Epoxidation of Olefins Catalyzed by Polyoxomolybdates Formed *in-situ* in Ionic Liquids

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Polyoxomolybdates were generated *in situ* by treating a carboxylic acid-functionalized ionic liquid with an aqueous solution of sodium molybdate. This reaction mixture was applied in the catalytic epoxidation of olefins using hydrogen peroxide as oxidant. The influence of acid and catalyst concentration as well as of the reaction temperature was investigated. The system showed a good performance for the epoxidation reaction and can be reused several times without a significant loss of activity. We present an easy, cheap and environmentally friendly catalytic system for the epoxidation of *cis*-cyclooctene.

Key words: Ionic Liquids, Homogeneous Catalysis, Epoxidation, Molybdenum

Introduction

The design and application of clean and efficient processes for the epoxidation of olefins on a large scale dwells on being an important objective in the fine chemical industry [1, 2]. There is a bulging need for the elaboration of catalytic systems that consume only cheap, ecologically friendly and readily available oxidants, such as hydrogen peroxide [3, 4]. In this context our group reported very recently about the ability of certain anions of ionic liquids, such as tetrafluoroborate and perrhenate, to activate hydrogen peroxide through only hydrogen bonding interactions [5, 6]. Olefin epoxidation with imidazolium perrhenates occurs *via* an outer-sphere mechanism, not involving the Re center [6]. This knowledge opens new reaction pathways for the epoxidation of olefins with stable, cheap and readily accessible compounds, which are isoelectronic and isostructural to $[ReO_4]^-$, offering a diversity of advantages towards the rather sophisticated and expensive commonly used molecular Mn, Mo, Re and Ti compounds [7].

As the price for rhenium salts is still 10 times higher than that for comparable molybdenum compounds, and the molybdate anion might be seen as a congener to the investigated perrhenate anion, further investigations were carried out in our group recently. A series of ionic compounds containing the polyoxomolybdate anion $[Mo_6O_{19}]^{2-}$ and a weakly coordinating cation have been used as catalysts for the epoxidation of olefins and the oxidation of sulfides to sulfoxides [8]. The catalysts show good yields for the oxidation of sulfides and the epoxidation of olefins and are reusable several times in the oxidation reaction without loss of activity. The catalysts were prepared by acid condensation into aqueous solution of the oxometalate anion followed by addition of the precipitating cation. The formation of polyoxomolybdates is conducted *via* self-assembly by covalent and non-covalent interactions. The resulting structures are dependent on the pH value of the reaction media and the starting materials. In solution, the simplest molybdate, $[MoO_4]^{2-}$, forms various polyoxomolybdate compounds in dependence of the pH. In aqueous solutions, molybdenum(VI) is present in form of the tetrahedral $[MoO_4]^{2-}$ ion. When lowering the pH value to 4–6, the heptamolybdate $[Mo_7O_{26}]^{4-}$ is primarily formed. In even more acidic reaction solutions (pH lower than 3) various polyoxomolybdate species coexist, but mostly Mo_{36} clusters are formed [9, 10]. Due to their verifiable redox and acidic properties, polyoxometalates are copiously used as the catalyst for a broad scope of organic transformations [11, 12]. Very recently, other groups reported on polyoxotungstate and polyoxomolybdate compounds as catalysts of the oxidation of sulfides with H_2O_2 [13–16]. These early systems suffer from difficulties in catalyst isolation and recycling due to being liquid-phase homogeneous or biphasic systems. Therefore, research efforts focused on the immobilization of polyoxometalates on porous carriers to provide recoverable heterogeneous catalysts. However, these systems deteriorate due to leaching of active components, give slow reaction rates or need elaborated steps in catalyst syntheses [17, 18].

At the same time ionic liquids are renowned catalysts and reaction media for a plethora of processes. Most of the time their immiscibility with most of the common organic solvents is used in two-phase homogeneous catalysis allowing an easier product separation and catalyst recycling [19, 20].

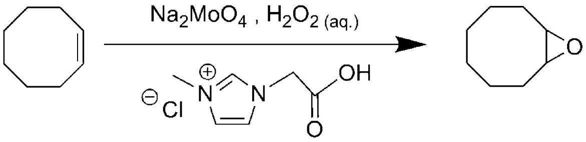
In recent times the usually monocharged anions of ionic liquids have been replaced with the multicharged polyoxometalate anions as counterions, and the new systems were tested in oxidation catalysis [21–24]. In 2012 Wang *et al.* synthesized several imidazolium polyoxometalate salts using Keggin-type polyoxometalate ions as counter-ions while varying the length of the carbon chains at the imidazolium cations. The salts provided good yields in the oxidation of sulfides with aqueous H_2O_2 [25].

Instead of using a "normal", not functionalized ionic liquid and an organic acid to lower the pH value we combined the advantages of both systems and used an acid-functionalized imidazolium-based ionic liquid to form *in situ* an active catalytic system which we examined for the epoxidation of cyclooctene with aqueous H_2O_2.

The resulting reaction mixture has led to the desired biphasic catalytic system, exhibiting good yields in the conversion of cyclooctene and providing the advantages of easy product separation, steady reuse and *in situ* formation of the active species.

Results and Discussion

The catalytic system reported herein was tested in the epoxidation of cyclooctene (Scheme 1). Typically a solution of 2.00 mmol *cis*-cyclooctene and 0.10 mmol sodium molybdate in 1.00 mmol of the ionic liquid [camim]Cl (camim = 1-carboxymethyl-3-methylimidazolium) dissolved in 3 mL deionized water was treated with 3.00 mmol aqueous hydrogen peroxide (50 %). A biphasic system was formed consisting of a yellow phase with the ionic liquid and the molybdate-containing aqueous phase and the colorless organic substrate phase.



Scheme 1. Epoxidation of *cis*-cyclooctene using *in situ*-prepared polyoxomolybdates.

To determine the optimum reaction conditions, the amount of acid-functionalized ionic liquid [camim]Cl (Table 1), the molybdate concentration (Table 2) and the reaction temperature (Fig. 1) were varied.

As can be seen from Table 1, the yield of epoxide is strongly dependent on the amount of [camim]Cl in the reaction mixture. This can be attributed to the fact that the amount of ionic liquid in the solution determines the pH value of the reaction media and therefore the formed polyoxomolybdate species [9, 10]. In 2005 Reedijk *et al.* showed that the catalytic activity of a tungstate-containing catalytic system is strongly pH dependent [15]. In recent years several polyoxotungstate-containing ionic liquids have been synthesized and tested in catalysis [21, 26–28]. In the experiments described in these reports the acidity plays an important role in catalyst synthesis. To the best of our knowledge there are so far no reports about the pH dependence of molybdate-containing reaction mixtures.

Conversions are very low ($< 20\,\%$) when less than 0.75 mmol of the acid-functionalized ionic liquid is added (entries 1 and 2). The best results were achieved when 1.00 mmol IL was added, and a pH value of *ca.* 3.5 was generated (entry 4). This system most presumably leads to the formation of $[Mo_xO_y]^{2-}$ clusters. Further investigations on the exact nature of the active species are underway. It is noteworthy that no cyclooctene-1,2-diols are formed during the reaction. Furthermore it can be stated that a greater excess of IL does not improve the yield of cyclooctene oxide (entry 6).

Table 1. Epoxidation of *cis*-cyclooctene using different amounts of [camim]Cl[a].

Entry	mmol (camim)Cl	pH	Conv. (%)[b]	Yield (%)[b]	Conv. (%)[b]	Yield (%)[b]
			after 4 h		after 24 h	
1	0.1	7.0	14	14	21	21
2	0.5	5.5	18	18	26	26
3	0.75	4.0	28	28	37	37
4	1	3.5	39	39	68	68
5	1.5	2.5	34	34	62	62
6	2	2.0	33	33	56	56

[a] Reaction conditions: 2.00 mmol *cis*-cyclooctene, 3.00 mmol H_2O_2, 20.5 mg (0.1 mmol) Na_2MoO_4, 3 mL deionized water, 60 °C; [b] determined by GC-MS analysis.

Table 2. Epoxidation of *cis*-cyclooctene using different amounts of Na_2MoO_4[a].

Entry	Na_2MoO_4 (mmol)	Conv. (%)[b]	Yield (%)[b]
1	0	6	6
2	0.05	23	23
3	0.10	39	39
4	1.00	27	27
5	5.00	8	8

[a] Reaction conditions: 2.00 mmol *cis*-cyclooctene, 3.00 mmol H_2O_2, 1.00 mmol [camim]Cl, 3 mL deionized water, pH = 3.50, 60 °C; [b] determined by GC-MS analysis.

In order to optimize the reaction conditions for olefin conversion, the catalyst concentration has also been varied. The catalytic system is sensitive to the applied amount of sodium molybdate as can be seen in Table 2.

Entry 1 validates that sodium molybdate is the precursor of the active species as the conversion is very low (conv. < 10 %) when no molybdate is involved in the catalytic reaction. This result also excludes that epoxidation takes place only *via* oxygen transfer from *in situ*-generated per-acids, as in this case the yield would be only determined by the amount of acid-functionalized ionic liquid involved in the catalytic system.

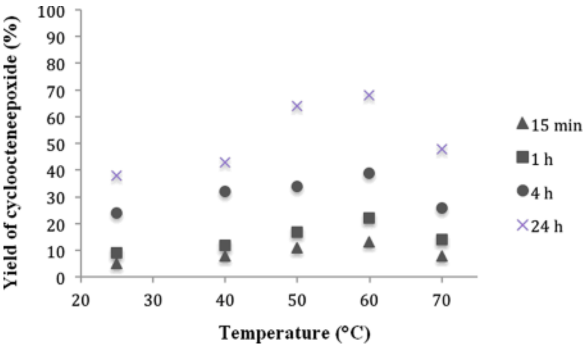


Fig. 1. Influence of reaction temperature on the yield of *cis*-cyclooctene oxide in the epoxidation of *cis*-cyclooctene. Reaction conditions: 2.00 mmol cyclooctene, 3.00 mmol H_2O_2, 0.1 mmol Na_2MoO_4, 1.00 mmol [camim]Cl, 3 mL deionized water.

Further, from entry 5 it can be seen that an excess of sodium molybdate also leads to low conversion. Most likely this can be attributed to solubility issues as the formation of a slurry is observed. The undissolved molybdate leads to a faster decomposition of hydrogen peroxide as a strong gas evolution was observed in this catalytic run.

Based on the data from Tables 1 and 2 it can be stated that the ideal molybdenum to ionic liquid ratio is 1 to 10 for the applied reaction conditions. Moreover, the reaction temperature plays a substantial role regarding the yield as can be seen in Fig. 1. This can most likely be ascribed to solubility issues on the one hand of the polyoxomolybdate in the water/IL phase and on the other hand of the substrate in the reaction mixture.

From the data in Fig. 1 it appears that 60 °C is the ideal reaction temperature for the catalysis. When tem-

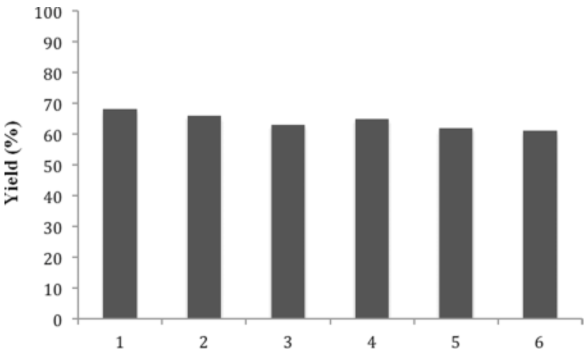


Fig. 2. Recycling studies for the epoxidation of *cis*-cyclooctene.

peratures below 50 °C were applied, the aqueous phase was a slurry due to a not adequate solubility of the ionic liquid in the aqueous phase. When an elevated temperature of 70 °C is adapted to the system the decomposition of hydrogen peroxide seems to be the favored reaction pathway as a strong gas evolution is observed.

A further point of investigation was catalyst recycling and reusability (Fig. 2). After 24 h at 60 °C with a molar ratio of sodium molybdate to [camim]Cl of 1 to 10 the product-containing organic phase was extracted with *n*-hexane. The aqueous phase containing the ionic liquid and the catalyst was dried in high vacuum at 80 °C and used for the next catalytic run. The systems remained active with a negligible loss of activity.

Conclusion

The epoxidation of *cis*-cyclooctene was achieved under relatively mild reaction conditions. Conversions and yields are not as high as for the well known molecular systems, but the active species is formed *in situ* from a cheap, commercially available catalyst precursor and can be reused for several runs without a significant loss of activity. The data presented here certainly warrant a more comprehensive study of this catalytic system for further improvement of its catalytic activity.

Experimental Section

General methods

Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit HP 3396 Series II. [camim]Cl was synthesized according to literature procedures [29].

General procedure for the epoxidation of olefins

In a typical reaction, 205 mg (0.1 mmol) sodium molybdate was dissolved in deionized water (3 mL) and 20 equiv. (353 mg) 1-carboxymethyl-3-methylimidazoliumchloride was added. Substrate (2 mmol) was added, followed by the addition of aqueous hydrogen peroxide (3 mmol). The reaction mixture was extracted with *n*-hexane (3 × 1 mL) and the organic phase dried over $MgSO_4$. The resulting slurry was filtered and the filtrate injected onto a GC column. The conversion of olefin and the formation of epoxides were calculated from calibration curves ($r^2 > 0.999$) recorded prior to the reaction.

The aqueous/ionic liquid phase was dried at 80 °C in vacuum for 4 h after substrate and product were extracted by the addition of *n*-hexane. 3 mL deionized water, fresh substrate and hydrogen peroxide were then added to start a new reaction cycle.

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