Catal Lett (2013) 143:1162–1165
DOI 10.1007/s10562-013-1088-1

Epoxidation of Alkenes with Aqueous Hydrogen Peroxide and Quaternary Ammonium Bicarbonate Catalysts

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Received: 4 June 2013 / Accepted: 19 August 2013 / Published online: 4 September 2013

Abstract A range of solid and liquid catalysts containing bicarbonate anions were synthesised and tested for the epoxidation of alkenes with aqueous hydrogen peroxide. The combination of bicarbonate anions and quaternary ammonium cations opens up for new catalytic systems that can help to overcome challenges with catalyst separation and reuse.

Keywords Green chemistry · Epoxidation · Alkenes · Oxidation · Liquid-phase oxidation

Epoxides are among the most versatile intermediates in organic synthesis and find use in the production of many bulk commodities, high-valuable fine chemicals and pharmaceuticals [1]. Unfortunately, epoxides are often synthesized using stoichio-metric amounts of strong organic oxidants such as peracetic acid [2], *tert*-butyl hydroperoxide [3] or *m*-chloro-peroxy-benzoic acid [4]. These oxidants are not particularly attractive on an industrial scale because of the poor atom economy and concerns for safety. The development of effective catalytic oxidations and epoxidations using more environmentally friendly oxidants is therefore highly desirable [5, 6]. In particular, much effort has been devoted to the use of aqueous hydrogen peroxide [7]. Beside molecular oxygen [8, 9], hydrogen peroxide is the most attractive oxidant, because it is cheap, easy to handle and produces water as the only by-product [10].

During the last 30 years several efficient methods for the epoxidation of alkenes with hydrogen peroxide using Ti [11], V [12], Mn [13, 14], Fe [15], W [16, 17] and Re [18, 19] metal catalysts have been reported. However, most of these catalysts are homogeneous and requires tedious separation procedures to reuse the expensive catalysts. Immobilization of the homogeneous catalysts is challenging and may lead to decreased activity, poor stability and leaching of the catalytically active species. Although, titanium-containing zeolites such as TS-1 have become well-known as effective heterogeneous catalysts for the epoxidation of linear alkenes [11], the microporous catalysts generally suffer from diffusion limitations when it comes to more bulky substrates [20].

In 2000, Yao and Richardson [21] reported the bicarbonate-catalyzed epoxidation of alkenes with aqueous hydrogen peroxide. In this simple and metal-free system, the active oxidant was proposed to be the peroxymonocarbonate anion HCO_4^- formed by the reaction of HCO_3^- with H_2O_2. Yao and Richardson found that bicarbonate activated peroxide (BAP) system could be used for the epoxidation of a range of alkenes in water and in aqueous solutions with acetonitrile using NH_4HCO_3 as the homogeneous catalyst. Moreover, Bulman Page et al. [22, 23] have demonstrated that electrochemically generated percarbonate can oxidize alkenes to the corresponding epoxides with high selectivity.

Here, we show that the use of quaternary ammonium cations opens up for new catalytic systems that can help to overcome the challenges with catalysts separation and reuse. The catalysts were prepared by a simple and cheap procedure, where CO_2 was bubbled through an aqueous solution of a quaternary ammonium hydroxide. In this way,

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Electronic supplementary material The online version of this article (doi:10.1007/s10562-013-1088-1) contains supplementary material, which is available to authorized users.

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tetra-methyl-ammonium-, tetra-ethyl-ammonium-, tetra-propyl-ammonium- and tetra-hexyl-ammonium bicarbonate were easily obtained from the commercially available hydroxides. During the CO_2 treatment, the bicarbonate salt with the longest and most hydrophobic alkyl groups, i.e. tetrahexylammonium bicarbonate, resulted in a fine white dispersion. After half an hour, the white dispersion separated into a two-phase system that consisted of an aqueous phase (bottom layer) and a room temperature ionic liquid (top layer). Ionic liquids have been used for catalytic epoxidations in several recent studies [19, 24] and a direct synthesis of ionic liquids containing bicarbonate anions have previously been reported by Rogers and co-workers [25].

In addition to the homogenous catalysts, we also prepared a heterogeneous bicarbonate catalyst. The heterogeneous catalyst was prepared from a commercial ion exchange resin (Amberlite CG-400 Cl) by treating it with a saturated aqueous solution of $NaHCO_3$. All catalysts were characterized by FTIR and ^{1}H-NMR (see Supporting Information). A schematic representation of the investigated bicarbonate catalysts is shown in Fig. 1.

Initially, we tested the quaternary ammonium cations with alkyl groups of increasing chain length to investigate the effect on catalytic activity. Cyclohexene was used as model substrate and the reactions were performed under ambient atmosphere and at room temperature with two equivalents of aqueous hydrogen peroxide in acetonitrile. During the reactions samples of 0.1 ml were periodically collected and analysed by GC–FID and GC–MS using a HP-5 column from Agilent Technologies Inc. The conversion and product selectivity was calculated from an internal standard.

Figure 2 shows that all investigated catalysts promoted the epoxidation of cyclohexene to cyclohexene oxide and that the nature of the cation only had a limited effect on the reaction progression. These results confirmed that the cation could be changed without significant loss of catalytic activity. All reactions occurred with excellent selectivity (>98 %) and no reaction occurred in the absence of catalyst. It should be mentioned that all the ammonium catalysts where fully soluble, while $NaHCO_3$ was only partially soluble under the given reaction conditions. After 24 h both $NaHCO_3$, NH_4HCO_3 and tetra-methyl-ammonium bicarbonate afforded 81 % yield, while tetra-ethyl-ammonium-, tetra-propyl-ammonium- and tetra-hexyl-ammonium bicarbonate afforded 69–73 % yield.

In contrast to Yao and Richardson [21] we found that acetonitrile acted as co-reactant and that relatively large amounts of acetamide were formed under the given reaction conditions. No reaction occurred in other solvents than acetonitrile and exchanging the bicarbonates with the corresponding hydroxides resulted in fast decomposition of the hydrogen peroxide under formation of water, oxygen and heat. The formation of acetamide indicates (although more detailed studies are needed) that the reaction may proceed by the well-known base-catalyzed Payne oxidation in acetonitrile [26] and that a peroxycarboximidic acid intermediate may be formed in addition to the peroxy-mono-carbonate anion as proposed by Yao and Richardson [21].

In an attempt to prevent the formation of acetamide we also tested the catalysts in a two-phase system without acetonitrile. However, although quaternary ammonium cations are well-known compounds in phase transfer catalysis [27], none of the investigated catalysts were active under solvent-free conditions.

By parallel screening of more than 30 d-block and f-block metals, Burgees and co-workers [28] previously showed that the combination of manganese and

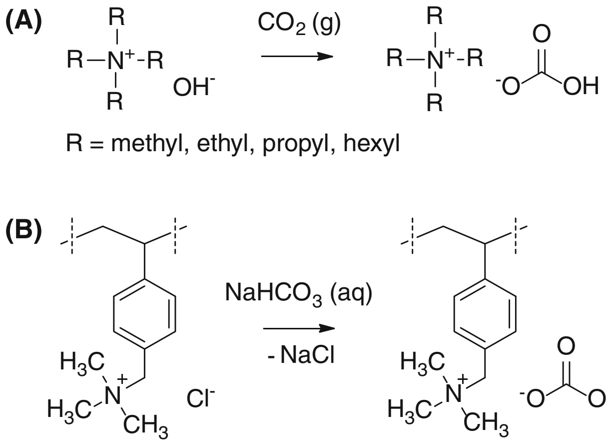


Fig. 1 Schematic representation of the investigated bicarbonate catalysts. **a** Homogeneous catalysts. **b** Heterogeneous catalyst

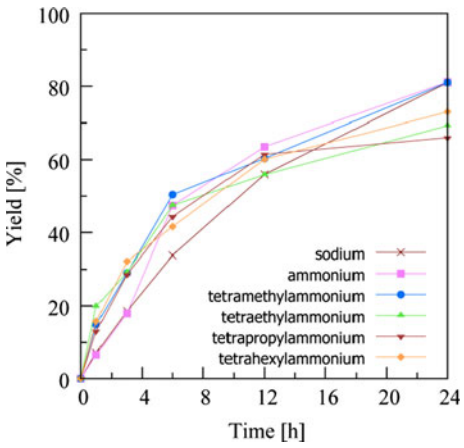
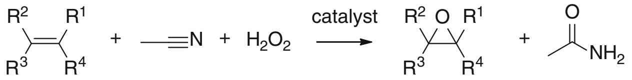
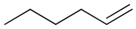
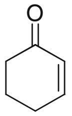
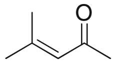
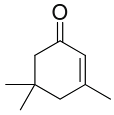
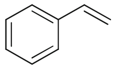
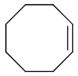
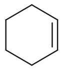
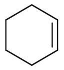


Fig. 2 Epoxidation of cyclohexene using quaternary ammonium bicarbonate salts as catalysts. Reaction conditions: cyclohexene (5 mmol), anisole (ref, 0.5 mmol), acetonitrile (5 ml), 35 % H_2O_2 (10 mmol), catalyst (0.5 ml, 1 M), room temperature

Table 1 Investigation of the substrate scope using the ion exchanged resin catalyst



Entry	Substrate		Time (h)	Conv. (%)	Sel. (%)	Yield (%)
1			24	82	99	81
2			24	99	99	98
3			24	19	94	18
4			24	0	–	–
5			24	32	51	16
6			24	78	99	77
7		1. run	24	68	99	67
		2. run	20	58	99	57
		3. run	20	41	99	41
8[a]			24	0	–	–

Reaction conditions: alkene (5 mmol), anisole (ref, 0.5 mmol), acetonitrile (5 ml), 35 % H_2O_2 (10 mmol), Amberlite-HCO_3 (0.5 g), room temperature

[a] Reference Amberlite-Cl (0.5 g)

bicarbonate forms a very efficient catalytic system for the epoxidation of alkenes with H_2O_2 in DMF or *tert*-BuOH. Considering the many interesting and tuneable properties of ionic liquids [29, 30], we believe that ionic liquids have a large potential as bi-functional solvents for the epoxidation of alkenes [31]. However, since heterogeneous catalysts can be separated by simple unit operations, such as filtration, we also prepared the ion exchanged bicarbonate resin shown in Fig. 1b. The catalyst was tested on a range of different alkenes to investigate the catalytic activity and substrate scope of the reaction, see Table 1.

From Table 1 it is seen that the ion exchanged bicarbonate resin is an active and highly selective catalysts for the epoxidation of simple alkenes. Entry 1 in Table 1 shows that the epoxidation of 1-hexene reached 82 % conversion after 24 h and that the desired product was obtained with excellent selectivity. The α,β-unsaturated ketone cyclohex-2-enone (Entry 2) reached full conversion, while the tri-substituted mesityloxide (Entry 3) only afforded 19 % conversion. Furthermore, no reaction occurred with the more rigid and sterically hindered isophorone molecule (Entry 4). The epoxidation of styrene (Entry 5) reached 32 % conversion in 24 h, but resulted in almost equal amounts of styrene oxide (51 %) and phenylacetaldehyde (49 %) due to isomerisation. Cyclooctene (Entry 6) and cyclohexene (Entry 7) reached 78 and 68 % conversion, respectively, and both epoxides were obtained with excellent selectivity. Entry 7 in Table 1 also shows the heterogeneous bicarbonate catalyst could be separated and reused, although the catalytic activity decreased. Entry 8 shows that no reaction occurred with the untreated resin on chloride-form and confirmed that the bicarbonate anions were the catalytically active species.

In conclusion, the use of quaternary ammonium cations opens up for new homogenous and heterogeneous catalytic systems that can help to overcome the challenges with catalyst separation and reuse in the bicarbonate-catalyzed epoxidation of alkenes with aqueous hydrogen peroxide in acetonitrile. Treating a commercially available ion exchanging resin (Amberlite CG-400 Cl) with $NaHCO_3$ formed an efficient heterogeneous bicarbonate catalyst. The catalyst was tested on a range of aliphatic, cyclic and aromatic alkenes and afforded the desired epoxides with excellent selectivity (up to 99 %) under room temperature and atmospheric pressure.

Acknowledgments We gratefully acknowledge the support of the Danish Council for Independent Research, Grant no. 10-093717L.

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