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Guanidinium-Based Phosphotungstates and Ionic Liquids as Catalysts and Solvents for the Epoxidation of Olefins with Hydrogen Peroxide

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Several penta- and hexaalkylated guanidinium-based ionic liquids (GILs) were tested as solvents for the epoxidation of cyclooctene using the Venturello catalyst, $[(C_8H_{17})_3N(CH_3)]_3[PO_4\{WO(O_2)_2\}_4]$, and hydrogen peroxide as the oxidant. Epoxide yields were obtained in a broad range between 13 and 79 % depending on both the anion and the substituents on the guanidinium moiety. Recycling experiments showed that the catalyst can be used at least three times. Furthermore, new guanidinium phosphotungstates with the $PW_{12}O_{40}^{3-}$ anion were synthesized and characterized. Their catalytic performance was evaluated, and GILs as well as acetonitrile were employed as the solvent. Results were compared to those obtained with the comparable ammonium-based catalysts $[NR_4]_3[PW_{12}O_{40}]$ (R = C_4H_9, C_6H_{13}) and the analogous imidazolium-based catalyst $[BMIM]_3[PW_{12}O_{40}]$ containing the 1-butyl-3-methylimidazolium cation. Employing different GILs as solvents, similar results were obtained for the guanidinium and imidazolium catalysts but significantly lower epoxide yields were obtained using the ammonium catalysts. On using acetonitrile as the solvent, guanidinium-based catalysts exhibited a better performance than the imidazolium catalyst in the case of linear and branched olefins and vice versa in the case of cyclic olefins.

Introduction

Catalytic oxidation with hydrogen peroxide is a highly attractive process and rapidly developing topic.[1] With regard to applications, enormous progress was made over the past few decades, and several benefits such as convenient handling, the favourable price of the oxidant and the formation of water as the only byproduct led to the successive substitution of some traditional oxidants, e.g. organic peroxides or inorganic salts, by hydrogen peroxide in several processes.

Recent investigations showed that oxidation reactions with hydrogen peroxide can be carried out favourably using ionic liquids as solvents. Such reaction systems afforded mild reaction conditions, efficient product separation by distillation or extraction, facile catalyst separation and multiple use.[2–5] Several examples of transition metal-catalyzed epoxidation reactions have been reported, e.g. the epoxidation of styrenes and cyclic olefins employing 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], and $MnSO_4$[6] and an iron(III) porphyrin complex employing a [BMIM][Br]/CH_2Cl_2 mixture under biphasic conditions.[7] Another example is the asymmetric epoxidation of limonene in [BMIM][BF_4] catalyzed by Jacobsen's manganese–salen complex.[8] Epoxidation reactions with a urea–hydrogen peroxide adduct as an oxidant have also been described, e.g. the epoxidation of various olefins in 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF_4], catalyzed by CH_3ReO_3[9–11] and the epoxidation of cyclooctene in [BMIM][PF_6] catalyzed by different Mo^{VI} compounds.[12]

Several epoxidation reactions without a transition metal catalyst have also been accomplished such as the epoxidation of α,β-unsaturated carbonyl compounds in a [BMIM][PF_6]/H_2O biphasic system containing NaOH,[13] the epoxidation of chromones and flavonoids in a [BMIM][BF_4]/H_2O/NaOH system,[14] the in situ epoxidation of cyclohexenones with electrogenerated H_2O_2 in [BMIM][BF_4]/H_2O/NaOH,[15] the epoxidation of cyclohexenones in [BMIM][PF_6] or [BMIM][BF_4] with alkaline H_2O_2,[16] styrene epoxidation using carboxyl-functionalized ionic liquids[17] and styrene epoxidation in the presence of KOH and CO_2 employing different ionic liquids as well as conventional organic solvents.[18]

Polyoxotungstates are a well known and efficient class of catalysts for the epoxidation of olefins with hydrogen peroxide.[19–22] Their use in combination with ionic liquids as solvents has been investigated recently. Examples are epoxidation reactions using the ammonium silicotungstate $(Bu_4N)_3K[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]$ as the catalyst and microwave heating of the reaction mixtures[23] and epoxidation reactions catalyzed by the imidazolium (phospho)tungstates $[BMIM]_3[PW_{12}O_{40}]$[24] and $[BMIM]_4[W_{10}O_{23}]$.[25] In these cases imidazolium salts of the type [BMIM][X] [X = BF_4^-, PF_6^-, $CF_3SO_3^-$, $N(CF_3SO_2)_2^-$] were used as solvents.

In contrast to the widely investigated imidazolium salts, significantly less work has been dedicated to guanidinium

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salts. Similar to imidazolium salts, several guanidinium salts exhibit typical ionic liquid characteristics and can be favourably employed as reaction media[18,26] as well as catalysts.[27,28] Recently, remarkable progress was made with respect to the optimization of synthetic strategies,[29–33] computational[34,35] and structural characterization[29,36] as well as a better understanding of their properties.[31,33,37–40] Based on these new insights, the applications of guanidinium salts can be vastly extended. Important examples are their use as solvents or additives, e.g. for the preparation of heterocycles,[41] for asymmetric Baylis–Hilman reactions[42] and for proline-catalyzed asymmetric aldol reactions.[43] Separation techniques employing guanidinium-based ionic liquids (GILs), e.g. the extraction of carbohydrates from aqueous solutions[44] and the absorption of organic vapours,[45] have also been investigated. Furthermore, their potential in liquid crystal applications has been evaluated.[46,47]

Within the work presented here we describe the use of guanidinium salts in epoxidation reactions with hydrogen peroxide as the oxidant. Penta- and hexaalkylated GILs were tested as solvents for the epoxidation of cyclooctene with a focus on the recyclability of the catalyst systems and multiple use in consecutive reactions. Furthermore, new guanidinium phosphotungstates were synthesized and characterized. Their catalytic performance was evaluated and the results were compared to those obtained with corresponding ammonium and imidazolium salts.

Results and Discussion

Synthesis and Characterization of Guanidinium Salts

Within this study guanidinium phosphotungstates (compounds **1** in Table 1), pentaalkylated guanidinium salts (compounds **2** in Table 1) and hexaalkylated guanidinium salts (compounds **3** in Table 1) were investigated. For comparison, ammonium phosphotungstates (compounds **4** in Table 1) and imidazolium phosphotungstate **5** were also employed.

The new guanidinium salts **1a** and **1b** (Table 1, n = 3) bearing the phosphotungstate anion $PW_{12}O_{40}^{3-}$ were prepared by ion exchange employing *N*,*N*,*N*′,*N*′-tetrahexyl-*N*′′,*N*′′-dimethylguanidinium chloride in the case of **1a** and the corresponding tetraoctyl compound in the case of **1b** with phosphotungstic acid, $H_3PW_{12}O_{40}$. Spectroscopic data are in accordance with the expected structures[48] and X-ray diffraction analysis of **1a** was carried out to elucidate its solid-state structure (Figure 1). According to the results of XRD analysis the three negative charges of the $PW_{12}O_{40}^{3-}$ cluster are compensated by three guanidinium counter cations. The cluster itself consists of a central PO_4 unit whose O atoms act as bridges to three W atoms completing their distorted octahedral environment to six O atoms. Four of

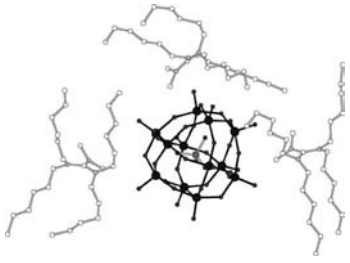
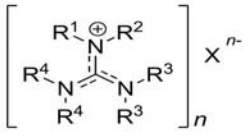
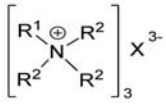


Figure 1. Solid-state structure of **1a** (cell content of the independent unit of the elementary cell). H atoms and numbering omitted for clarity. W–OP: 242.5(6)–245.2(7) pm, W–OW: 188.7(7)–193.5(6) pm, W–O(terminal): 168.7(7)–171.2(7) pm; C(central guanidinium atom)–N: 133(1), 133(1), 135(1), 133(1), 133(1), 135(1), 134(1), 132(1), 136(1) pm.

Table 1. Catalysts, solvents and labelling.

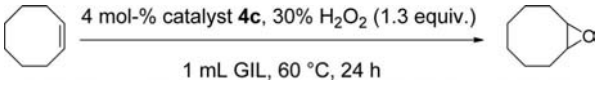
	R^1	R^2	R^3	R^4	X	Labelling
	CH_3	CH_3	C_6H_{13}	C_6H_{13}	$PW_{12}O_{40}$	**1a**
	CH_3	CH_3	C_8H_{17}	C_8H_{17}	$PW_{12}O_{40}$	**1b**
	H	C_2H_5	CH_3	CH_3	CF_3SO_3	**2a**
	H	C_2H_5	CH_3	CH_3	$C_6F_{13}PF_5$	**2b**
	H	C_2H_5	CH_3	CH_3	$C_2H_5OSO_3$	**2c**
	$C_2H_4OCH_3$	$C_2H_4OCH_3$	CH_3	C_2H_5	CF_3SO_3	**3a**
	CH_3	CH_3	C_6H_{13}	C_6H_{13}	CF_3SO_3	**3b**
	CH_3	CH_3	C_6H_{13}	C_6H_{13}	$N(CF_3SO_2)_2$	**3c**
	CH_3	CH_3	C_6H_{13}	C_6H_{13}	BF_4	**3d**
	CH_3	CH_3	C_6H_{13}	C_6H_{13}	PF_6	**3e**
	CH_3	CH_3	C_6H_{13}	C_6H_{13}	$C_7H_4NO_3S$	**3f**
	C_4H_9	C_4H_9	C_2H_5	C_2H_5	CF_3SO_3	**3g**
	C_4H_9	C_4H_9	–	–	$PW_{12}O_{40}$	**4a**
	C_6H_{13}	C_6H_{13}	–	–	$PW_{12}O_{40}$	**4b**
	CH_3	C_8H_{17}	–	–	$PO_4\{WO(O_2)_2\}_4$	**4c**
	CH_3	C_4H_9	–	–	$PW_{12}O_{40}$	**5**

these O atoms are involved in the formation of W–O–W bridges and the remaining O atom completes the oxygen rich surface of the $PW_{12}O_{40}^{3-}$ unit. Bond lengths and angles (Figure 1) are characteristic for this type of oxygen rich cluster and in agreement with literature data.[49–56]

In the cationic guanidinium counterions of **1a**, it can be noted that the central, planar guanidinium unit exhibits C–N bond lengths indicating π-electron delocalization in accordance with other crystallized guanidinium salts.[29,36,57–63] The hexyl substituents at the N-atoms appear in different conformations in the solid state showing their flexible conformational behaviour and build a lipophilic environment around the catalytically active metal oxygen cluster. With these structural findings one could expect an acceptable catalytic activity in the epoxidation of cyclooctene.

Guanidinium-Based Ionic Liquids as Reaction Media for the Epoxidation of Cyclooctene with Hydrogen Peroxide

Numerous guanidinium salts were tested as solvents for the epoxidation of cyclooctene with hydrogen peroxide catalyzed by the Venturello catalyst, **4c**.[64,65] Various water-soluble and insoluble ionic liquids were employed (Scheme 1 and Table 2). In all cases control reactions under the same reaction conditions but without catalyst were performed and no significant reactions were observed.



Scheme 1. Epoxidation of cyclooctene catalyzed by the Venturello catalyst (**4c**) in different guanidinium salts.

Table 2. Epoxidation of cyclooctene catalyzed by the Venturello catalyst (**4c**) in different guanidinium salts.

Entry	Solvent	Solubility in H_2O	Epoxide yield [%]
1	**2a**	+	79[a]
2	**2b**	–	48
3	**2c**	+	30
4	**3a**	+	76
5	**3b**	+	21
6	**3c**	–	13
7	**3d**	–	64
8	**3e**	–	56
9	**3g**	+	38[b]

[a] 5% cyclooctene diol byproduct. [b] Reaction time: 68 h.

Considerable fluctuations were observed for the cyclooctene conversions, which could be due to the activity of the catalyst system, the viscosity of the solvent, the miscibility and phase behaviour of the components as well as the solubility of the catalyst in the reaction system. Highest conversions were obtained using water soluble GILs **2a** (Table 2, entry 1, 83%) and **3a** (entry 4, 76%). In all reactions epoxide selectivities were 99% and higher except for those using **2a**. Employing **2a** led to the formation of significant amounts of cyclooctene diol as a byproduct and the epoxide selectivity reached only 95%. Employing the water soluble GILs, **2a**, **2c**, **3a**, **3b** and **3g**, small amounts (≤ 1%) of the diol were detected and when the water insoluble variants, **2b**, **3c**, **3d** and **3e**, were used formation of cyclooctenone (≤ 1%) was observed. Time dependence of the reactions was investigated and, as an example, the catalytic performance of **4c** in **2a** was monitored over 24 h (Figure 2). The cyclooctene conversion increased remarkably within the first five hours and there was still an increase of 3% between 19 and 24 h. Other reactions showed similar kinetic profiles and thus reaction times of 24 h were mostly chosen. Usually, the oxidant was completely consumed after 24 h.

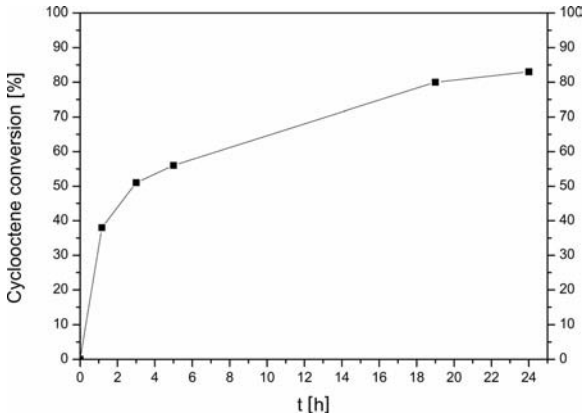


Figure 2. Cyclooctene epoxidation catalyzed by **4c** in **2a** as a function of time.

Obviously, the catalytic performances are largely influenced by the anion used. Considering the pentaalkylated GILs, **2a**, **2b** and **2c**, which bear the same substituents at the guanidinium cation, catalytic activities decrease in the following order: $CF_3SO_3^- > C_6F_{13}PF_5^- > C_2H_5OSO_3^-$. With respect to the hexaalkylated GILs, **3b**, **3c**, **3d**, **3e** and **3g**, bearing the same or at least very similar substituents at the guanidinium moiety, catalytic activities decrease in the order: $BF_4^- > PF_6^- > CF_3SO_3^- > N(CF_3SO_2)_2^-$. Considering the GILs with the trifluoromethanesulfonate anion, **2a**, **3a**, **3b** and **3g**, the catalytic performance of the system based on the pentaalkylated GIL **2a** is superior to systems based on the hexaalkylated GILs, **3a**, **3b** and **3g**. A drop from 76% conversion employing **3a** to 21 and 38% employing **3b** and **3g** was observed and indicates a significant influence of the substituents at the guanidinium cation on the catalytic performance.

Comparatively high conversions were observed using the water-miscible GIL **3a** and the immiscible GILs **3d** and **3e**. Recycling experiments were carried out using these three GILs and the catalyst was tested in three consecutive reactions (Table 3). After each catalytic run the product was separated from the reaction mixture by repeated extraction with hexane and the residue was diluted with CH_2Cl_2. The hexane solution and the CH_2Cl_2 phase were filtered through MnO_2/Al_2O_3 and analyzed by GC. After removal of CH_2Cl_2 in vacuo, the resulting residue was subjected to the next run without further purification. Employing the GILs **3d** and **3e**, similar epoxide yields of around 90% were observed and the epoxide yield in the second run remained

the same as in the first. Employing **3a**, the epoxide yield increased from 88 in the first run to 97% in the second. Third runs were performed after storage of the catalyst systems for two months and significantly lower epoxide yields were obtained. No significant amounts of byproducts were detected in any of these reactions.

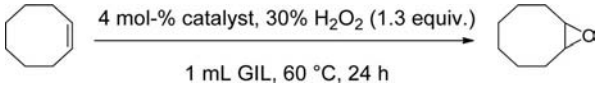
Table 3. Recovery and repeated use of the Venturello catalyst (**4c**) in different guanidinium salts.

Solvent	Epoxide yield in each run [%][a]		
	1	2	3[b]
3a	88	97	67
3d	90	90	68
3e	87	87	53

[a] The catalyst was activated in a previous run. [b] The catalyst was not used during a period of two months between runs 2 and 3.

Guanidinium and Ammonium Phosphotungstates as Catalysts for the Epoxidation of Cyclooctene in Guanidinium-Based Ionic Liquids

The guanidinium phosphotungstate **1a** was tested as an epoxidation catalyst in the GILs **3d**, **3e** and **3f** (Scheme 2 and Table 4). Catalyst recycling experiments comprising three consecutive reactions were carried out as described above for **4c**. The catalytic performance was significantly influenced by the GIL. In the case of **3d**, cyclooctene conversion increased from 73 in the first run to 91% in the third, whereas a decrease from 83 to 75% was observed using **3e** as solvent. Employing the GIL with the saccharinate anion, **3f**, conversion increased firstly from 65 to 83% and decreased subsequently to 77% in the last reaction. Epoxide selectivities were 99% and higher, in all reactions.



Scheme 2. Epoxidation of cyclooctene catalyzed by guanidinium and ammonium phosphotungstates in GILs.

Table 4. Epoxidation of cyclooctene catalyzed by guanidinium and ammonium phosphotungstates in GILs.

Catalyst	Solvent	Cyclooctene conversion in each run [%][a]		
		1	2	3
1a	**3d**	73 (≥99)[b]	81 (≥99)	91 (≥99)
	3e	83 (≥99)	77 (≥99)	75 (≥99)
	3f	65 (≥99)	83 (≥99)	77 (≥99)
4a	**3e**	28 (92)[c]	59 (96)[d]	19 (≥99)
4b	**3e**	34 (93)[e]	25 (≥99)	25 (≥99)
4c	**3e**	87 (≥99)	87 (≥99)	53 (≥99)

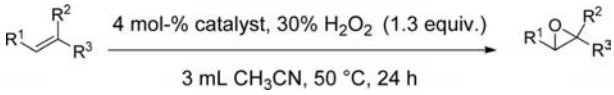
[a] The catalyst was activated in a previous run. [b] Values in parentheses are epoxide selectivities. [c] Byproducts: 5% cyclooctene diol and 3% cyclooctenone. [d] Byproducts: 3% cyclooctene diol and 1% cyclooctenone. [e] Byproducts: 3% cyclooctene diol and 4% cyclooctenone.

For comparison, the ammonium-based catalysts[66] **4a** and **4b** bearing the same anion as **1a** were also studied with **3e** as the solvent (Scheme 2 and Table 4). Olefin conversions were low and reached only 59% in the second run of the reactions catalyzed by **4a**. Significant amounts of byproducts, cyclooctene diol and cyclooctenone, were detected in the initial runs and epoxide selectivity increased in the following reactions to 99% and higher. In contrast, cyclooctene conversions were higher in reactions catalyzed by **4c** (Table 3 and Table 4) and epoxide selectivities were 99% and higher. However, cyclooctene conversions decreased from 87 in the first run to 53% in the third.

The analogous catalyst with the [BMIM] cation (catalyst **5**, Table 1) was tested by Zhao et al. using [BMIM][PF_6] as solvent.[24] Employing a catalyst loading of 0.3 mol-%, 1.5 equiv. of H_2O_2, a reaction time of 1 h and a reaction temperature of 60 °C, cyclooctene oxide yield was 87% with 99% epoxide selectivity. ^{31}P NMR spectra indicated the formation of the Venturello anion $PO_4[WO(O_2)_2]_4^{3-}$ as the catalytically active species during these reactions and it was suggested that formation of this species was promoted by using [BMIM][PF_6] as the solvent. Corresponding salts with the anions $N(CF_3SO_2)_2^-$ and BF_4^- were also investigated as reaction media but the catalytic performance decreased in the order [BMIM][PF_6] > [BMIM][$N(CF_3SO_2)_2$] > [BMIM][BF_4]. It was claimed that the catalyst system could be used in five recycling experiments without significant decrease in reactivity and selectivity.

Guanidinium Phosphotungstates as Catalysts for the Epoxidation of Olefins in Acetonitrile

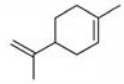
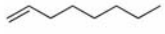
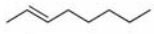
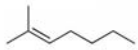
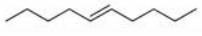
Due to the good solubility of all reaction components in acetonitrile, it was chosen as solvent for the epoxidation of several cyclic, linear and branched olefins using the guanidinium phosphotungstate **1b** as a catalyst. For direct comparison, analogous reactions catalyzed by the corresponding imidazolium phosphotungstate **5**[24] were also carried out (Scheme 3 and Table 5). In all cases, test reactions under the same reaction conditions but without catalyst showed no significant olefin conversion.



Scheme 3. Epoxidation of different olefins catalyzed by the phosphotungstates **1b** and **5** in acetonitrile.

The catalytic performance of **5** in the epoxidation of cyclooctene using acetonitrile as solvent has already been described by Zhao et al.[24] However, a short reaction time of 1 h and a low catalyst loading of 0.3 mol-% led to an epoxide yield of only 1% with 77% selectivity. Only trace amounts of cyclooctene oxide were observed when MeOH or CH_2Cl_2 were employed as solvents. In our own experiments under the same reaction conditions using catalyst **1b**, i.e. a catalyst loading of 4 mol-% and an extended reaction time of 24 h, an olefin conversion of 74% with 96% epoxide selectivity could be reached (entry 5, Table 5). In the case of the analogous guanidinium catalyst **1b** a significantly higher cyclooctene conversion of 91% with 95% epoxide selectivity

Table 5. Epoxidation of different olefins catalyzed by the phosphotungstates **1b** and **5** in acetonitrile.

Entry	Substrate	Catalyst			
		1b		**5**	
		Conv. [%]	Sel. [%]	Conv. [%]	Sel. [%]
1		84	97[a]	94	99
2		71	40[b]	89	47[b]
3		50	77[c]	85	86[d]
4		25	99	32	99
5		91	95[e]	74	96[e]
6		33	85[f]	41	98[f]
7		66	97[g]	57	96[g]
8		73	97[e]	92	96[e]
9		86	87[b]	50	98[b]
10		10	86[e]	2	72[e]

[a] 1% Cyclohexenone and 2% cyclohexanediol as byproducts. [b] Ketone as major byproduct: Entry 2, 60% (**1b**) and 35% (**5**); Entry 9, 13% (**1b**) and 2% (**5**). [c] 7% dioxide, 11% diol and 5% ketone. [d] 3% dioxide, 11% diol. [e] Diol as byproduct: Entry 5, 5% (**1b**) and 4% (**5**); Entry 8, 3% (**1b**) and 4% (**5**); Entry 10, 14% (**1b**) and 28% (**5**). [f] Diepoxide as byproduct: 15% (**1b**) and 2% (**5**). [g] Aldehyde as byproduct: 3% (**1b**) and 4% (**5**).

was observed. However, in the epoxidation of all other cyclic olefins a different behaviour was observed and catalyst **5** led to significantly higher conversions compared to **1b**. Conversions of cyclic olefins were usually 70% and higher with the exception of 2-norbornene (entry 4, Table 5) and 1,5-cyclooctadiene (entry 6, Table 5). In the epoxidation of these two olefins both catalysts, **1b** and **5**, gave conversions in the range of 25 to 41% with high epoxide selectivities of 98% and higher.

Conversely, in the case of linear and branched olefins, except for *trans*-2-octene, **1b** performed better than **5** with respect to olefin conversion. Good results were obtained in the epoxidation of 1-octene with **1b**, (entry 7, Table 5), and olefin conversion increased with increasing number of alkyl substituents at the double bond thus facilitating electrophilic epoxidation. Olefin conversion increased from 66% in the case of 1-octene to 73% in the case of *trans*-2-octene (entry 8, Table 5) and to 86% using 2-methyl-2-heptene as substrate (entry 9, Table 5). In the case of the long-chain olefin *trans*-5-decene (entry 10, Table 5) low conversion was observed, most probably due to steric hindrance. These results indicate that the catalyst cation has a significant influence on the catalytic performance of the reaction system. Concerning epoxide selectivities, both catalysts gave similar results.

To elucidate the nature of the active species, catalysts **1a** and **1b** were also investigated by ^{31}P NMR spectroscopy. The catalysts were dissolved in acetonitrile and a signal typical of the $PW_{12}O_{40}^{3-}$ anion was observed at around –14 ppm. After addition of H_2O_2 (50 equiv.) the spectrum changed and new peaks at around 25, –28 and –44 ppm emerged in addition to the peak at –14 ppm. The Venturello anion, which typically shows a peak at around 4 ppm,[24] was not detected. Thus, the nature of the active species remains unclear and will be investigated in future work.

Conclusions

Guanidinium-based ionic liquids are suitable solvents for epoxidation reactions with H_2O_2 as the oxidant. The compounds are oxidation resistant and, employing the Venturello catalyst, the catalyst system can be recovered after the reaction and used repeatedly. Guanidinium phosphotungstates with the $PW_{12}O_{40}^{3-}$ anion exhibit remarkable activity in epoxidation reactions with H_2O_2 and their performance is similar to the analogous imidazolium phosphotungstate [BMIM][$PW_{12}O_{40}$]. The corresponding ammonium compounds showed a significantly lower catalytic performance. Recyclable catalyst systems can be obtained by combining guanidinium phosphotungstate catalysts with guanidinium-based ionic liquids as solvents. Further experiments will clarify the relationship between the structure of guanidinium-based catalysts and solvents and their performance in catalytic epoxidation reactions.

Experimental Section

General: GC analyses were carried out using an Agilent 6890N gas chromatograph with FID detector equipped with a DB-5 (5% phenyl siloxane und 95% methyl siloxane) capillary column. NMR spectra were recorded with a Bruker Avance 250 or a Varian Unity INOVA 400 spectrometer. FTIR measurements were carried out using a Varian 660-IR spectrometer in the transmission mode. Spectra were recorded from KBr pellets. Melting points were measured by differential scanning calorimetry employing a Mettler Toledo DSC822^e device. Tungsten and phosphorus contents of the catalysts were determined by inductively coupled plasma-atomic emission spectroscopy with a Varian Liberty 150 instrument. Electrospray ionization-mass spectrometry (ESI-MS) was carried out using a Hewlett–Packard Series 1100MSD device. X-ray diffraction data were collected using a Siemens SMART 1000 CCD diffractometer at 200 K. Calculations were performed using SHELXS-97 and SHELXL-97.[67] Crystal data, data collection and refinement parameters are summarized in Table 6. CCDC-808202 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

N,*N*,*N*′,*N*′-tetrahexyl-*N*′′,*N*′′-dimethylguanidinium chloride and *N*,*N*,*N*′,*N*′-tetraoctyl-*N*′′,*N*′′-dimethylguanidinium chloride were synthesized as described by Afonso et al.[44] The pentaalkylated *N*′′-ethyl-*N*,*N*,*N*′,*N*′-tetramethylguanidinium triflate **2a** and the corresponding guanidinium salt with the tris(pentafluoroethyl)trifluoro phosphate anion **2b** were obtained from Merck KGaA. The

Table 6. Crystallographic data and refinement details for **1a**.

Empirical formula	$C_{81}H_{174}N_9O_{40}PW_{12}$
Formula weight	4151.46
Crystallization	acetonitrile
Crystal size	0.35 × 0.25 × 0.2 mm
Space group	$P2_1/n$ (No. 14)
Crystal system	monoclinic
Unit cell dimensions	a = 29.338(2) Å
	b = 15.504(1) Å
	c = 29.514(2) Å
	β = 116.459(1)°
Volume	12018(1) Å^3
Z	4
Density (calculated)	2.294 gcm^{-3}
Wavelength	0.71073 Å
Temperature	200(2) K
θ-Range	$1.52 \leq \theta \leq 28.29$
Index ranges	$-38 \leq h \leq 38$, $-20 \leq k \leq 20$, $-38 \leq l \leq 39$
Reflections	
collected / unique / observed	143523 / 29524 / 20998 ($I > 2\sigma$)
Largest diff. peak and hole	2.789 and –2.913 Å^{-3}
Refinement method	full-matrix least-squares on F^2
GooF	1.060
R indices	R_1 = 0.0489 (I > 2σ), wR_2 = 0.0989 (all data)

analogous compound with the ethyl sulfate anion **2c** was obtained from Prof. Kantlehner et al. (University of Stuttgart). The hexaalkylated guanidinium salts **3a** and **3g** were purchased from Prof. Maas et al. (University of Ulm). Further hexaalkylated salts **3b**–**3f** were prepared according to methods described in the literature.[44,45,68,69] The ammonium phosphotungstates **4a** and **4b**,[66] the Venturello catalyst **4c**[64,65] and the imidazolium salt **5**[24] were also synthesized according to literature methods. Other compounds were commercially available and used without further purification.

Preparation of the Phosphotungstate Salts 1a and 1b

Synthesis of 1a: Phosphotungstic acid (2.88 g, 1.0 mmol) was dissolved in water (30 mL) and *N*,*N*,*N*′,*N*′-tetrahexyl-*N*′′,*N*′′-dimethylguanidinium chloride (1.39 g, 3.0 mmol) was added. The suspension was stirred for 72 h at room temperature and water was removed by filtration. After washing with water and drying in vacuo, the product was obtained as a yellow solid (3.00 g, 72%); m.p. 91 °C. ESI-MS: *m*/*z* (%) = 424 (100) [M$^+$], 425 (20) [M$^+$ + H]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (m, 12 H, CH_2CH_3), 1.32–1.74 (m, 32 H, CH_2), 2.98–3.39 (m, 14 H, N–CH_2, N–CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.6, 22.7, 26.7 (CH_2, CH_3), 31.7, 40.8 (N–CH_2, N–CH_3) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = –14.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 2903 (br., NCH_3), 1558, 1456, 1416, 1378, 1080 (PO), 981 (W=O), 844 (O–O) cm^{-1}.

Synthesis of 1b: Phosphotungstic acid (3.37 g, 1.2 mmol) was dissolved in a water/dichloromethane mixture (40 mL, H_2O:CH_2Cl_2 4:1) and *N*,*N*,*N*′,*N*′-tetraoctyl-*N*′′,*N*′′-dimethylguanidinium chloride (2.00 g, 3.5 mmol) was added. The reaction mixture was stirred for 72 h at room temperature, filtered and the solid was washed with water until a neutral pH was reached. The product was dried at 75 °C and a yellow solid (4.00 g, 76%) was obtained; m.p. 73 °C. ESI-MS: *m*/*z* (%) = 536 (100) [M$^+$], 554 (50) [M$^+$ + H_2O]. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.80 (m, 12 H, CH_2CH_3), 1.20–1.94 (m, 48 H, CH_2), 2.70–3.20 (m, 14 H, N-CH_2, N-CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.0, 26.8, 26.9, 27.4, 27.7, 29.0, 29.1, 29.2, 29.4, 31.7, 31.8 (rotamer signals, CH_2, CH_3), 38.7, 40.7, 48.0, 48.2, 49.4, 49.8 (rotamer signals, N–CH_2, N–CH_3), 163.4 (C=N) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = –14.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 2956, 2925, 2903, 2855, 1570, 1546, 1467, 1427, 1079 (PO), 986, 977 (W=O), 896, 819 (O–O), 595, 522 (W–O–O) cm^{-1}.

Epoxidation of Olefins: Reactions were carried out in a 10 mL glass tube equipped with a magnetic stirrer. Typically, reaction temperatures of 60 °C and reaction times of 24 h were chosen. The reported amounts of catalyst, substrate, internal standard for GC analysis (decane) and hydrogen peroxide (30% aqueous solution) were dissolved in the respective solvent and reactions were monitored by sampling and GC–MS as well as GC–FID analyses. Product quantification was carried out by comparison of the product mixtures with calibration curves obtained from standard solutions. Recycling experiments were carried out by removal of the products by extraction. Catalyst recovery was achieved by separation of the ionic liquid phase with the dissolved catalyst and the catalyst solution was reused in the next catalytic run. The error range of the given yields, conversions and selectivities was ±4%, mainly due to GC measurements and slightly diverging product workup.

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