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Oxidation of Cyclooctene to Suberic Acid Using Perrhenate-Containing Composite Ionic Liquids as Green Catalysts[1]

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Abstract—A series of quaternary ammonium perrhenate/3-hexyl-1-methyl-imidazolium hydrogen sulfate ([Hmim]HSO_4) composite ionic liquids has been prepared. For the first time, the composite ionic liquids are used both as catalyst and solvent in oxidation of cyclooctene to suberic acid in the presence of hydrogen peroxide as a green oxidant. It was found that organic perrhenate salts play the important role in improving the selectivity of cyclooctene oxidation to suberic acid. The yield of suberic acid under the mild conditions is from good to high.

Keywords: oxidation, suberic acid, organic perrhenate, composite ionic liquid

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INTRODUCTION

Dicarboxylic acids are the important key raw materials, widely used in the preparation of nylon, lubricants, electrolyte, cosmetics, polyamides, adhesives, greases, polyesters, and many other fine chemicals [1, 2]. Among them, adipic acid has found the most wide industrial application as precursor for nylon-6,6 production [3, 4]. To important succinic, suberic, azelaic, dodecanedioic and other acids belong to dicaboxylic acids. The above dicarboxylic acids, for example adipic and suberic acids, can be produced by the oxidation of castor oil, cyclic diols, or ketones in the presence of nitric acid as oxidant [5, 6]. Some other long-chain dicarboxylic acids, such as dodecanedioic acid, can be prepared by the alkali fission or fermentation of long-chain alkanes [7, 8]. However, nitric acid oxidation includes air pollution and corrosive processes [9–11]. Due to the environ-mental restrictions, replacement of conventional methods is desirable. An alternative method would be the replacement of nitric acid for aqueous hydrogen peroxide, which gives only water as byproduct [12, 13] and, therefore is a comparatively "green" method. For preparing adipic acid under mild conditions, various "green" catalytic methods using cyclohexene as substrate and aqueous hydrogen peroxide as oxidant have been reported. WO_3 [14, 15], H_2WO_4 [16, 17], $Na_2WO_4{\cdot}2H_2O$ [18, 19], organic peroxytungstates [20, 21], and other compounds [22] are widely used efficient catalysts. Small amount of $Na_2WO_4{\cdot}2H_2O$, as metal salt catalyst, $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, as phase-transfer catalyst, and 30% hydrogen peroxide, as oxidant, are applied in oxidation of cyclohexene to acidic acid in the Noyori's et al. method [18, 19]. Further, Deng et al. have developed similar method for direct oxidation of cyclohexene with 30% aqueous hydrogen peroxide, in which organic peroxotungstate with the anion structure of $[W(O)(O_2)_2L_2]^{2-}$ served as green catalyst, with the yield by adipic acid under mild conditions also comparable [20, 21].

Li et al. [23] have shown that in oxidation of cyclohexenes in the presence of quaternary ammonium salts as co-catalysts, the highest catalytic activity among three polyoxometalates (POMs), $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, has $H_3PW_{12}O_{40}$. Compared to well-known catalytic methods of cyclohexene oxidation, the oxidation of cyclooctene, which is also an important industrial raw material, is studied little. Although the Novori's method is efficient for cyclohexene, in the case of cyclooctene it provides only 9% yield by suberic acid.

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[1] The text was submitted by the authors in English.

It is known that many high-oxidation state transition metal complexes show good catalytic activity in oxidation reactions. In particular, a versatile organorhenium compound, methyltrioxorhenium (MTO), which was first synthesized by Beattie and Jones in 1979 [24] and was first used as oxidation catalyst in 1991 [25], has received considerable attention during the past decades [26–30]. However, such homogeneous catalysts are expensive and must be recycled. Unfortunately, immobilization of MTO onto heterogeneous carriers is difficult and a significant amount of the catalyst is commonly lost upon leaching [31].

An alternative method is the immobilization of MTO and related compounds in ionic liquids (ILs) [32]. Due to negligible volatility, excellent thermal stability, marked solubility, and a variety of the available structures, ILs have received great attention as environmentally benign solvents to replace volatile organic solvents in a wide variety of chemical reactions, and in separation and manufacturing processes [33–36]. ILs are already used in industrial catalytic processes [37], in BASF-BASIL process in particular [38]. However, the decomposition of MTO to perrhenates may occur in the ionic liquid-mediated catalytic reactions. For decades, perrhenates have been considered as notorious "dead end" compounds for most catalytic processes. However, it was surprising to find that many perrhenate-based ionic liquids can activate olefin epoxidation reactions, ensuring from good to excellent yield by epoxide for a variety of olefin substrates. More important, the perrhenate-based ionic liquids can be repeatedly recycled and reused without significant loss of activity, which provides an easy-handle and solvent-free oxidation method [39]. The above results have stimulated us to perform a further study on the catalytic behavior of the perrhenate-based ionic liquids. Recently, a series of quaternary ammonium perrhenate ionic liquids was synthesized in our group and then combined with Hmim[HSO_4], which was used both as efficient catalyst and a solvent in cyclooctene oxidation.

Herein, we report our original study on a green oxidation of cyclooctene to suberic acid in the presence of perrhenate-containing composite ionic liquids as catalysts and a 30% aqueous hydrogen peroxide as oxidant.

RESULTS AND DISCUSSION

Synthesis and properties. The quaternary ammonium perrhenate salts bearing alkyl chains of different lengths were prepared in our studies, according to the published procedures [40–42]. The structures are shown in Scheme 1.

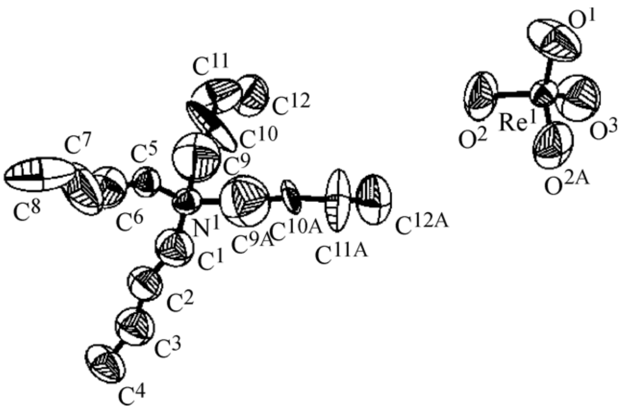
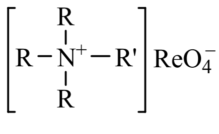


Fig. 1. ORTEP view of $[(n\text{-}C_4H_9)_4N]ReO_4$ (**4**) showing vibrational ellipsoids at the 50% probability level. H atoms are omitted for clarity.

The synthesized perrhenate salts were characterized by the FT-IR, ^{1}H NMR, and elemental analyses (see Experimental). The melting point was determined with a micromelting point apparatus and the decomposition temperature, by the thermogravimetric analysis (TGA). These organic salts are not conventional ionic liquids, since they are solids below 100°C. However, these salts can be completely dissolved in [Hmim]HSO_4 to form colorless or yellow composite ionic liquids, which were used both as catalyst and a solvent in cyclooctene oxidation. The TGA data indicate that compounds **1–5** have good thermal stability and start to decompose between 220–300°C. The compounds' spectra have strong bands due to the Re–O bond vibrations between 890–920 cm^{-1}, which are typical of ReO_4 [43].

The solid-state single crystal structure of the compound **4** is shown in Fig. 1. The structure is somewhat disordered with respect to the carbon atoms on the butyl groups, which sets the limit for the determination of bond lengths and bond angles.

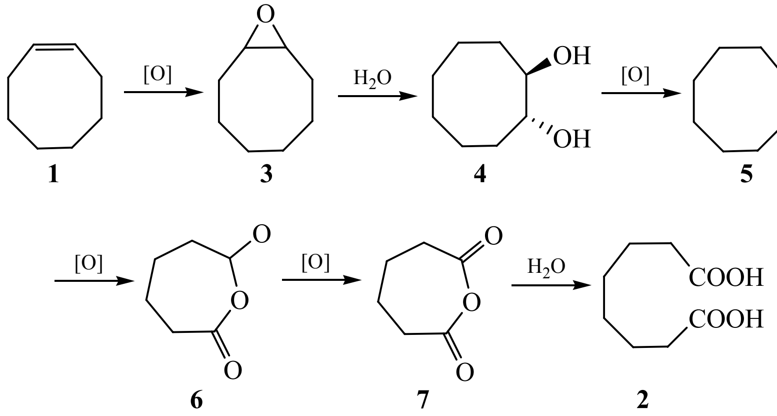
Scheme 1. Structures of quaternary ammonium perrhenate salts.



$$\left[\begin{array}{c} R \\ | \\ R-N^{+}-R' \\ | \\ R \end{array}\right] ReO_4^-$$

1: R, R' = CH_3, **2**: R, R' = C_2H_5, **3**: R = C_2H_5, R' = n-C_4H_9, **4**: R, R' = n-C_4H_9, **5**: R = CH_3, R' = n-C_4H_9.

Scheme 2. Pathway of the oxidation of cyclooctene to suberic acid.



Oxidation of cyclooctene. According to our previous study [39], the H_2O_2 molecules can be activated by organic perrhenate salts through hydrogen bonding between ReO_4^- and H_2O_2, thus enabling epoxidation of a variety of olefins with the forming active species under mild conditions. According to the literature data [18, 19], the oxidation of cyclooctene to suberic acid includes several processes, such as formation of epoxide, its hydrolysis to diol, oxidation of diol to cyclic α-hydroxy ketone, the Baeyer–Villiger oxidation of α-hydroxy ketone to α-hydroxy lactones, and formation of suberic acid by hydrolysis (Scheme 2).

According to [39], the imidazolium-based perrhenates assist cyclooctene epoxidation, providing an almost 100% selectivity towards the formation of epoxides. Therefore, it can be concluded that catalytic oxidation of cyclooctene to suberic acid will proceed under more violent conditions.

Moreover, the existence of a phase-transfer catalyst is also crucial for H_2O_2 oxidation reactions to provide transfer of the forming active species or the reactants between the inorganic and organic phases. In our study, the acidic ionic liquid ([Hmim]HSO_4) was combined with compounds **1–5** into the composite ionic liquids, which were used both as solvent and catalyst for the oxidation of *cis*-cyclooctene to suberic acid in the presence of a 30% aqueous hydrogen peroxide as oxidant.

Details concerning the catalytic reaction are given in the Experimental. No cyclooctene conversion was observed in blank reactions proceeding in the presence

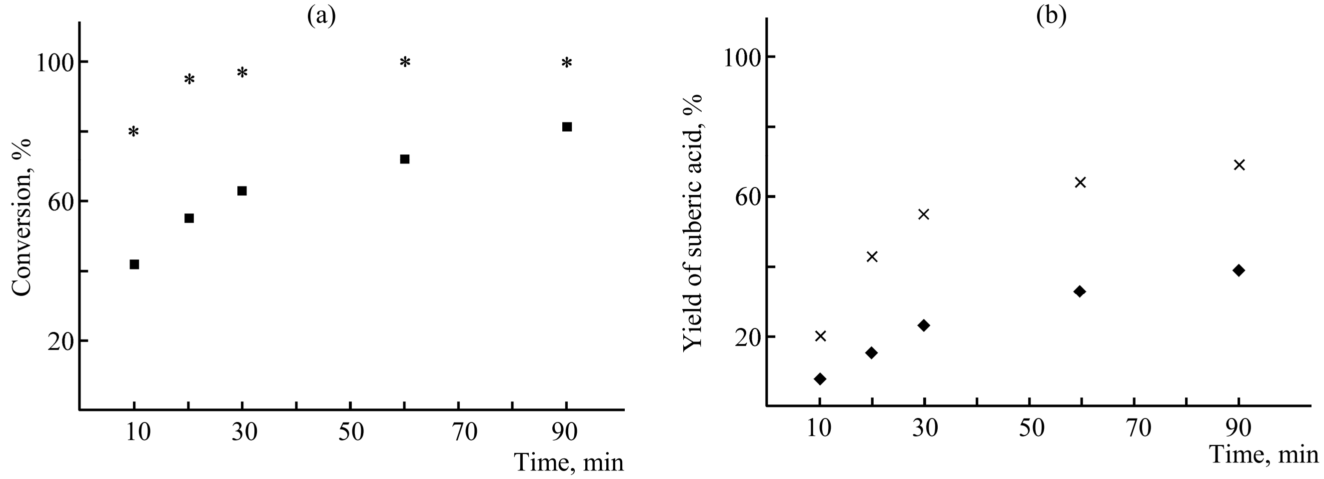


Fig. 2. (a) Conversion vs. time and (b) yield of suberic acid vs. time curves for cyclooctene oxidation at 60°C: (■, ♦) without **1** and (*, ×) with 5 mol % of **1**. Reactants: *cis*-cyclooctene (1 mmol, 0.11g), H_2O_2 (5 mmol, 0.5 mL), and [Hmim]HSO_4 (1 mL).

Table 1. Optimization of the reaction conditions[a]

Run no.	Amount of composite ionic liquid		Temperature, °C	Conversion[c], %	Yield[d,e], %
	1, mol %[b]	[Hmim]HSO$_4$, mL			
1	0	1.0	60	81	38 (31)
2	1	1.0	60	92	47 (36)
3	3	1.0	60	98	69 (10)
4	5	1.0	60	100	69 (10)
5	5	0.1	60	33	3 (25)
6	5	0.3	60	73	17 (50)
7	5	0.5	60	79	20 (45)
8	5	0.8	60	100	54 (25)
9	8	1.0	60	100	70 (10)
10	5	1.0	25	65	0 (60)
11	5	1.0	40	87	5 (58)
12	5	1.0	50	95	43 (41)
13	5	1.0	70	100	71 (10)
14	5	1.0	80	100	75 (15)
15	5	1.0	100	100	70 (15)

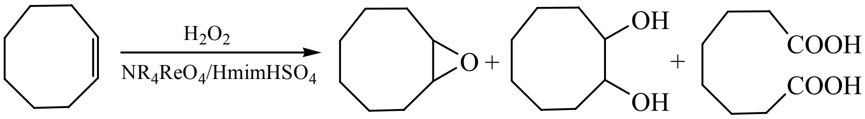
[a] The reactions were carried out using cis-cyclooctene (1 mmol, 0.11 g) and H_2O_2 (5 mmol, 0.5 mL) for 6 h. [b] Compound **1** was applied according to the molar percentage of cyclooctene. [c] The conversion and yield were calculated based on GC analysis. [d] Yield of cyclooctene epoxide is given in the brackets. [e] <5% of 1,2-cyclooctanediol and small amount of other unidentified byproducts can be detected.

of excess amount of H_2O_2 and 1 mL of dichlorometane as solvent and in the absence of the catalyst at 60°C. When 1 mL of [Hmim]HSO$_4$ is introduced into the system as the catalyst and solvent (Fig. 2a), the conversion reaches ca. 81% after 4 h of reaction. However, the reaction product is a complicated mixture, with the suberic acid yield only 38% (Fig. 2b). To our delight, the reaction can be accelerated in the presence of the compound **1** containing [Hmim]HSO$_4$ composite ionic liquid as catalyst and solvent, and the selectivity of suberic acid can be also significantly improved (Fig. 2b), i.e., organic perrhenates are suitable to promote cyclooctene oxidation. In the subsequent optimization of the reaction, we used the compound **1** containing the composite ionic liquid as the catalyst and solvent, and 30% aqueous hydrogen peroxide as the oxidant.

The data on the influence of reaction temperature, composition of the ionic liquid, and amount of the composite ionic liquid are given in Table 1.

Theoretically, 4 equiv. of H_2O_2 is necessary to transfer the cyclooctene to suberic acid. In order to completely convert the substrate, 5 equiv. of the oxidant was applied in our experiments. All the reactions give cyclooctene epoxide and suberic acids as major products. Moreover, a small amount of 1,2-cyclooctanediol, product of epoxide hydrolysis and other non-identified products were also detected. In general, the conversion of cyclooctene is significantly affected by the amount of [Hmim]HSO$_4$. The conversion in the presence of 0.8 mL [Hmim]HSO$_4$ at 60°C is 100% (Table 1). The yield by suberic acid increases with the increase of the amount of perrhenate. Moreover, the temperature is also the crucial parameter to control the composition of the products. At lower temperature of the reaction, epoxide is major product (Table 1, nos. 10, 11). The yield by suberic acid rapidly increases with increasing temperature. The highest yield (75%) is obtained in the presence of 5 mol % of perrhenate and 1 mL of [Hmim]HSO$_4$ at 80°C. However, with temperature

Table 2. Cyclooctene oxidation in the presence of different composite ionic liquids[a]



Run no.	Organic perrhenates	Conversion[b], %	Yield[b,c], %		
			epoxide	diol	suberic acid
1	–	81	31	11	38
2	$[(CH_3)_4N]ReO_4$ (**1**)	100	10	3	75
3	$[(C_2H_5)_4N]ReO_4$ (**2**)	100	8	3	72
4	$[(C_4H_9)(C_2H_5)_3N]ReO_4$ (**3**)	100	15	3	58
5	$[(n\text{-}C_4H_9)_4N]ReO_4$ (**4**)	100	4	3	81
6	$[(C_{16}H_{31})(CH_3)_3N]ReO_4$ (**5**)	100	20	4	57

[a] The reactions were carried out using *cis*-cyclooctene (1 mmol, 0.11 g), H_2O_2 (5 mmol, 0.5 mL), Compounds **1**–**5**: (0.05 mol), [Hmim]HSO_4 (1 mL) at at 80°C. [b] Conversion and yield were calculated based on GC analysis. [c] <5% of 1,2-cyclooctanediol and small amount of other un-identified byproducts can be determined.

increased further to 100°C, the yield is decreased, which may be due to the decomposition of the oxidant at the evaporation temperature.

Based on the above studies, we performed the cyclooctene oxidation with different perrhenate-containing ionic liquids in order to compare the catalytic performance of the perrhenate salts. The results are summarized in Table 2. It was found that compounds **1, 2**, and **4** with the symmetric cationic structure have higher selectivity towards suberic acid and better solubility in the ionic liquid [Hmim]HSO_4 than compounds 3 and 5. Dissolution of compounds **3** and **5** in [Hmim]HSO_4 yields a composite ionic liquid solution of a comparatively high viscosity, which might be responsible for the low catalytic activity in cyclooctene oxidation.

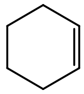
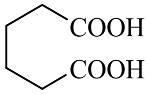
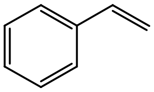
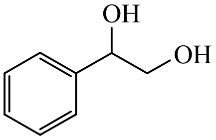
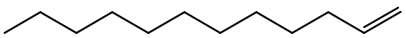
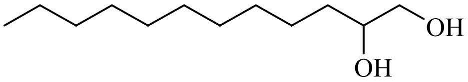
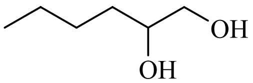
The recycling and reusability of composite ionic liquids were also studied. After completing the reactions, the products were extracted by ethyl acetate and the residual composite ionic liquids were further purified by extraction with *n*-hexane, dried under vacuum below 80°C for 2 h, and used directly as the catalyst and solvent for the next catalytic run. However, the recycled ionic liquid became dark and somewhat more viscous, as compared to the first run, and its activity was also decreased, which may due to the paritial decomposition of [Hmim]HSO_4 during the catalytic reactions. In the case of the compound **1** containing a composite ionic liquid as the catalyst, the yield by suberic acid is decreased from 75 to 53% after recycling.

Oxidation of other olefins. The catalytic system was also applied for other olefins, including cyclohexene, styrene, 1-hexene, and 1-dodecene1-Dodecene in order to further evaluate the catalytic performance of the composite ionic liquids. The results indicate that the catalytic system is also applicable for the oxidation of cyclohexene, with a 88% yield by adipic acid achieved in the presence of compound **1** containing a composite ionic liquid. At the same time, in the case of styrene, 1-hexene, and 1-dodecene, all reactions yield diols as major products (Table 3).

EXPERIMENTAL

General Remarks. All chemicals and solvents were purchased from Sinopharm Chemical Reagent Co. or Acros and used as received. Microanalyses of the obtained products were performed with a Flash EA 1112 series elemental analyzer. ^1H NMR spectra were recorded on a 500-MHz Bruker Avance DPX-500 spectrometer. IR spectra were measured on a PerkinElmer Frontier FT-IR spectrometer. ESI-MS spectra were taken on a Finnigan LCQ Classic mass spectrometer. Melting points were determined by an X-6 micro melting point apparatus (Beijing Tech Instrument). Thermogravimetric (TGA) and differential scanning (DSC) analyses were conducted on a Netzsch-STA 409 PC Instrument. Each sample (about

Table 3. Oxidation of other olefins using compound **1** containing a composite ionic liquid[a]

Run no.	Olefin	Product	Conversion[b], %	Yield[b], %
1			100	88
2			100	64
3			56	58
4			84	76

[a] The reactions were carried out using olefin (1 mmol), H_2O_2 (5 mmol, 0.5 mL), compound 1 (0.05 mmol), [Hmim]HSO_4 (1 mL) at 80°C.

[b] Conversion and yield were calculated based on GC analysis.

10 mg weight) was heated from 25 to 1000°C at a step of 10 K/min. The catalytic runs were monitored by the GC methods on an Agilent 6890 instrument equipped with a FID detector (capillary column 30 m × 0.25 mm × 0.25 μm).

Preparation of quaternary ammonium perrhenates. 1.2 equiv. of KOH (0.269 g, 4.8 mmol) was added to a solution of the quaternary ammonium bromine salts (4 mmol) in 20 mL ethanol in argon, and the mixture was stirred at room temperature for 6 h. The resulting mixture was filtered through a Gooch funnel to remove KBr and residual KOH, then 1.1 equiv. of NH_4ReO_4 (1.18 g, 4.4 mmol) was added, and after that, the reaction temperature was increased to 80ºC and the mixture was stirred for 2 h to remove NH_3. After the reaction was complete, the resulting solution was concentrated to about 3 mL-volume and cooled down to 0ºC, the obtained white precipitate was filtered, triply washed with ethanol, and dried under vacuum at 70ºC to give the quaternary ammonium perrhenates.

Compound 1. IR spectrum, cm^{-1}: 908 (Re=O), 1411, 1866, 3218. ^{1}H NMR spectrum (D_2O, 400 Hz, r.t., ppm): 3.114 s (12H, $4CH_3$). Calculated, %: C 14.81, H 3.73, N 4.32. $C_4H_{12}NO_4Re$. Found, %: C 14.79, H 3.75, N 4.36. *M* 324.35.

Compound 2. IR spectrum, cm^{-1}: 908 (Re=O), 1488, 2919, 3413. ^{1}H NMR spectrum (D_2O, 400 Hz, r.t., ppm): 3.201–3.158 q (8H, $4CH_2$), 1.197–1.170 t (12H, $4CH_3$). Calculated, %: C 25.26, H 5.30, N 3.68. $C_8H_{20}NO_4Re$. Found, %: C 25.21, H 5.30, N 3.66. *M* 380.46.

Compound 3. IR spectrum, cm^{-1}: 910 (Re=O), 1463, 2918, 3435. ^{1}H NMR spectrum (D_2O, 400 Hz, r.t., ppm): 3.218–3.174 q (6H, $3CH_2$), 3.095–3.061 t (2H, CH_2), 1.610–1.546 m (2H, CH_2), 1.343–1.314 m (2H, CH_2), 1.299–1.185 t (9H, $3CH_3$), 0.896–0.867 t (3H, CH_3). Calculated, %: C 29.40, H 5.92, N 3.43. $C_{10}H_{24}NO_4Re$. Found, %: C 29.42, H 5.90, N 3.45. *M* 408.51.

Compound 4. IR spectrum, cm^{-1}: 906 (Re=O), 1389, 1474, 2965. ^{1}H NMR spectrum ($CDCl_3$, 400 Hz, r.t., ppm): 3.232–3.176 t (8H, $4CH_2$), 1.680–1.577 m (8H, $4CH_2$), 1.479–1.358, m (8H, $4CH_2$), 1.013–0.965 t (12H, $4CH_3$). Calculated, %: C 39.01, H 7.37, N 2.84. $C_{16}H_{36}NO_4Re$. Found, %: C 38.89, H 7.36, N 2.88. *M* 492.67.

Compound 5. IR spectrum, cm^{-1}: 909 (Re=O), 1492, 2985, 3219. ^{1}H NMR spectrum ($CDCl_3$, 400 Hz, r.t., ppm): 3.466–3.432 t (2H, CH_2), 3.350 s (9H, $3CH_3$), 1.732–1.701 q (2H, CH_2),1.348 m (4H, $2CH_2$), 1.246 m (22H, $11CH_2$), 0.881 t (3H CH_3). Calculated, %: C 42.67, H 7.92, N 2.62. $C_{19}H_{42}NO_4Re$. Found, %: C 42.70, H 7.93, N 2.60. *M* 534.75.

Catalytic reactions. In a typical reaction, *cis*-cyclooctene (110 mg, 1 mmol) and the composite ionic liquid containing 1–5 mol % of quaternary ammonium perrhenates (**1**–**5**) and 1 mL of [Hmim]HSO_4 ionic liquid (catalyst and solvent) were mixed in the reaction vessel at 80°C. The reaction was started with the addition of hydrogen peroxide (5 mmol, 0.5 mL). The course of the reactions was monitored by the quantitative GC analysis. Samples were taken at regular time intervals, extracted with ethyl acetate, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the unreacted H_2O_2. The resulting slurry was filtered, and then filtrate was injected into a GC column. The conversion of olefins and the formation of epoxides were calculated from calibration curves ($r^2 > 0.999$) recorded prior to the reaction. The residual solution was treated by washing with ethyl acetate and then with dry *n*-hexane, and finally, it was dried under vacuum at 70°C for 6 h to obtain the recycled composite ionic liquid. The composite ionic liquid was used directly for the next catalytic run. The fresh substrate and H_2O_2 were then added for a new reaction cycle.

Single-crystal X-ray structure determination. A single crystal of the compound 4 was mounted on the diffractometer (Bruker XRDR3M/ESYSTCM model, 50 kV, 30 mA, MoK_α radiation, $\lambda = 0.71073$ Å). The data were collected at 273(2) K with a ω/φ diffraction measurement and data reduction was performed using the SMART and SAINT software with frames of 0.3° oscillation in the θ range $1.5° < \theta < 26.2°$. The structures were solved by direct methods and all non-hydrogen atoms were subjected to the anisotropic full-matrix least-squares refinement on F^2 using the SHELXTL package [44, 45].

CONCLUSIONS

Five alkyl quaternary ammonium perrhenates are prepared. The perrhenates are combined with [Hmim] HSO_4 to form the composite ionic liquids, which are used as the catalyst and solvent for the oxidation of cyclooctene to suberic acid. The results indicate that the introduction of perrhenates can not only accelerate the reaction but also increase the selectivity towards suberic acid, with a highest product yield of 75% obtained under the optimal conditions. To the best of our knowledge, this is the first report on the oxidation of cyclooctene to suberic acid, in which pherrhenate-containing composite ionic liquids are used as effective catalyst and hydrogen peroxide, as a green oxidant.

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