These TSILs are air- and water-stable.

[a] Department of Chemistry, East China Normal University, Shanghai, 200062, China
Fax: +86-21-62233503
E-mail: ykshan@chem.ecnu.edu.cn



Scheme 1. Preparation of $[C_n\text{mim}]_2[\text{S}_2\text{O}_8]$ by ion exchange ($[C_n\text{mim}] = 1\text{-alkyl-3-methylimidazolium}$, $n = 4, 6, 8, 10$).

There were variations in the methods of preparation of the TSILs because of their different hydrophobicity. TSIL-4, which is a hydrophobic ionic liquid, was prepared in aqueous solution, because the reactants are soluble in water. The product spontaneously separated from the aqueous solution, which further promoted the formation of the product and led to higher yields. TSIL-1, -2, and -3, which are hydrophilic ionic liquids, were prepared in acetone solution, because the byproduct, KCl, is insoluble in acetone. KCl spontaneously separated from the reaction system as a precipitate, which also promoted the formation of the ionic liquid and led to higher yields. Using these preparation methods, four new task-specific ionic liquids were obtained in high yield. The chloride content in all of the ionic liquids produced was less than 0.1 % w/w. Some physical characteristics of the ionic liquids are listed in Table 1.

Table 1. Some physical characteristics of the ionic liquids produced.

Ionic liquid	Density ^[a] (g cm ⁻³)	Conductivity ^[a] (10 ⁻⁴ S cm ⁻¹)	Viscosity ^[a] (mPa s)	T_m (°C)
TSIL-1	1.17	2.80	700	—
TSIL-2	1.15	2.00	960	—
TSIL-3	1.12	1.40	1450	25
TSIL-4	1.10 ^[b]	1.70 ^[b]	—	48

[a] Measured at 40.0 °C. [b] Measured at 50.0 °C.

Thermal Properties

Melting points (T_m) measured by the capillary tube method are shown in Table 1. The fluid ionic liquids showed a strong tendency to form a supercooled state when they were cooled, especially $[C_4\text{mim}][\text{S}_2\text{O}_8]$ (TSIL-1), which remains fluid even on cooling to -20 °C. The melting point of an ionic liquid is governed by many factors, including Coulombic, van der Waals, and H-bonding interactions. The ionic liquids prepared here contain the same anion and cation cores; therefore, the only difference between them is the different alkyl chain length. The melting points of these TSILs become higher with the increased alkyl chain length on the imidazolium ring. This may be attributed to enhanced van der Waals interactions and is in agreement with previous reports.^[11] The thermal behavior of the ionic liquids was investigated by means of thermogravimetry/differential thermal analysis (TG/DTA) measurements. In the analysis of the samples, a prominent exothermal peak at 95 °C combined with a little weight loss (about 3%) was observed (Figure 1). This was attributed to the decomposition of the peroxydisulfate anion, resulting in the release of oxygen. Further degradation and obvious mass loss that occurred between 300 and 360 °C may be attributed to the

decomposition of the alkylimidazolium and sulfate ions. In general, for strong oxidants such as peroxydisulfate salts, a lower decomposition temperature means a higher reactivity. Thus, the lower decomposition temperatures of TSILs containing peroxydisulfate indicate that these task-specific ionic liquids may possess high reactivities.

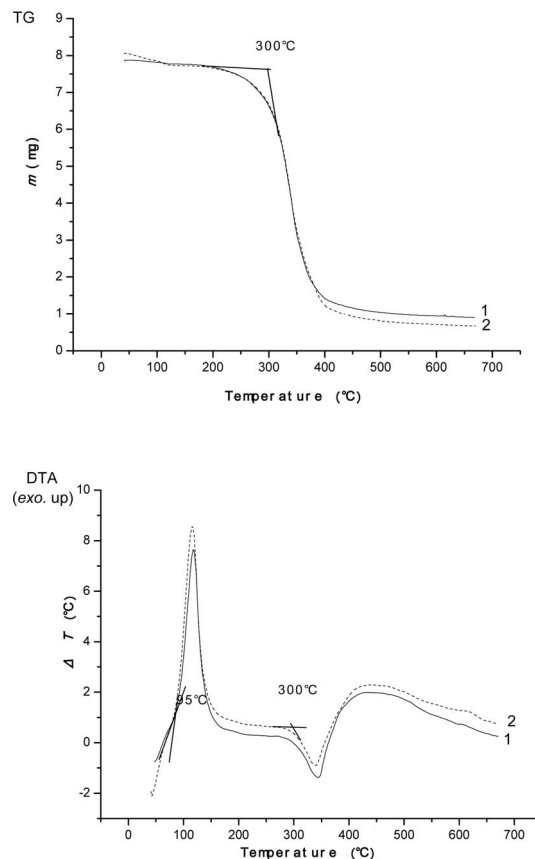


Figure 1. TG/DTA analysis for (1) $[C_6\text{mim}]_2[\text{S}_2\text{O}_8]$ (TSIL-2) and (2) $[C_8\text{mim}]_2[\text{S}_2\text{O}_8]$ (TSIL-3). ΔT is the difference between sample and reference temperatures.

Conductivity

Figure 2 shows the temperature dependence of the ionic conductivity (δ) of the TSILs. The ionic conductivity depends strongly on temperature and increases exponentially with the rise in temperature. This can be ascribed to fast ion transfer at high temperatures. The length of the alkyl chain on the cation also has an influence on the conductivities of the TSILs: as the length of the alkyl chain increases, the cation size increases, and the ionic transfer rate decreases, which results in a lower conductivity. Moreover, Arrhenius-type plots of δ show convex upward curves for TSIL-1 and TSIL-2 (Figure 2), whose ion-conducting behavior was analyzed with the Vogel–Tammann–Fulcher (VTF) equation [Equation (1)].^[12]

$$\delta = \delta_0 T^{-1/2} \exp[-B/(T - T_0)] \quad (1)$$

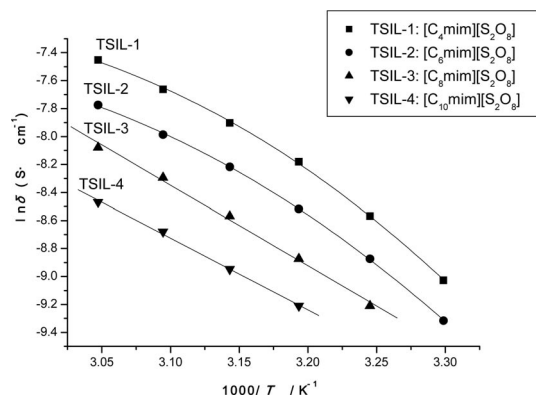


Figure 2. Temperature dependence of ionic conductivity (δ) for $[C_n\text{mim}]_2[\text{S}_2\text{O}_8]$ ($n = 4, 6, 8, 10$).

In Equation (1), δ_0 is a pre-exponential constant proportional to the number of carrier ions at infinitely high temperature, B is the pseudo-activation energy for ion conduction, and T_0 is the ideal glass transition temperature. Straight lines obtained from this analysis are depicted in Figure 3. These results illustrate that the temperature dependencies of the ionic conductivity for these TSILs do not obey the Arrhenius equation; however, they do obey the VTF equation. The migration of the carrier ions was dominated by a cooperative transport mechanism in the temperature range studied.^[13] For TSIL-3 and TSIL-4, the experimental data result in a straight line when plotted in Arrhenius coordinates as shown in Figure 2. This demonstrates that the temperature dependence of their ionic conductivities obeys the Arrhenius equation, which implies that migration of the carrier ions is dominated by an activated jump mechanism in the temperature range studied.^[13c,14]

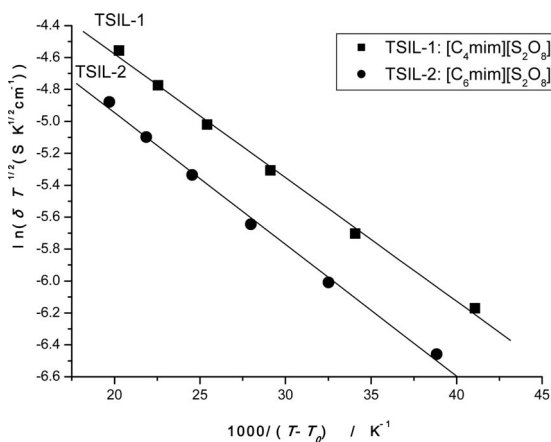


Figure 3. VTF plots of the ionic conductivity of TSIL-1 ($\delta_0 = 0.048 \text{ SK}^{1/2} \text{ cm}^{-1}$, $B = 77.6 \text{ K}$, $T_0 = 278.8 \text{ K}$) and TSIL-2 ($\delta_0 = 0.037 \text{ SK}^{1/2} \text{ cm}^{-1}$, $B = 77.6 \text{ K}$, $T_0 = 277.4 \text{ K}$).

Cyclic Voltammetry

The electrochemical behavior of the TSILs was investigated by cyclic voltammetry. Figure 4 shows the cyclic voltammogram of $[C_6\text{mim}]_2[\text{S}_2\text{O}_8]$ (TSIL-2) in an electrochem-

ical window of about 1.2 V at 25 °C. Such redox stability of the imidazolium cation and the oxidation potential of the peroxydisulfate anion. The reduction reaction involving the imidazolium cation begins at approximately -0.6 V . Although the standard oxidation potential of the peroxydisulfate ion is 2.01 V in aqueous solution, its reduction process on a Pt electrode begins at about 0.6 V in an ionic liquid and is an irreversible electrode reaction. Its narrow electrochemical window is related to its strong oxidizing ability. The electrochemical window of an ionic liquid is an important indicator of its ability to act as both the reactant and the medium in a solvent-free reaction system.

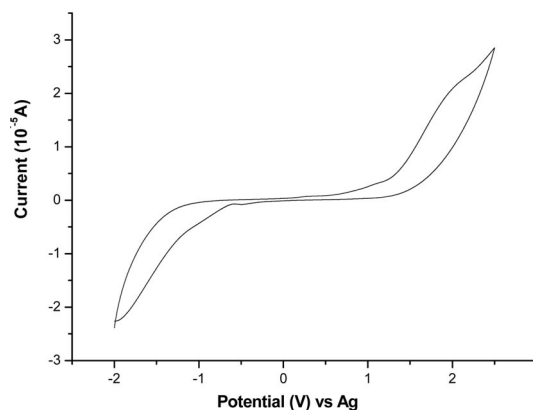


Figure 4. Cyclic voltammogram of $[C_6\text{mim}]_2[\text{S}_2\text{O}_8]$ at 25 °C; scan rate: 0.1 V s^{-1} .

Dynamic Viscosity

Figure 5 shows the temperature dependence of dynamic viscosity (η) for $[C_n\text{mim}]_2[\text{S}_2\text{O}_8]$ ($n = 4, 6, 8$) in the temperature range 298.15–333.15 K under atmospheric pressure. In general, the viscosity of an ionic liquid is strongly governed by Coulomb forces, van der Waals interactions, and hydrogen bonding.^[15] Compared with common ionic liquids, these TSILs have a high relative viscosity [700–1450 mPa s (25 °C), Figure 5]. A possible reason for this is the enhancement of Coulombic interactions between the ionic species as a result of the introduction of the divalent peroxydisulfate anion. The increase in alkyl chain length also makes the TSILs more viscous due to increased van der Waals interactions. This may be the reason why the viscosity of $[C_8\text{mim}]_2[\text{S}_2\text{O}_8]$ is higher than those of $[C_4\text{mim}]_2[\text{S}_2\text{O}_8]$ and $[C_6\text{mim}]_2[\text{S}_2\text{O}_8]$ (Figure 5) and comparable to that of $[C_2\text{mim}][\text{BF}_4]$.^[16] Deviations from the Arrhenius law are observed in the temperature range studied for TSIL-1 and TSIL-2 (Figure 6). Arrhenius-type plots of η show convex downward curves, which suggests that these data can be fitted by the empirical VFT equation [Equation (2)].^[12c]

$$\eta = \eta_0 T^{-1/2} \exp[B/(T - T_0)] \quad (2)$$

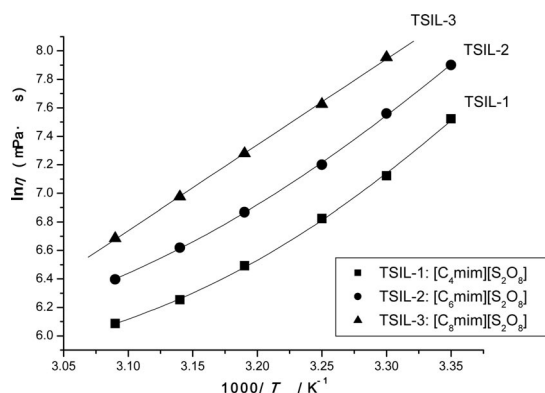


Figure 5. Temperature dependence of viscosity for $[C_n\text{mim}]_2[\text{S}_2\text{O}_8]$ ($n = 4, 6, 8$).

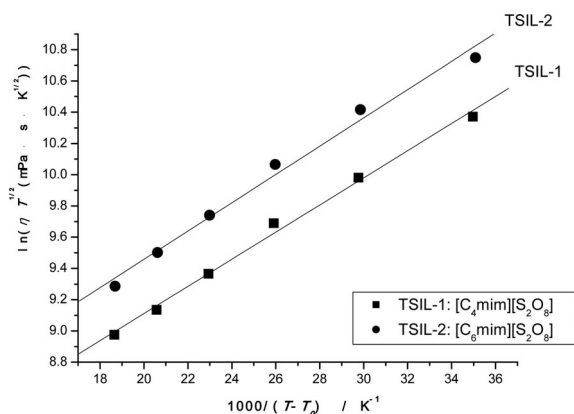


Figure 6. VTF plots of the viscosity of TSIL-1 ($\eta_0 = 1603 \text{ mPa s K}^{1/2}$, $B = 86.5 \text{ K}$, $T_0 = 269.4 \text{ K}$) and TSIL-2 ($\eta_0 = 2101 \text{ mPa s K}^{1/2}$, $B = 90.2 \text{ K}$, $T_0 = 269.5 \text{ K}$).

In Equation (2), η_0 (mPa s) is a pre-exponential constant proportional to the viscosity coefficient, B (K) is the pseudo-activation energy for viscous behavior, and T_0 (K) is the ideal glass transition temperature.

However, the temperature dependence of the viscosity of TSIL-3 shown in Figure 3 is in agreement with Equation (3).

$$\eta = \eta_0 \exp[E_\eta/RT] \quad (3)$$

In Equation (3), η_0 is a constant, T is the absolute temperature, and E_η is the energy of activation of viscous flow. The data for TSIL-3 (Figure 5) fit Equation (3) well ($r = 0.996$) and yield a value for E_η of 46.2 kJ mol^{-1} . This is larger than that of conventional molecular liquids but comparable to those of other room-temperature ionic liquids.^[17] It should be noted here that the sequence of viscosity in this series of TSILs has close similarity with that of T_m (see Table 1) and may be governed by the van der Waals force and the electrostatic interaction force.

Solubility

Ionic liquids have attracted considerable attention for their wide application in organic synthesis, catalysis, and

materials preparation.^[18] Most of these applications correlate closely with the solubility of ionic liquids in solvents or the solubility of solutes in ionic liquids. In the present study, the solubility of the ionic liquids in water and common organic solvents was investigated. The water solubility of the ionic liquids was strongly dependent on the length of the alkyl chain on the cation and followed the order $[\text{C}_4\text{mim}] > [\text{C}_6\text{mim}] > [\text{C}_8\text{mim}] > [\text{C}_{10}\text{mim}]$, which is similar to that of $[\text{C}_n\text{mim}][\text{BF}_4]$ ionic liquids.^[12] On the contrary, the solubility in trichloromethane followed the order $[\text{C}_{10}\text{mim}] > [\text{C}_8\text{mim}] > [\text{C}_6\text{mim}] > [\text{C}_4\text{mim}]$. All the ionic liquids studied here were immiscible with nonpolar solvents such as toluene, benzene, ethyl ether, and hexane, and were completely miscible with polar solvents such as acetone, acetonitrile, and ethanol due to their high polarity (see Table 2). The solubility of other substances in these ionic liquids was also investigated, and phenol and amines (triethylamine, aniline, etc) were found to be soluble. This solvent property could make these ionic liquids an ideal new medium for chemical reactions.

Table 2. Miscibility of new ionic liquids in some common solvents at room temperature (M: miscible, I: immiscible).

Ionic liquids	H ₂ O	EtOH	Acetone	CH ₃ CN	CHCl ₃	Et ₂ O	Toluene
TSIL-1	M	M	M	M	I	I	I
TSIL-2	M	M	M	M	I	I	I
TSIL-3	M	M	M	M	M	I	I
TSIL-4	I	M	M	M	M	I	I

Oxidation Reactions

The selective oxidation of cysteine to cystine is a fundamentally important laboratory and commercial procedure and is conventionally carried out with stoichiometric amounts of metallic complex ions such as $[\text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2]^+$,^[19] $[\text{IrIVCl}_6]^{2-}$,^[20] $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$,^[21] $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$,^[22] and $[\text{Co}_2(\text{CN})_{10}(\text{O})_2]^{5-}$ ^[23] in volatile organic solvents. From both an economic and environmental point of view, developing a green process for converting cysteine to cystine on an industrial scale has been an important objective for chemists. In order to search for an appropriate oxidant and medium for the development of a cost-effective and environmentally benign synthesis, the ability of the ionic liquids prepared to act as both reactive oxidant and medium was scrutinized in the oxidation reaction of thiols. The experimental results are shown in Table 3. The reactive system comprises the ionic liquid and cysteine or 1-pentanethiol as the substrate. The reaction takes place in the homogeneous phase and has the advantages of being a solvent- and catalyst-free system. The product of the reaction with cysteine was isolated in 92% yield with 100% selectivity under moderate reaction conditions (see footnotes in Table 3). At the end of the reaction, the ionic liquid was easily recovered by extraction. Its regeneration was realized by the electrolytic method,^[24] because the hydrogen ion has a higher reduction potential on the Pt electrode and the imidazolium ring is inactive to oxidation at the anode.

Furthermore, by using this reactive system, benzyl alcohol was converted to benzyl aldehyde in 96% yield and 100% selectivity at room temperature after 1 h (Table 3). Secondary alcohols were oxidized to ketones with a lower yield, whereas aliphatic primary alcohols (such as *n*-hexyl and *n*-heptyl alcohol) were not oxidized to the corresponding aldehydes under the same conditions (Table 3). Unlike conventional methods, this solvent- and catalyst-free reaction system has many advantages including reduced pollution, lower costs, and simplicity in process and handling. These factors are especially important in industry.

Table 3. Oxidation of substrates by ionic liquids.^[a]

Entry	Substrate	Product	Ionic liquid	Selectivity (%)	Yield ^[b] (%)
1	PhCH ₂ OH	PhCHO	TSIL-1	94%	94%
2	PhCH ₂ OH	PhCHO	TSIL-2	95%	95%
3	PhCH ₂ OH	PhCHO	TSIL-3	96%	96%
4	<i>n</i> -C ₅ H ₁₁ CH ₂ OH	<i>n</i> -C ₅ H ₁₁ CHO	TSIL-3	<1%	<1%
5	<i>n</i> -C ₆ H ₁₃ CH ₂ OH	<i>n</i> -C ₆ H ₁₃ CHO	TSIL-3	<1%	<1%
6	2-propanol	acetone	TSIL-3	15%	15%
7	cyclohexanol	cyclohexanone	TSIL-3	40%	40%
8	1-pentanethiol	dipentyl disulfide	TSIL-3	85%	85%
9 ^[c]	cysteine	cystine	TSIL-3	100%	92% ^[d]

[a] Molar ratio of substrate to ionic liquid = 1:2; reaction time = 1 h; temperature = 80 °C. [b] Yields determined by GC based on the substrate. [c] Room temperature. [d] Isolated yield.

Conclusions

Four oxidizing ionic liquids based on peroxydisulfate anions were synthesized and characterized. These ionic liquids have the desired oxidizing properties for given oxidation reactions of alcohols and thiols and perform exceptionally well as both oxidant and medium in a solvent- and catalyst-free reaction system. They make the oxidation processes more environmentally benign and cost-effective. This research work will enrich the knowledge of ionic liquid chemistry and extend the range of applications of ionic liquids.

Experimental Section

Chemicals and Analysis: 1-Chlorodecane, 1-chlorooctane, 1-chlorohexane, and 1-chlorobutane (Shanghai Reagent Co. China) were distilled before use. 1-Methylimidazole was vacuum-distilled prior to use. Reagent grade ethyl acetate, acetone, dichloromethane, acetonitrile, absolute ethanol, alcohols, and K₂S₂O₈ were obtained from Sinopharm Chemical Reagent Co. Ltd. China and used without further purification. ¹H NMR spectra were recorded with a Bruker DRX-500 spectrometer in CDCl₃ or D₂O relative to a TMS internal standard. IR spectra were recorded as liquids or as solid KBr disks with a NEXUS 670 FTIR infrared spectrometer (Nicolet). Elemental analysis was performed with a Vario EL III elemental instrument. The thermal stability of the ionic liquids was investigated with a TG/DTA851 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ with nitrogen as the purge gas. Conductivity was measured with a DDS-11 conductivity meter. Electrochemical stability was analyzed by cyclic voltammetry, in which a

Pt working electrode was used with Ag as quasi-reference electrode and platinum as the counter electrode. Dynamic viscosities of these ionic liquids were measured with a NDJ-79 rotating viscometer. GC-MS analysis was completed with a CP-3900 GC/Saturn 2100 MS system. The product yields were determined with a GC-14C instrument. The conditions for the GC run are listed in Table 4. Melting points were measured with a SGW X4 microscopic melting point instrument. The content of chlorine ion was determined by an ICS-5200 Ion Chromatography System (Dionex IonPac AS11-HC, 2 × 250 mm). Constant potential electrolysis of the spent ionic liquids was performed with a CHI760 electrochemistry workstation equipped with Pt as cathode and anode. The cell was put in a water bath to avoid overheating during the electrolysis.

Table 4. The conditions and retention times for the GC runs.

Samples	Column	Column temp. (°C)	Detector temp. (°C)	Retention time (min)
PhCH ₂ OH	RTX-1	120	250	4.05
PhCHO				3.64
<i>n</i> -C ₅ H ₁₁ CH ₂ OH	DB-WAX	120	250	6.18
<i>n</i> -C ₅ H ₁₁ CHO				4.64
<i>n</i> -C ₆ H ₁₃ CH ₂ OH	DB-WAX	120	250	8.55
<i>n</i> -C ₆ H ₁₃ CHO				6.49
Isopropyl alcohol	DB-WAX	50	250	4.73
Acetone				3.32
Cyclohexanol	DB-WAX	120	250	7.34
Cyclohexanone				5.80
1-Pentanethiol	RTX-1	120–300 ^[a]	320	3.44
Dipentyl disulfide				9.76

[a] Programmed temperature.

Synthesis

1-Alkyl-3-methylimidazolium chloride compounds ([C_{*n*}mim][Cl], *n* = 4, 6, 8, 10) were prepared by an adaptation of a reported procedure^[25] and were characterized by ¹H NMR and IR spectroscopy. 1-Alkyl-3-methylimidazolium peroxydisulfate ([C_{*n*}mim]₂[S₂O₈]) compounds were synthesized by the metathesis reaction of the appropriate 1-alkyl-3-methylimidazolium chloride with potassium peroxydisulfate in acetone solution or water (Scheme 1).

[C₄mim]₂[S₂O₈] (TSIL-1): This compound was prepared by the reaction of [C₄mim][Cl] (0.1 mol, 17.5 g) with K₂S₂O₈ (0.055 mol, 14.8 g) in acetone (150 mL). The solution was stirred for 24 h at room temperature and then filtered. The solvent was removed under reduced pressure at room temperature. The product was further dried under high vacuum for 24 h. The product was obtained as a light-yellow liquid in 82% yield. The same method was used to prepare [C₆mim]₂[S₂O₈] (TSIL-2; yield: 88%) and [C₈mim]₂[S₂O₈] (TSIL-3; yield: 88%).

[C₁₀mim]₂[S₂O₈] (TSIL-4): This ionic liquid was prepared by the reaction of a solution of K₂S₂O₈ (0.055 mol, 14.8 g) in water (150 mL), which was added dropwise to a rapidly stirring solution of 1-decyl-3-methylimidazolium chloride (0.1 mol, 25.8 g) in water (100 mL) at 0 °C over 30 min. The reaction mixture separated into two phases; the lower phase was collected, washed with water (2 × 100 mL), and dried under high vacuum at room temperature for 24 h. After drying, [C₁₀mim]₂[S₂O₈] was obtained as a white solid in 80% yield (25.5 g).

TSIL-1: C₁₆H₃₀N₄O₈S₂ (470.57); calcd. C 40.9, H 6.4, N 11.9, S 13.6; found C 41.2, H 6.1, N 12.0, S 12.8. IR: $\tilde{\nu}$ = 3150, 3098, 2930, 2859, 1659, 1612, 1384, 1285, 1167, 1135, 1066, 1002, 728, 622,

591, 561 cm^{-1} . ^1H NMR (500 MHz, D_2O , 25 $^\circ\text{C}$): δ = 0.80 [t, $^3J_{\text{H,H}}$ = 7.5 Hz, 3 H], 1.20 (q, $^3J_{\text{H,H}}$ = 7.5 Hz, 2 H), 1.73 (m, $^3J_{\text{H,H}}$ = 7.5 Hz, 2 H), 3.77 (s, 3 H), 4.08 (t, $^3J_{\text{H,H}}$ = 7.5 Hz, 2 H), 7.30 (s, 1 H), 7.35 (s, 1 H), 8.58 (s, 1 H) ppm.

TSIL-2: $\text{C}_{20}\text{H}_{38}\text{N}_4\text{O}_8\text{S}_2$ (526.67): calcd. C 45.6, H 7.2, N 10.6, S 12.2; found C 46.2, H 6.7, N 11.0, S 12.3, IR: $\tilde{\nu}$ = 3150, 3095, 2925, 2855, 1636, 1573, 1384, 1283, 1170, 1064, 723, 620, 591, 561 cm^{-1} . ^1H NMR (500 MHz, D_2O , 25 $^\circ\text{C}$): δ = 0.76 (t, $^3J_{\text{H,H}}$ = 6.5 Hz, 3 H), 1.20 (m, 6 H), 1.78 (m, $^3J_{\text{H,H}}$ = 6.5 Hz, 2 H), 3.80 (s, 3 H), 4.10 (t, $^3J_{\text{H,H}}$ = 7 Hz, 2 H), 7.33 (s, 1 H), 7.38 (s, 1 H), 8.60 (s, 1 H) ppm.

TSIL-3: $\text{C}_{24}\text{H}_{46}\text{N}_4\text{O}_8\text{S}_2$ (582.78): calcd. C 49.5, H 7.9, N 9.6, S 11.0; found C 49.2, H 7.7, N 9.4, S 10.8, IR: $\tilde{\nu}$ = 3146, 3090, 2926, 2855, 1636, 1575, 1466, 1298, 1169, 1062, 704, 621, 592, 562 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 0.87 (t, $^3J_{\text{H,H}}$ = 8 Hz, 3 H), 1.24–1.29 (m, 10 H), 1.85 (t, $^3J_{\text{H,H}}$ = 7 Hz, 2 H), 4.02 (s, 3 H), 4.26 (t, $^3J_{\text{H,H}}$ = 7.5 Hz, 2 H), 7.20 (s, 1 H), 7.28 (s, 1 H), 9.34 (s, 1 H) ppm.

TSIL-4: $\text{C}_{28}\text{H}_{54}\text{N}_4\text{O}_8\text{S}_2$ (638.89): calcd. C 52.6, H 8.5, N 8.8, S 10.0; found C 51.7, H 7.9, N 9.1, S 9.5, IR: $\tilde{\nu}$ = 3147, 3091, 2926, 2855, 1572, 1467, 1295, 1169, 1117, 1063, 704, 622, 592, 562 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 0.87 (t, $^3J_{\text{H,H}}$ = 7 Hz, 3 H), 1.24–1.28 (m, 14 H), 1.84 (t, $^3J_{\text{H,H}}$ = 7 Hz, 2 H), 3.99 (s, 3 H), 4.24 (t, $^3J_{\text{H,H}}$ = 7 Hz, 2 H), 7.26 (s, 1 H), 7.36 (s, 1 H), 9.25 (s, 1 H) ppm.

IR and ^1H NMR Spectra: The infrared spectra of all the TSILs prepared are similar. A typical IR spectrum for a TSIL is shown in Figure 7. The characteristic bands of the imidazolium cation^[26] and peroxydisulfate anion are clearly observed. In the FTIR spectra of TSIL-4, the bands at 1295, 1063, and 704 cm^{-1} were ascribed to the characteristic bands of the $[\text{S}_2\text{O}_8]$ anion. The bands at 3147 and 3091 cm^{-1} were attributed to a C–H stretching vibration of the imidazolium ring, whereas C–H stretching bands of the alkyl chain on the imidazolium ring were observed at 2926 and 2855 cm^{-1} . This characteristic spectrum is similar to those of other ionic liquids containing an imidazolium ring.^[27] The absorption band in the 3500–3800 cm^{-1} region of the infrared spectra shows the presence

of adsorbed water in samples. It indicates that storage in vacuo was required to obtain the ionic liquid containing little or no water. The ^1H NMR spectrum of TSIL-3 (Figure 8) revealed nine very strong, well-resolved resonance lines. The resonances with the chemical shifts δ = 7.26, 7.36, and 9.25 ppm were attributed to the protons in the imidazolium ring. The singlet at δ = 4.24 ppm corresponds to the protons of the methyl group on the imidazolium nitrogen atoms (NCH_3). The chemical shifts of protons of the octyl group on the imidazolium ring were δ = 0.86 (3 H), 1.24–1.28 (m, 10 H), and 1.84 ppm (t, 2 H), similar to the ^1H NMR spectrum of 1-octyl-3-methylimidazolium tetrafluoroborate.^[27]

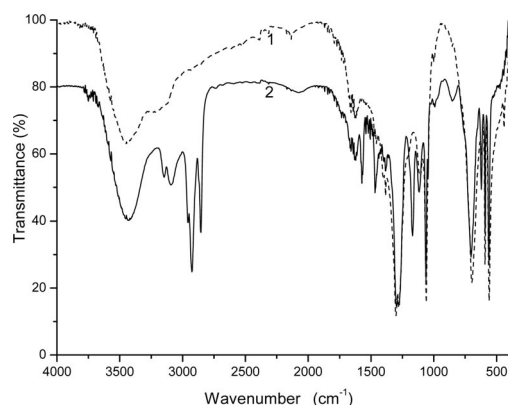


Figure 7. FTIR spectra of (1) $\text{K}_2\text{S}_2\text{O}_8$ and (2) $[\text{C}_{10}\text{mim}]_2[\text{S}_2\text{O}_8]$.

Oxidation of Benzyl Alcohol and Cysteine

Benzyl alcohol (5 mmol, 0.54 g) and $[\text{C}_8\text{mim}]_2[\text{S}_2\text{O}_8]$ (10 mmol, 5.82 g) were combined in a 50 mL three-necked flask equipped with a reflux condenser and a magnetic stirrer. The solution was heated under reflux for 1 h at 80 $^\circ\text{C}$. The reaction mixture was cooled to room temperature, and the product was extracted into diethyl ether (3×10 mL). The yield of the reaction was measured by GC without further purification. All products were identified by GC–MS by comparison with the retention time of authentic samples.

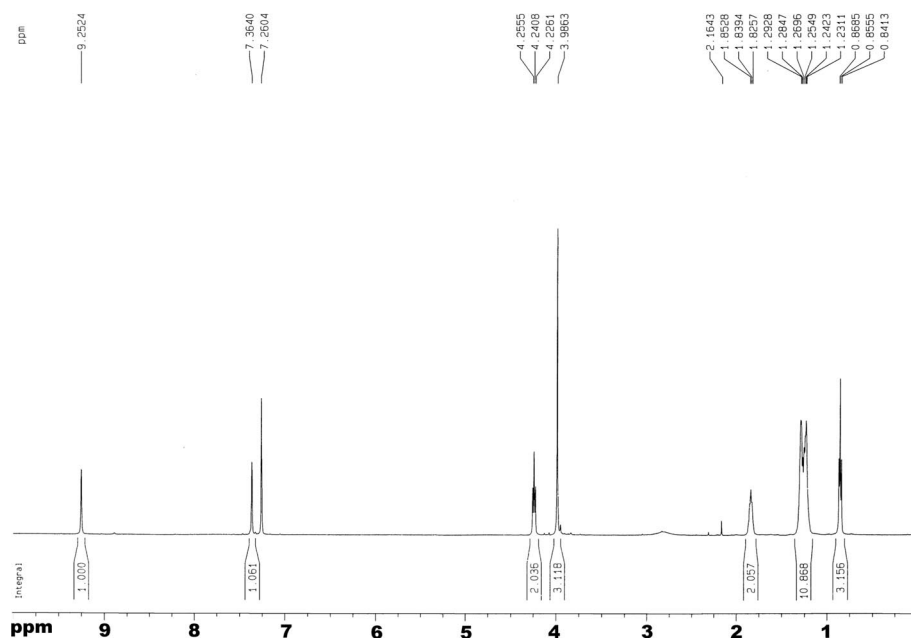


Figure 8. ^1H NMR spectrum of $[\text{C}_8\text{mim}]_2[\text{S}_2\text{O}_8]$.

Cysteine (1 mmol, 0.121 g) was added to $[\text{C}_8\text{mim}]_2[\text{S}_2\text{O}_8]$ (2 mmol, 1.16 g) and stirred at room temperature for 1 h. Sodium hydrogen carbonate solution (0.1 mol L^{-1}) was added to neutralize the reaction mixture. The precipitate was filtered, washed with water, and recrystallized from water.

After the separation of the products, the used TSIL (about 1 mL) was regenerated by electrolysis by maintaining a potential of 4.0 V at 40 °C for 24 h in an electrolytic cell.

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