Catalytic epoxidation of olefins using MoO$_3$ 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 MoO$_3$ and TBHP as terminal oxidant. Conversions of up to 92% and epoxide selectivities of up to ≥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 (≥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 homogenous 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(O$_2$)$_2$L$_n$] (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(O$_2$)$_2$O–ER$_3$, E = N, P, As; R = *n*-dodecyl, which were used for the epoxidation of simple olefins with H$_2$O$_2$ in a biphasic medium [15]. Thiel has successfully developed a series of pyrazole–pyridine oxodiperoxo 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 H$_2$O$_2$. Bhattacharyya and coworkers have prepared a MoO(O$_2$)$_2$(saloxH) catalyst which was successfully used with H$_2$O$_2$ and catalytic NaHCO$_3$ 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

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% H_2O_2 [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–peroxo Mo(VI) complexes in situ in an anhydrous medium. To achieve this objective we considered the use of MoO_3 and anhydrous TBHP as the terminal oxidant in an 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 MoO_3 (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 H_2O_2. 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 MoO_3/α-Al_2O_3 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 ($\geq$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	$\geq$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).

and. Pyrazole was substituted by the stronger heterocyclic amine base, pyridine, and an analogous study to the previous was undertaken. It was established that pyridine, too, accelerated the reaction, but to a lesser extent than pyrazole. An increase of 21% relative to the reaction without ligand was registered after 1 h (entry 4). However, the selectivity increased by about 10% relative to the reaction without ligand, presumably due to preservation of the olefin from Lewis acid catalysed oxirane ring opening. The conversion after 17 h (entry 6) was slightly higher than the reaction without ligand, but the selectivity was slightly lower than both the reaction with pyrazole and the reaction with no ligand. In an attempt to gain an insight into the effect of these ligands on the epoxidation reaction, pyrazole loadings of 0.5 and 5 mol% were used. The effect of increasing the amine additive, was to lower the olefin conversion. For instance, on increasing the pyrazole loading from 0.17 to 0.5 mol% the conversion dropped by 7% (entry 7) and from 0.17 to 5 mol% it dropped by 15% (entry 8). Occupation of vacant sites on the metal by the amine thus impeding alkyl peroxy complex formation is presumably the reason for this drop in olefin conversion. The selectivities remained constant, thus implying that the effect of increased pyrazole was to perhaps deactivate the putative alkyl peroxy Mo(VI) complex. In the case of pyridine, the situation was similar, increased ligand concentration led to a drop in olefin conversion. For instance, at a loading of 6.6 mol% when compared with the 0.17 mol% loading level after 1 h the conversion dropped by 12% (entry 10) and the selectivity dropped by 8%. However, after 17 h the conversion was roughly the same as that carried out at the 0.17 mol% loading level (entry 6), but the selectively dropped by 20%. These results would imply that instead of protecting the oxirane ring, at increased concentrations pyridine would appear to actually promote activation of the Mo(VI) species responsible for oxidative cleavage of the epoxide [21,27].

From an experiment aimed at determining the temperature dependence of this reaction, styrene was reacted at 50 °C with 5 mol% pyrazole over a 17 h period (entry 9). It was established that at this temperature the epoxidation reaction was sluggish (17% conversion), but surprisingly the oxidative cleavage reaction of the epoxide was quite active, as the selectivity dropped from 86% to 63%.

Both 4-methylstyrene and β-methylstyrene gave lower conversions than styrene, 42% and 62% over a 17 h period (entries 12 and 13), respectively. The epoxide selectivity obtained with β-methylstyrene was excellent (≥99%) but in the case of 4-methylstyrene it was lower than that obtained using styrene.

With the more nucleophilic olefin: cyclohexene, the conversions after 1 and 17 h were, 21% and 72%, respectively (entries 14 and 18). In the first instance, on adding both pyridine and pyrazole (at the 0.17 mol% level) the conversion increased by 10% over a 1 h period (entries 15 and 16), and later by increasing the quantity of pyrazole to 5 mol% the conversion rose to 44% (an increase of 22% on the reaction without ligand). These results clearly demonstrate ligand acceleration in the epoxidation reaction. However, after 17 h the conversions were lower, 49 and 52%, respectively (entries 19 and 20). This is presumably due to pronounced ligand induced deactivation of the active Mo(VI) species over longer periods. The selectivities were poor, the best selectivity (33%) was obtained with pyrazole (0.17 mol%) over a 17 h period (entry 19). A number of epoxide decomposition products like: 2-cyclohexen-1-ol (**2**), 2-cyclohexen-1-one (**3**), *trans*-1,2-cyclohexanediol (**4**), and in all cases a substantial amount of 1-(*tert*-butylperoxy)-2-cyclohexene (**5**), a compound that is also formed in the catalytic epoxidation of cyclohexene with alumina-supported Mn(II), Co(II), Ni(II) and Cu(II) bis(2-hydroxyanil)acetylacetone complexes and TBHP [27], but as far as we are aware, has never been reported in catalytic epoxidations using Mo(VI) complexes. The distribution of the decomposition products, including the epoxide **1** is shown in Table 2.

One can see from both Tables 1 and 2 that the epoxide selectivity increases over time. This fact may be a consequence of deactivation of the catalytic species responsible for oxirane ring opening and other oxidative reactions. In all cases the major product was 1-(*tert*-butylperoxy)-2-cyclohexene (**5**). The results would seem to indicate that peroxide **5** is formed rapidly via decomposition of the initial epoxide **1**. There appears to be little difference between the reaction with and without ligand as regards the amount of compound **5** formed, as both the ligand catalysed reactions and non-ligand catalysed reactions gave roughly equal percentages of this compound (Table 2; entries 1,

Table 2
Products obtained from the Mo(VI) catalysed epoxidation of cyclohexene
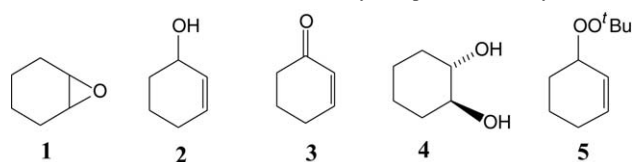
| Entry	Ligand (mol%)	Time (h)	Conversion (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)	**5** (%)
1	None	1	21	5	3	0	6	86
2	None	17	72	24	5	1	15	55
3	Pyrazole (0.17)	1	31	7	0	2	5	86
4	Pyrazole (0.17)	17	49	33	8	7	11	41
5	Pyrazole (5)	1	44	6	2	5	1	86
6	Pyridine (0.17)	1	32	5	2	0	4	89
7	Pyridine (0.17)	17	52	19	4	7	0	70
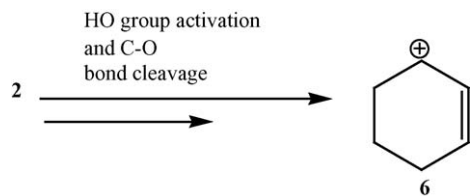
Scheme 1.

3 and 6). We believe that peroxide **5** is formed via S_N1 attack of TBHP on the putative reactive cyclohexenyl cation **6** which could be formed by suitable activation of 2-cyclohexen-1-ol (**2**) followed by cleavage of the O–C bond (Scheme 1). Over longer reaction times the diol **4** is formed, however, in the presence of pyridine over the 17 h period no diol **4** was detected, presumably it was converted to 2-cyclohexen-1-ol (**2**) which should result from dehydration of this diol.

At this juncture one can only speculate on the mechanism of these catalytic epoxidation reactions. As the reaction mixtures were yellow in colour we assumed that oxo–peroxo complexes might be present. In their study of the mechanism of the Mo(VI) catalysed epoxidation of olefins using alkylperoxides, Sharpless and Chong first considered the possibility of peroxo complexes being the active catalysts for the epoxidation of the olefins and proposed the following mechanistic pathways for the formation of peroxo complexes (Scheme 2) [24]. However, in the same paper Sharpless and Chong discounted the role of peroxo complexes in the epoxidation of the olefins, on the basis of experimental evidence using ^{18}O labelled Mo catalysts (the terminal oxo groups of the pre-catalyst were expected to contain an ^{18}O label) in favour of a mechanism which included as the active catalyst a coordinated alkyl hydroperoxide complex of the type 7 or 9 (Scheme 2).

In our particular case it was important to try and identify the active catalytic species involved in the reaction. Was the active catalyst a peroxo species of the type **8** (Scheme 2) or was it a coordinated alkyl hydroperoxide complex of the type **7** (Scheme 2) or **9**? Could di-peroxo complexes be formed? As a preliminary study we decided to carry out a reaction between MoO$_3$ and TBHP to establish if *tert*-butanol was formed in this reaction. The presence of *tert*-butanol would be an indication of the presence of peroxo species based on the mechanistic pathways shown in Scheme 2. MoO$_3$ and TBHP (2.1 equiv.) were heated at 100 °C for several hours, the yellow coloured solution obtained was filtered and analysed quantitatively by GC. *tert*-Butanol was indeed found (to show that all the *tert*-butanol did not come from the TBHP solution used we also analysed this solution to determine the amount of *tert*-butanol it contained) and we determined the yield of *tert*-butanol to be 19% (relative to the MoO$_3$), which would imply that peroxo intermediates were highly likely to be present and in reasonable amounts. The same solution was evaporated to dryness giving a yellow gum, which upon spectroscopic analysis appeared to contain a mixture of compounds whose identity is not known at this point. We also detected TBHP in solution (72% relative to the starting quantity) and our analysis showed that the amount of TBHP that reacted relative to the MoO$_3$ used was 60%. The filtered solid (84% based on the initial mass of MoO$_3$) was analysed spectroscopically and apart from containing MoO$_3$ it appeared to contain other species whose identity at this juncture is not certain. These findings were interesting and would support the hypothesis that both peroxo (presumably an oxo–peroxo species) and a coordinated alkyl hydroperoxide species were present. Mimoun et al. [28] have previously evoked such an hypothesis. These results would seem to indicate that most of the catalytic species involved in the reaction are adsorbed on the
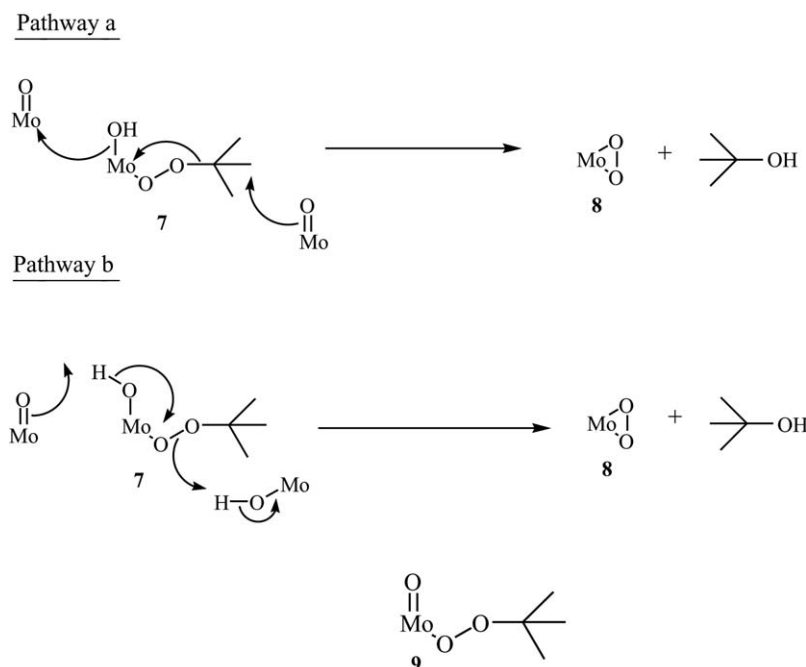
Scheme 2.
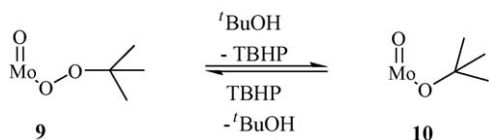
Scheme 3.

solid phase and the epoxidation reaction, takes place principally on the liquid–solid interface. In the actual epoxidation reaction coordination of the peroxo or coordinated alkyl hydroperoxide species with the olefin should solublise the active catalytic species. It must be noted that that the ratio of solvent to MoO_3 in this reaction (ca. 11.5:1) is much lower than that for the actual epoxidation reaction (ca. 4×10^4:1). Although the fine details of this particular reaction mechanism at this point remain elusive, it would be safe to assume on the basis of the Sharpless–Chong [24] study that the active catalyst is a coordinated alkyl hydroperoxide species. These authors also referred to the possibility of exchange between coordinated alkyl hydroperoxides and oxo alkoxides, and on this basis an equilibrium of the type shown in Scheme 3, between an alkyl oxo-hydroperoxide (**9**) and an oxo-*tert*-butoxide (**10**) might be possible.

The reaction acceleration observed in these epoxidation reactions could be the result of one or a combination of the following: (1) activation of the active Mo(VI) catalyst(s) by the amine, (2) activation of the oxygen transfer from the peroxo Mo(VI) or coordinated alkyl hydroperoxide complex to the olefin by amine coordination or (3) deprotonation of the TBHP forming the more reactive alkyl peroxide intermediate.

3. Conclusions

A range of olefin substrates was epoxidised using a catalytic system consisting of MoO_3 and TBHP in anhydrous toluene with and without the presence of aromatic amines like pyridine and pyrazole. Some very good conversions and excellent selectivities were obtained. Ligand acceleration was observed in these reactions. In the case of styrene the greatest ligand acceleration was obtained using 0.17 mol% pyrazole and in the case of cyclohexene both pyrazole and pyridine gave comparable acceleration rates. A preliminary experiment was conducted to gain an insight into the nature of the catalytic species involved in this epoxidation reaction and it indicated that both peroxo (most likely oxo–peroxo species) and coordinated alkyl hydroperoxide species appeared to be present. The results reported here are of a preliminary nature and currently we are trying to: (1) identify the putative peroxo and coordinated alkyl hydroperoxide species present in the reaction and (2) to establish the identity of the key catalytic active species involved in the epoxidation reaction.

4. Experimental

4.1. General information

The MoO_3 99.5% used was purchased from Sigma, all other reagents were obtained from Sigma-Aldrich, Lancaster-Synthesis or Acros. ca. 5.5 M TBHP in nonane (Fluka) stored over molecular sieves was used. Toluene was dried using a standard procedure [29].

Gas chromatographic (GC) analyses of the products obtained from the epoxidation reactions were performed on a Hewlett Packard (HP) 6890 series instrument equipped with a flame ionization detector (FID). The chromatograph was fitted with a cyclosil-B capillary column (30 m, 250 μm, 0.25 μm) (Agilent 112-6632) or alternatively with a Hewlett Packard HP-5 column (30 m, 320 μm, 0.25 μm).

The ^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AMX300 (^1H: 300.13 MHz and ^{13}C: 75 MHz) or a Bruker Avance (^1H: 400.13 MHz and ^{13}C: 100.61 MHz) instrument using $CDCl_3$ as solvent and TMS as internal standard (for measurements made with the Bruker AMX300 instrument) and the signal from residual $CHCl_3$ as an internal standard (for the measurements made with the Bruker Avance instrument).

Infra-red spectra were measured with a Perkin-Elmer Paragon 1000 model.

In all cases, the olefin conversions were calculated by simply determining the ratio of the peak areas for the olefin substrate and the reaction products.

Quantitative GC analysis was used to determine the yield of *tert*-butanol (from a calibration curve with $R^2 = 0.9993$) and the conversion of TBHP in the mechanistic study.

4.2. Catalytic reactions

4.2.1. General procedures for the Mo(VI)/TBHP catalysed epoxidation of olefins

To a two-necked flask fitted with a reflux condenser was added: MoO_3 (2.4 mg, 0.017 mmol), ligand (0.017 mmol), TBHP (2 mL, 11 mmol), dry toluene (1 mL) and the olefin (10 mmol) as a solution in 3 mL of toluene. The mixture was heated to 100 °C under an atmosphere of nitrogen. At the end of the reaction period the reaction mixture was analysed by GC. See Tables 1 and 2 for the results.

The reaction was performed in exactly the same manner without ligand.

4.3. Mechanistic study

MoO_3 (0.26 g, 1.81 mmol) was added to TBHP (0.7 mL, 3.85 mmol) followed by the addition of toluene (2–3 mL) and the suspension heated to 100 °C for 17 h. The white solids were filtered washed with toluene and the filtrate analysed by GC.

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