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Review

Chiral oxoperoxomolybdenum(VI) complexes for enantioselective olefin epoxidation: Some mechanistic and stereochemical reflections

Anthony J. Burke*

Departamento de Química and Centro de Química de Évora, Universidade de Évora, Rua Romão Romalho 59, 7000 Évora, Portugal

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Contents

Abstract

Ever since the discovery of oxidation catalysts of the type $MoO(O_2)_2L_n$, ($n = 1–2$, L = H_2O, DMF, HMPA, Py) concerted efforts have been made by various groups to prepare or generate in situ chiral versions that lead to high asymmetric induction in either stoichiometric or catalytic olefin epoxidation reactions. To-date the highest enantioselectivity obtained was 81% obtained using a pre-prepared chiral Mo(VI)-oxodiperoxo containing chiral α-hydroxyamide ligand. Reports on using chiral Mo(VI)-oxodiperoxo complexes prepared in situ are exceedingly rare and what has been reported mentions no enantioselectivity. In this review we look at these efforts, highlighting their inherent limitations and suggest some new approaches which might enhance the asymmetric inductive powers of these catalysts in olefin epoxidation.

Keywords: Oxodiperoxomolybdenum(VI); Asymmetric catalysis; Epoxidation; Chiral ligands

1. Introduction

Transition metal peroxo and peroxy complexes have played for some time now an important role in the epoxidation of alkene substrates to their respective epoxide products. In this regard Mo(VI) complexes are an important class of oxidants for this type of reaction and quite a number of studies have been conducted [1]. Much of the impetus for this research has in many ways been due to the seminal contributions by Mimoun et al. in 1969 [2] and the development earlier of the Arco process [3] and the Halcon process [4]. Despite the enormous effort that has gone into developing these processes, far lesser progress has been made over the years in obtaining highly stereoselective versions of this reaction using oxoperoxo Mo(VI) chiral complexes at either the stoichiometric or catalytic level. In this review, (i) we look at the efforts that have been made to date on the synthesis and application of oxoperoxo Mo(VI) chiral complexes for the epoxidation of olefins (chiral dioxomolybdenum(VI) complexes have already recently been reviewed elsewhere [5] and thus does not warrant review here) and (ii) highlight the main difficulties that prevent the attainment of high enantioselectivities with this system.

2. Chiral oxoperoxomolybdenum(VI) complexes and the enantioselective epoxidation of olefins

After Mimoun et al. [2] demonstrated the use of molybdenum(VI)-oxodiperoxo complexes of the general formula **1** ($n = 1–2$, L = H_2O, DMF, HMPA, Pyr) (Fig. 1) for the epoxidation of olefins using molecular oxygen as the terminal oxidant [2], it became an open challenge to obtain a chiral analogue of this type of complex and conduct the first enantioselective epoxidation of olefins with such chiral oxidants.

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* Tel.: +351 266745310; fax: +351 266744971.
E-mail address: ajb@dquim.uevora.pt.

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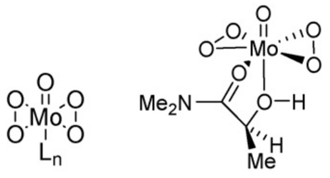
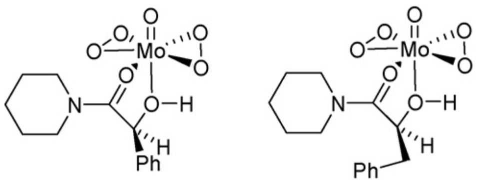


1 **2**

Fig. 1. The Mimoun Mo(VI)-oxodiperoxo complex **1** and Schurig's chiral Mo(VI)-oxodiperoxo analogue **2**.



3 **4**

Fig. 2. The Mo(VI)-oxodiperoxo complexes developed by Yoon and co-workers.

In 1978 Schurig et al. [6a] reported the preparation of an optically active Mo(VI)-oxodiperoxo complex **2** (Fig. 1) and it's application in the enantioselective epoxidation of *trans*-but-2-ene [6a]. X-ray crystallographic studies have shown that complex **2** had a pentagonal-bipyramidal structure with the (*S*)-*N*,*N*-dimethyl-lactamide (DMLA) moiety responsible for the introduction of chirality in the molecule [6b]. The olefin could be transformed to in all cases the *trans*-(1*R*,2*R*)-but-2-ene oxide with a yield of 70% and an ee of up to 34%. Shortly afterwards, Kagan et al. [7] reported a catalytic version of this reaction, when they showed that a range of olefins could be epoxidized enantioselectively using only 10 mol% of **2**. The highest ee obtained was only 35%, again for the epoxidation of *trans*-but-2-ene. It was argued that this result was due to enantiofacial discrimination of the olefins and that kinetic resolution leading to enrichment of the enantiomers was not likely [7].

Mimoun then tested some chiral monodentate ligands and discovered that there was no observable asymmetric induction [8]. In attempts to decipher the mechanism of oxygen transfer in this epoxidation reaction, Modena and co-workers carried out a series of reactions with chiral Mo(VI) catalysts as chiral tools to probe it's mechanism. The highlight of this work was the use of complex **2** for the epoxidation of *trans*-oct-2-ene under the same conditions as used by Schurig et al. to give the major enantiomer with 36% ee [9]. These workers have also shown, that certain chiral monodentate ligands, like, (−)-menthyl-phosphoric triamide and *N*,*N*-dimethyl-(−)-menthylamine *N*-oxide, can be used to give enantioselective epoxidations (albeit low, 7–9% ee) which was contrary to the findings of Mimoun [8]. However, unfortunately, these studies were unable to provide clear-cut evidence on the mechanism of oxygen transfer from the Mo(VI)-peroxo complex.

Besides reactions using complex **2**, Schurig et al. [10] prepared a number of other chiral Mo(VI)-oxodiperoxo complexes based on a series of enantiomerically pure hydroxyamides like, (*S*)-piperidine lactamide (PLA), (*S*)-*N*,*N*-dimethyl-3-phenyllactamide (DMPLA), (*S*)-2-hydroxy-3-methylbutanoic acid piperidineamide (HMBPA), (2*S*,3*S*)-2-hydroxy-3-methylpentanoic acid piperidineamide (HMPPA), (*S*)-3-hydroxybutanoic acid piperidineamide (HBPA), (*S*)-*N*-acetylprolinol (AcPro) and (*S*)-*N*-benzoylprolinol (BzPro) and evaluated them in a series of stoichiometric epoxidations of olefins. Prochiral, chiral racemic and chiral non-racemic olefins were used in this study. The best results were obtained using *trans*-but-2-ene with the complex derived from (*S*)-piperidinelactamide, [$MoO(O_2)_2$·PLA, (49% ee)] and (*S*)-3-methylpent-1-ene with either $MoO(O_2)_2$·PLA (51% ee for the 2*S*,3*S* diastereomer and 49% for the 2*R*,3*S* diastereomer) or with $MoO(O_2)_2$·DMLA **2** (51% for the 2*S*,3*S* diastereomer and 49% for the 2*R*,3*S* diastereomer). It was also found that the reaction enantioselectivity was inversely dependent on the degree of alkyl substitution present in the olefin substrate, as the reaction ee decreased in the following order: prop-1-ene > but-1-ene > 3-methylbut-1-ene. There was a preferential formation of (*R*)-alkyloxiranes. The chiral hydroxyamide ligands mentioned above with a variety of structural differences were screened with an objective at gaining some insight into the influence of: (a) the size of the amide component, (b) the degree of branching of the alkyl substituents, (c) presence of an additional stereogenic centre, and (d) the type of chelate ring formed by the ligand with the metal, on the enantioselectivity of the reaction. These effects were studied in reactions with *trans*-but-2-ene at 23 and 0 °C. It was established that when the steric bulk in the main chain of the ligand was increased depending on the type of amide ligand there was an increase or decrease in the ee. For example, in the case of the dimethyl amide series there was a significant increase at 23 °C on going from (*S*)-DMLA to (*S*)-DMPLA, but on the contrary, in the piperidinamide series there was a significant decrease at 0 °C on going from (*S*)-PLA to (*S*)-HMBPA. The presence of a second stereogenic centre in the ligand [present in (*2S,3S*)-HMPPA] gave inferior enantioselectivities compared to the single stereogenic centred ligands. The type of chelate ring the ligand formed with the metal was also shown to affect the enantioselectivity of oxirane formation, as the enantioselection increased in the following order: seven-membered chelate [(*S*)-BzPro and (*S*)-AcPro], six-membered chelate [(*S*)-HBPA], five-membered chelate [(*S*)-DMLA and (*S*)-PLA].

It was also established that the addition of optically pure 1,2-alkanediol additives enhanced the ees of the oxirane products. For instance, in the case of the epoxidation of *trans*-but-2-ene with $MoO(O_2)_2$·PLA and one equivalent of (2*S*,3*S*)-butanediol the corresponding enantiomeric epoxide was obtained with 93% ee. It was suggested that subsequent kinetic resolution of the oxirane products by a hitherto unknown Mo-diol catalyst led to this enantiomeric enrichment.

In 2000, Yoon and co-workers reported the preparation of the Mo(VI)-oxodiperoxo complexes based on (*R*)-piperidinylphenylacetamide **3** (Fig. 2) and (*R*)-piperidinylmandelamide **4** (Fig. 2) and the first report of a catalytic epoxidation using this type of complex when both (*E*)- and (*Z*)-β-methylstyrene were transformed to the corresponding epoxides [11].

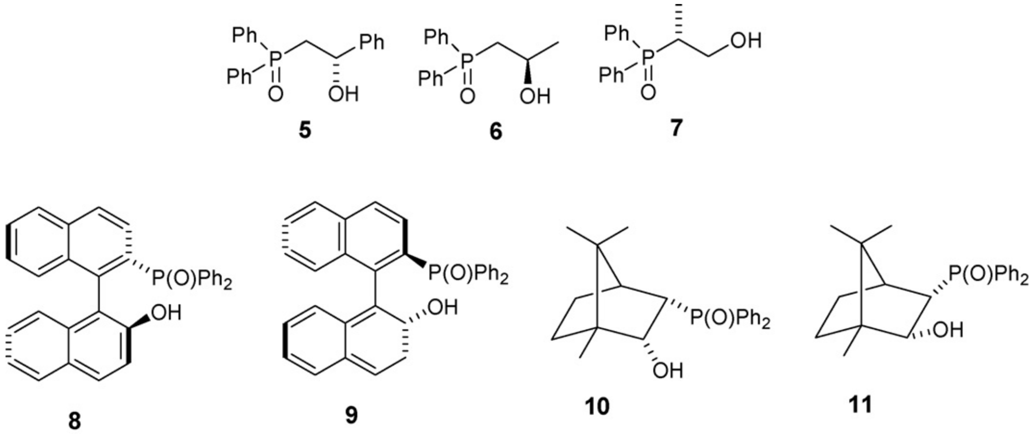


Fig. 3. The phosphinoylalcohol ligands used by Stirling and co-workers [12].

Using only 10 mol% of the isolated Mo(VI)-oxodiperoxo complexes **3** and **4** in concert with *tert*-butylhydroperoxide (TBHP) which was used as the terminal oxidant, they were able to achieve moderate to good ees (26–81%). The highest ee (81%) was obtained using (*E*)-β-methylstyrene and complex **4**. The yields were moderate.

Shortly before, Youn and co-workers reported their results, Stirling and co-workers reported their work on the use of chiral phosphinoylalcohol complexes of Mo(VI) for the epoxidation of a number of olefins [12]. The complexes were obtained from the chiral phosphinoylalcohols (Fig. 3) and $MoO(O_2)_2$ using a modification of the procedure of the Mimoun protocol. It was suggested that the P=O group coordinates with the Mo centre (see Fig. 4). The resulting complexes were screened in a number of epoxidation reactions with both terminal and di-substituted olefins using two types of conditions, stoichiometric and catalytic. The ees determined fell in the range 2–39% (see Table 1, for some selected results). In the case of complex $MoO(O_2)_2\cdot$**11** the epoxidation was conducted with both hept-1-ene and 3,3-dimethylbut-1-ene using both stoichiometric conditions (the mechanism most likely involves a direct attack of the olefin on one of the peroxo oxygen atoms [13]) and catalytic conditions, using TBHP as terminal oxidant, and though the ees were very low, approx. 3% in both cases, it was the catalytic reaction with it's different mechanism (most probably that which has been suggested by Thiel [14a,b]) that gave the best results (Table 1, compare entries 7 and 8).

The authors ruled out a mechanism of coordination of the olefin to the metal centre and opted for a scenario in which two or more mechanisms were at work for which the predominance of a single one being determined by the actual reaction conditions used. They also suggested with the aid of a model (Fig. 4) that both O_1 and O_3 should be the transferred oxygen atoms as they lie nearest the chiral ligand, and they asserted that given the fact that the environment near O_1 is different to that around O_2 it is the rate of oxygen transfer that dictates the degree of enantioselectivity in the reaction.

Table 1
Stoichiometric and catalytic epoxidation of hept-1-ene using $MoO(O_2)_2$ **5**–**11** [12]

Entry	Complex	Conversion (%)	ee (%)
1	$MoO(O_2)_2$**5**	72	<2
2	$MoO(O_2)_2$**6**	55	0
3	$MoO(O_2)_2$**7**	77	<2
4	$MoO(O_2)_2$**9**	39	9
5	$MoO(O_2)_2$**10**	47	23
6	$MoO(O_2)_2$**11**	80	8
7	$MoO(O_2)_2$**12**	35	3
8	$MoO(O_2)_2$**12**	>70	3

The reactions in entries 1–7 were performed under stoichiometric conditions, 10 equivalents of olefin were used relative to complex. In entry 8 catalytic conditions were used (5 mol% catalyst).

In 2004, Brito et al. [15] reported the preparation of the first chiral Mo(VI)-oxodiperoxo complex **12** containing a pyridine–oxazoline ligand (Fig. 5) for which an X-ray crystal structure was obtained (the structure shown in Fig. 5 is based on this analysis). This was used in the catalytic epoxidation (2.5 mol% catalyst) of cyclooctene and (*R*)-limonene **14** using

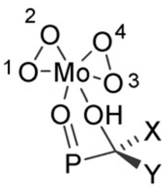


Fig. 4. Model presented by Stirling and co-workers to explain the asymmetric induction observed in this reaction (the Mo=O bond is hidden by the Mo atom).

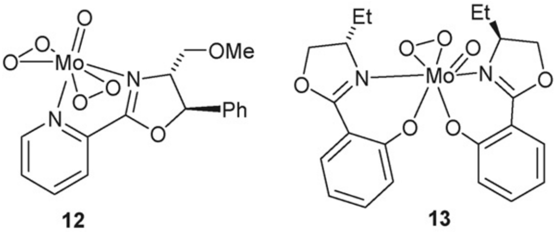
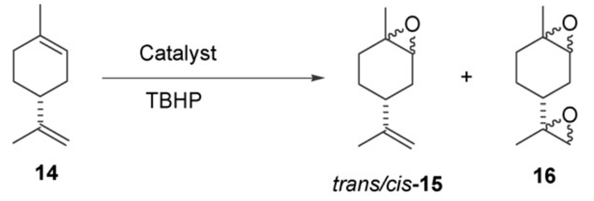


Fig. 5. The chiral Mo(VI)-oxodiperoxo pyridine–oxazoline complex **12** and Mo(VI) oxo-monoperoxo bis(pyridine–oxazoline) **13** of Brito et al. [15].



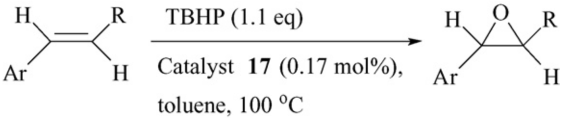
Scheme 1. Epoxidation of (*R*)-limonene using Mo(VI) catalysts **12** and **13** by Brito et al. [15].

TBHP as terminal oxidant. In the case of the latter substrate **14** (Scheme 1), only the mono epoxide **15** (22% combined yield) was obtained as a 1:1 mixture of the *cis* and *trans* isomers. No ees were described [15]. These workers also isolated and characterised the novel chiral bis(phenolate–oxazoline) monoperoxo Mo(VI) complex **13** with a pseudopentagonal bipyramidal geometry (the structure shown in Fig. 5 is based on X-ray crystal analysis), that was also used to epoxidise cyclooctene and (*R*)-limonene **14**. In this case both *trans*- and *cis*-**15** (62% combined yield) were obtained in a ratio of 3:2 along with some di-epoxide **16** (2%) and a trace amount of alcoholic products. Again, there was no mention of the ees for either *trans*- or *cis*-**15**, nor any mention of the types and ratios of di-epoxide **16** stereoisomers formed (enantiomers or diastereomers).

In 2006, Carreiro et al. [16] reported the synthesis of the first chiral 2-(1-pyrazole)pyridineoxodiperoxomolybdenum(VI) complex **17** (Fig. 6, including the X-ray crystal structure), which was used in a series of stoichiometric and catalytic olefin epoxidations.

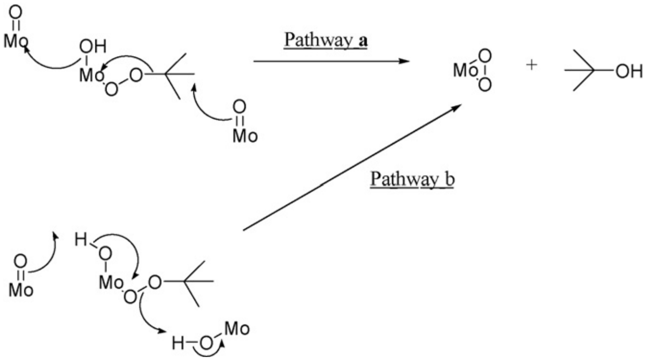
In the case of the catalytic epoxidation reactions, TBHP was used as the terminal oxidant and poor ees of 1–6% were obtained (Table 2). An excess of styrene was treated with complex **17** and although no epoxide was isolated, only benzaldehyde, it was suggested that this was the result of epoxide decomposition due to the severe reaction conditions used. Later an excess of cyclohexene was reacted with complex **17** and in this case the corresponding epoxide was obtained along with cyclohexane-1,2-diol. This result led the authors to suggest that in catalytic olefin epoxidations with complex **17** and TBHP there could be two possible mechanisms at work: (i) that suggested by Thiel [14] which involves oxygen transfer from the coordinated alkylperoxide appendage and (ii) direct transfer of an oxygen to the olefin from one of the peroxo oxygen atoms of complex **17** [13].

Table 2
Catalytic epoxidation of simple olefins using complex **17**



Entry	Olefin	Time (h)	Conversion	Epoxide ee (%)
1	Styrene	1	31	2
2	Styrene	17	86	1
3	*trans*-β-Methylstyrene	5	28	0
4	4-Methylstyrene	1	37	5
5	4-Methylstyrene	6	44	6
6	4-Methylstyrene	17	49	nd

nd = not determined, due to the small quantity of epoxide formed.



Scheme 2. Mechanisms for the conversion of a coordinated alkyl hydroperoxide Mo(VI) species to an oxoperoxo Mo(VI) complex [20].

In an attempt to develop a novel procedure of enantioselectively epoxidising olefins using in situ formed chiral complexes by mixing MoO_3, TBHP and a chiral ligand, Carreiro and Burke [17] on the basis of literature precedent [18,19], conducted a study to determine the feasibility of this approach after they showed that for the epoxidation of a number of olefins with MoO_3 and TBHP some heterocyclic aromatic amines (e.g. pyridine and pyrazole) accelerated the reaction. From the observation of the presence of significant quantities of *tert*-butanol in the product mixture it was postulated that both oxoperoxo Mo(VI) (the proposed mechanism for the formation of the oxoperoxo Mo(VI) complex is shown in Scheme 2 [20]) and coordinated alkyl hydroperoxide Mo(VI) species were present

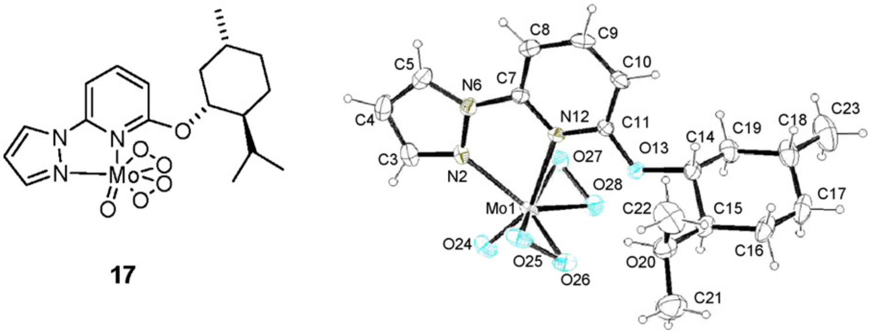


Fig. 6. (Left) Complex **17**. (Right) X-ray crystal structure of complex **17**. This drawing has previously appeared in Ref. [16].

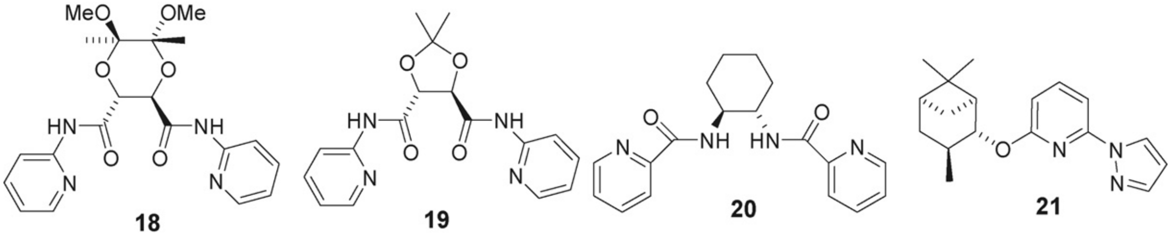


Fig. 7. Chiral bis-pyridinamides and pyridine–pyrazole ligands for Mo(VI) catalysed olefin epoxidations.

[17]. However, it was emphasised that the active oxidant should be the coordinated alkyl hydroperoxide Mo(VI) species.

In the follow-up publication by this group [21], a series of chiral pyridines and pyrazoles were used in order to try and form chiral alkyl hydroperoxide Mo(VI) species in situ. The ligands studied are shown in Fig. 7.

No enantioselectivity was observed in these reactions. Given the fact that it was not possible to isolate or even detect the presence of any catalytic species (despite the realisation of extensive NMR studies) the observation of ligand acceleration (which was especially noticeable using ligand **20**) and an increase in reaction conversion on increasing the quantity of ligand **20** by 0.5 mol% in one particular epoxidation, implied the presence of a chiral catalytic species [21]. This result was not unexpected from literature precedent, as Sharpless and co-workers reported that chiral molybdenyl bishydroxymates $[O_2Mo(hydroxymate)_2]$ gave enantioselectivities of <2% [22]. Lack of enantioselectivity was put down to the following reasons: (1) perhaps there were other chiral or achiral Mo(VI) peroxy or peroxo species in solution competing with the principal oxoperoxy complex (multiple catalytically active species, which had been alluded to by Mitchell and Finney [23]), (2) the labile nature of the peroxy appendage, particularly at the high temperature applied during the reaction, leading to the generation of a number of competing diastereomeric transition states and (3) fast on/off exchange of the ligands or part of the ligands from the coordination sphere of the Mo(VI) peroxy complex. In fact, weak coordination was suggested recently by Yamamoto and co-workers [24] to explain the lack of success achieved with this epoxidizing system and Chong and Sharpless had also suggested that there might be exchanges between coordinated alkyl hydroperoxides and alkoxides [20] which has recently been substantiated by Veiros et al. [25] on the basis of some DFT calculations.

Very recently Burke and Monteiro [26] conducted a study to establish if an actual Mo(VI) peroxo complex was formed in the reaction, this study was conducted with H_2O^{18} to form $O^{18}MoO_2$ using the same approach as Chong and Sharpless [20] only with styrene as the olefin substrate. It was determined from high resolution mass spectrometric analysis that there was no incorporation of O^{18} into the styrene oxide product, thus eliminating the possibility that Mo(VI) peroxo complexes are formed in this reaction.

Up until now on the basis of the findings of Carreiro and Burke [17], it had been assumed that a Mo(VI)-oxoperoxo complex was present during the reaction due to the presence of significant quantities of *tert*-butanol in the product mixture. The mechanism for its formation was suggested to be one or both of the mechanisms shown in Scheme 2 [17]. However, what was not considered by this group at the time was the propensity of certain transition metal complexes containing Fe(III) [27], Ru(II) [28], V(V) [29] and others [30] to decompose TBHP to the corresponding *tert*-butoxyl radical giving *tert*-butanol after proton abstraction. Given the similarity of the Mo(VI) oxidising system to such systems, a free radical pathway to *tert*-butanol with the formation of a hitherto unknown oxo-Mo complex is a distinct possibility. In fact, Mimoun et al. [31] have alluded to the presence of radical intermediates in the epoxidation of olefins by vanadium(V) oxo peroxo complexes.

3. Asymmetric induction: why isn't it better?

It was mentioned above that fast on/off exchange of the ligands or part of the ligands from the coordination sphere of the Mo(VI) peroxy complex could have been the reason for the lack of enantioselection in the system studied by Carreiro et al. [21]. This is perhaps the key reason why only poor to moderate enantioselectivities are obtained using oxoperoxo Mo(VI) catalysts for olefin epoxidation. Over the last ten years Thiel and co-workers have conducted in depth studies on this catalytic reaction using 2-(pyrazol-3-yl)pyrdinyloxodiperoxo Mo(VI) complexes in both homogenous [14] and heterogeneous phases [32]. In one particular study by this group [33] using both NMR experiments (temperature-dependent two dimensional NOESY experiments) and DFT calculations, evidence was obtained to show that ligand dissociation appeared to occur (the activation energies necessary (89–110 KJ/mol in Thiel's study) for this ligand dissociation are provided by the high temperatures required for the successful epoxidation reactions). This finding by Thiel and co-workers quite probably identifies the principle reason why the asymmetric induction is so weak in such systems. Another important reason in the case of the oxodiperoxo Mo(VI) complexes, a point which has previously been alluded to by Stirling and co-workers [12], is that in principle the two electrophilic oxygen atoms are disposable to the incoming nucleophilic olefin and due to the symmetric disposition of the two peroxo groups both enantiomers of the oxirane product should be obtained (see the model depicted in Fig. 8). Obviously, in most cases, the rates of oxygen transfer to olefin are different, but not enough to provide high enantioselectivities and perhaps ligand dissociation from the metal is the reason why the rates of oxygen transfer are not significantly different. This

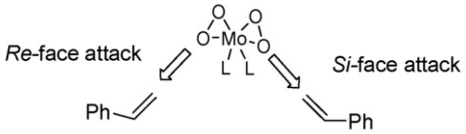


Fig. 8. Model to show that differential oxygen transfer leads to opposite enantiomers (for the sake of clarity styrene is chosen as the olefin substrate).

could also be the reason why good ees have been impossible to obtain using MTO with chiral ligands [5a,34], as in this case a reactive oxodiperoxo Re(VII) species is involved and ligand coordination is known to be weak [5a,34].

4. Conclusions and perspectives

In this review, we have encountered a number of chiral oxoperoxo Mo(VI) complexes which have been used in various stoichiometric and catalytic reactions, the general problem encountered in almost all cases is the paucity of good enantioselectivity. This is probably the result of ligand dissociation, and in the case of the diperoxo complexes the availability two transferable oxygen atoms that lead to opposite enantiomers of the oxirane product. The solution to this problem may be attainable if: (1) stronger non-dissociating chiral ligands are used, (2) in the case of the diperoxo complexes the difference in rate of oxygen transfer from the two peroxo ligands is accentuated and (3) more effort is expended on the synthesis and evaluation of chiral monoperoxo ligands bearing strongly coordinating chiral ligands.

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