

Catalytic epoxidation of olefins using MoO₃ and TBHP: Mechanistic considerations and the effect of amine additives on the reaction

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Abstract

Efforts were made at developing a simple catalytic epoxidation system for olefins using MoO₃ and TBHP as terminal oxidant. Conversions of up to 92% and epoxide selectivities of up to $\geq 99\%$ were obtained. The epoxidation reaction was accelerated by the addition of catalytic quantities of pyridine and pyrazole. The highest conversion was obtained with styrene (92%) and the highest selectivity with β -methylstyrene ($\geq 99\%$). For the epoxidation of cyclohexene a number of decomposition products were obtained including a large proportion of 1-(*tert*-butylperoxy)-2-cyclohexene. Preliminary investigations appear to indicate the presence of peroxo Mo(VI) complexes in the epoxidation reaction mixture.

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1. Introduction

The metal catalysed epoxidation of olefins giving epoxides is an important reaction in organic synthesis as such compounds serve as useful intermediates that can be transformed into a variety of other compounds [1,2].

Over the last number of decades transition metal peroxo complexes have been shown to be particularly useful for the homogeneous catalytic epoxidation of olefins most notably the peroxo complexes of early transition metals, like Ti(IV), Mo(VI), W(VI) and Re(VII) [3–5]. Of these metals Re has shown much promise, particularly in the case of methyltrioxorhenium(VII) (MTO), which has shown some excellent results for the epoxidation of olefins [6–11]. However, the use of this catalyst for epoxidation on a large scale is limited by its cost and difficult synthesis. On the other hand, the use of Mo(VI) complexes came to prominence after the discovery in 1969 by Mimoun and coworkers of stable oxo-diperoxo molybdenum(VI) complexes [MoO(O₂)₂L_{*n*}] (L = HMPA, DMF, pyridine etc and *n* = 1,2) capable of epoxidising olefins [12]. Considerable work has been devoted over the last 35 years to the use of such catalysts for olefin epoxidation [13]. One of the high points of this research has been the development of the

Halcon process for the epoxidation of propylene to propylene oxide [14]. Over the years there has been some variation of the Mimoun molybdenum(VI) complex in order to optimise the epoxidising power of the oxo-peroxo Mo(VI) catalyst. Recently Sundermeyer and Wahl have prepared Mimoun molybdenum(VI) complexes of the type, MoO(O₂)₂O-ER₃, E = N, P, As; R = *n*-dodecyl, which were used for the epoxidation of simple olefins with H₂O₂ in a biphasic medium [15]. Thiel has successfully developed a series of pyrazole-pyridine oxidiperoxo molybdenum(VI) complexes bearing various apolar appendages on the pyrazole moiety to enhance the solubility of the complex in organic solvents, and used them in concert with TBHP for the epoxidation of olefins [13]. However, such catalysts have failed to activate H₂O₂. Bhattacharyya and coworkers have prepared a MoO(O₂)₂(saloxH) catalyst which was successfully used with H₂O₂ and catalytic NaHCO₃ for the epoxidation of olefins [16]. Brégeault and coworkers have used anionic mononuclear and dinuclear oxo-diperoxo Mo(VI) complexes for the epoxidation of olefins [17]. Chiral oxo-diperoxo molybdenum(VI) complexes have also been prepared and used in stoichiometric olefin epoxidations [18–20]. In fact, we recently introduced a new chiral oxo-diperoxo-[2-(1-pyrazolyl)-6-menthylpyridine]molybdenum(VI) complex which was screened in both catalytic and stoichiometric asymmetric epoxidation reactions [21]. In these catalytic reactions we have used TBHP as the terminal oxidant. As a simpler

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approach the oxo–diperoxo molybdenum(VI) complexes have been formed in situ for the catalytic epoxidation of olefins. For example, a clever system was devised by Modena and coworkers where the oxo–diperoxo Mo(VI) complex was formed in situ and the reaction conducted in a semi-aqueous environment in the presence of a neutral lipophilic agent. Some good results were achieved, despite the use of 70% H₂O₂ [22].

Taking the lead from Modena and others [22–24] we became interested in the possibility of generating the desired oxo–peroxy and possibly oxo–peroxy Mo(VI) complexes in situ in an anhydrous medium. To achieve this objective we considered the use of MoO₃ and anhydrous TBHP as the terminal oxidant in a non-aqueous solvent on the basis of literature precedence [23,24]. We singled out such a system for these studies owing to the cheap and readily available nature of MoO₃ (also in the literature methods alluded to above, toxic Mo(CO)₆ was used as the pre-catalyst) and the superior solubility of TBHP in hydrocarbon solvents compared with H₂O₂. Our main incentive for developing such a system was to conduct the reaction under anhydrous conditions to avoid any unwanted epoxide ring-opening, particularly in the case of acid sensitive epoxides.

2. Results and discussion

With this strategy in mind, we set about screening a number of simple olefins using our new system (Table 1). This system was based on the system used by Thiel et al. [25] where the olefin, Mo catalyst and TBHP were used in the following ratio—1:0.17:1.1. The reactions were carried out in the first instance without an

added ligand and later in the presence of a ligand to determine if there was ligand acceleration in the reaction like that observed in the analogous MTO epoxidations [6–11]. Of note was the recent report by Imamura and coworkers [26] showing that the heterogenous phase epoxidation of allyl acetate using MoO₃/α-Al₂O₃ and TBHP was accelerated by the addition of pyridine and derivatives.

The reactions were carried out over periods of 1 and 17 h, respectively. For all the reactions studied, the best conversions were obtained after a reaction time of 17 h. It was observed that in the reactions without amine additive the highest reaction conversions (olefin conversion) were obtained with styrene, a conversion of 85% was obtained. The best epoxide selectivity (≥99%) was obtained using β-methylstyrene. Surprisingly in the case of both styrene and cyclohexene, the selectivity increased with reaction time. For example, for styrene the selectivity increased from 85% to 91% (entries 1 and 2) and for cyclohexene increased from 5% to 24% (entries 14 and 18). This could be due to the slowing down of the epoxide decomposition reaction relative to the olefin epoxidation reaction, possibly because of catalyst deactivation.

Pyrazole was the first amine additive to be explored in the epoxidation of styrene due to its pronounced ligand acceleration effect in MTO epoxidations [7] and the loading level used was generally 0.17 mol%. An increase in the reaction conversion from 11% to 44% for the epoxidation of styrene (entries 1 and 3), showed that there was indeed ligand acceleration. The selectivity increased slightly. The conversion and selectivities after 17 h (entry 5) were about the same as for the reactions without any lig-

Table 1
Mo(VI) catalysed epoxidations of simple olefins^a

Entry	Olefin (mmol)	Ligand (mol%)	Reaction time (h)	Conversion ^b (%)	Selectivity ^c (%)
1	Styrene	None	1	11	85
2	Styrene	None	17	85	91
3	Styrene	Pyrazole (0.17)	1	44	91
4	Styrene	Pyridine (0.17)	1	32	96
5	Styrene	Pyrazole (0.17)	17	83	89
6	Styrene	Pyridine (0.17)	17	88	86
7	Styrene	Pyrazole (0.5)	17	76	85
8	Styrene	Pyrazole (5)	17	68	86
9	Styrene ^d	Pyrazole (5)	17	17	63
10	Styrene	Pyridine (6.6)	1	20	88
11	Styrene	Pyridine (6.6)	17	92	65
12	4-Methylstyrene	None	17	42	81
13	β-Methylstyrene	None	17	62	≥99
14	Cyclohexene	None	1	21	5 ^e
15	Cyclohexene	Pyrazole (0.17)	1	31	7 ^e
16	Cyclohexene	Pyridine (0.17)	1	32	5 ^e
17	Cyclohexene	Pyrazole (5)	1	44	6 ^e
18	Cyclohexene	None	17	72	24 ^e
19	Cyclohexene	Pyrazole (0.17)	17	49	33 ^e
20	Cyclohexene	Pyridine (0.17)	17	52	19 ^e

^a The reactions were carried out in dry toluene at 100 °C.

^b Conversion refers to the transformation of olefin to epoxide and decomposition products in some cases.

^c In the case of styrene and 4-methylstyrene the accompanying product was the corresponding aldehyde and in the case of the cyclohexene reactions a number of decomposition products were obtained.

^d Reaction temperature = 50 °C.

^e A number of decomposition products were obtained including a large proportion of 1-(*tert*-butylperoxy)-2-cyclohexene (see Table 2).

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