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Metal catalyzed oxidations. Part 5. Catalytic olefin epoxidation with seven-coordinate oxobisperoxo molybdenum complexes: a mechanistic study [1]

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Abstract

Oxobisperoxo molybdenum complexes with chelating pyrazolylpyridine ligands catalyze the epoxidation of olefins by activation of the oxidizing agent (*t*-BuOOH or H_2O_2). The reaction mechanism is supported by spectroscopic and kinetic investigations.

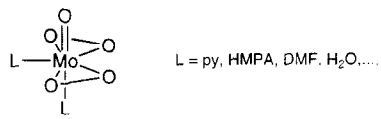
Keywords: Epoxidation; Peroxo complexes; Molybdenum; Mechanism

1. Introduction

Epoxides are usually obtained by oxygen transfer from an 'active oxygen species' to the olefin. Percarboxylic acids are normally used as stoichiometric reagents in organic syntheses, mostly generated in-situ from H_2O_2 and the corresponding carboxylic acids. Hydrogen peroxide and alkyl hydroperoxides can be activated for epoxidation by catalytic amounts of a multitude of high valent transition metal compounds [2]. Enantioselective olefin epoxidation, catalyzed by chiral transition metal complexes, is just one milestone in the rapid progression of this area of research [3].

In 1969, Mimoun et al. described new seven-coordinate molybdenum peroxo complexes (Scheme 1) [4], leading to a new class of epoxidation catalysts.

Stabilized by strong σ-donating monodentate ligands, these complexes can either act as epoxidation catalysts or as stoichiometric reagents. While the mechanism of the stoichiometric reaction was subject of a number of publications, the mechanism of the catalytic reaction is still controversially discussed [5]. Monodentate ligands undergo dissociation reactions and therefore cause problems in spectroscopic and kinetic investigations. On the other hand bidentate ligands, like 2,2′-bipyridine, give insoluble complexes [6]. Consequently, the optimization of



Scheme 1.

[1] For Part 4 of the series: see [1].

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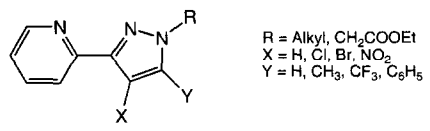
catalytic activity and selectivity of these systems was not described yet. We therefore decided to synthesize new chelating ligands, substituted with long aliphatic side chains. With these ligands, structurally defined and soluble peroxo complexes for NMR investigations should be accessible.

2. Results and discussion

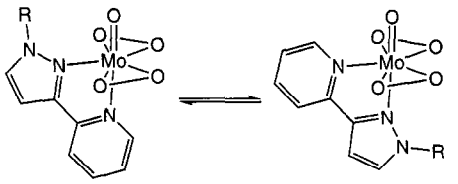
Starting from *N*-alkylsubstituted 2-(pyrazol-3-yl)pyridines (Scheme 2), we were able to synthesize a whole series of molybdenum oxobisperoxo complexes, which turned out to be high active catalysts for olefin epoxidation [7]. The ligands can be obtained in high yields from commercially available starting materials.

Due to long alkyl side chains (octyl or octadecyl) these catalysts are well soluble in nonpolar organic solvents, even in *n*-hexane or toluene. This is essential for the synthesis of sensitive epoxides, as the ringopening reaction is suppressed in these solvents [8]. Besides, the high solubility enables detailed spectroscopic investigations on the reaction mechanism. Electron donating or withdrawing substituents (see Scheme 2) allow the optimization of the activity of these catalysts, which will be discussed later on.

One crucial question of these investigations concerned the coordinative stability of the chelate complexes. EXCY experiments proved that the two isomers, which result from the asymmetric structure of the chelate ligand, are in equilibrium in solution (Scheme 3) and that this process does not proceed via a dissociation of the ligand [9]. Even in trifluoroacetic acid the peroxo complexes are only slowly protolyzed [1]. Therefore no dissociation of the chelate



Scheme 2.



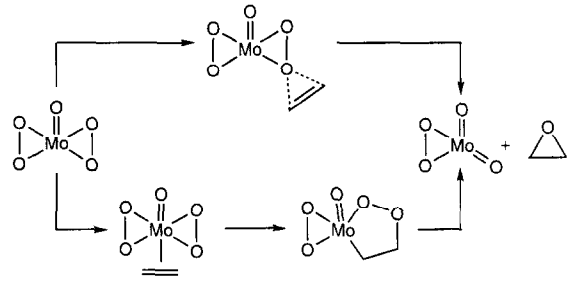
Scheme 3.

ligand should take place under the conditions of the catalytic olefin epoxidation.

However, a dissociation of the ligand is required for one of the two reaction mechanisms accepted in literature (Scheme 4). It enables the coordination of the olefin to the Lewis-acidic molybdenum center, followed by an insertion into a Mo–O bond and release of the epoxide by a cycloreversion reaction [5]a. The oxygen atom is transferred from a η^2-peroxo ligand. It is obvious that this can not be the proper mechanism for our chelate complexes. The alternative mechanism bases on a spirocyclic transition state, the oxygen atom is again transferred from a η^2-peroxo ligand to the olefin [5]b.

To get a deeper insight into the oxygen transfer step, we synthesized a series of pyrazolylpyridine ligands with olefinic side chains and investigated the corresponding molybdenum peroxo complexes [10]. Fig. 1 shows the X-ray structure analysis of the propenyl derivative. No inter- or intramolecular interactions of the olefinic group with the molybdenum center or one of the oxygen atoms of the oxo or the peroxo ligand were observed. These complexes are completely stable in the solid state.

For NMR investigations of the oxygen transfer step we synthesized the highly soluble cy-



Scheme 4.

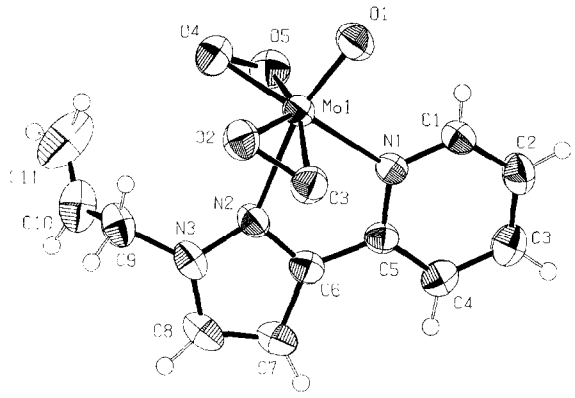


Fig. 1. Crystal structure of the propenyl substituted molybdenum peroxo complex.

clooctenylmethyl derivative. The results are shown in Fig. 2.

Again this complex is remarkably stable, as 60 min after the start of the NMR experiment no autoepoxidation is observed. However, the oxidation of the olefinic moiety starts immediately after the addition of *t*-butylhydroperoxide. Both isomers of the starting compound are converted into the corresponding epoxides, which can be assigned by the signals of two methylene units with diastereotopic protons for each isomer. From this experiment it is obvious that an oxygen atom of the hydroperoxide is transferred to the olefin, the peroxo complexes act as activators of the oxidizing agent. Therefore the mechanism should be complementary in its fundamental steps to the mechanism of the 'Sharpless epoxidation' of allylic alcohols [5]c. In the first step the oxidizing agent coordinates to the Lewis acidic Mo(VI) center (A) followed by proton transfer from the hydroperoxide to a peroxo ligand (B). η^2 coordination activates the alkyl hydroperoxide (C) for oxygen transfer (D). The resulting alcoholato ligand abstracts the proton from the hydroperoxo ligand, which regenerates the bisperoxo complex (Scheme 5).

This reaction mechanism requires a high Lewis acidic metal center coordinated with proton accepting ligands (peroxo, alcoholato, carboxylato, acetylacetonato or halogeno ligands). The influence of the solvent and the oxidizing agent on the catalytic activity of the system can

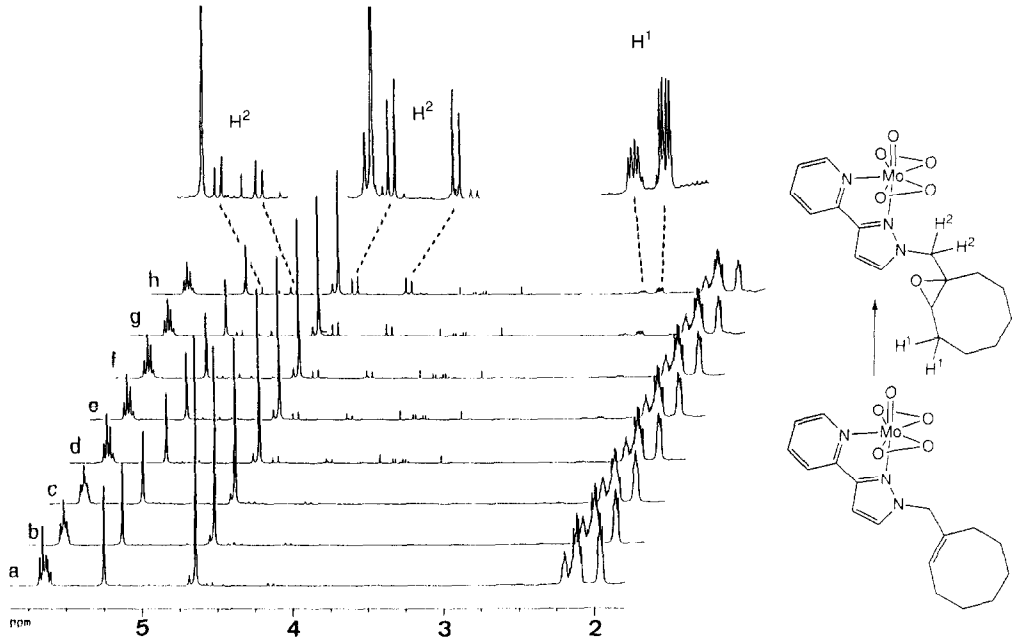
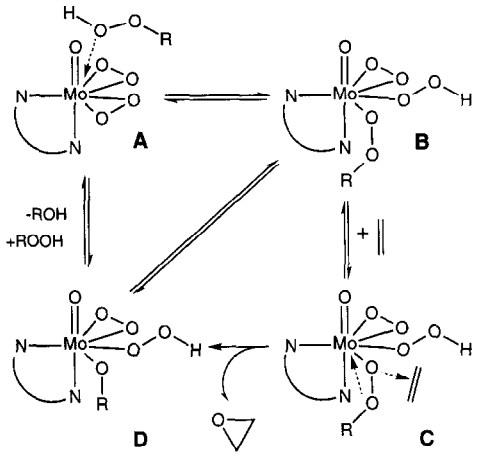


Fig. 2. Reaction of the cyclooctenylmethyl substituted molybdenum peroxo complex with *t*-BuOOH (NMR experiment): (a) peroxo complex in $CDCl_3$, (b) after 15 min, (c) after 1 h, (d) after addition of 4.3 equiv. of *t*-BuOOH, (e) 30 min after addition, (f) 1 h after addition, (g) 2 h after addition, (h) 3 h after addition; the signals of the aromatic protons and a part of the cyclooctenylprotons are omitted.



Scheme 5.

be understood from this mechanism. Coordinating solvents compete with the hydroperoxide for a coordination site at the molybdenum center and therefore decrease the activity of the system. Higher reaction rates are observed for the more basic *t*-butylhydroperoxide than for H_2O_2.

Kinetic investigations proved a temperature depending activation period, which is characteristic for the formation of an active species (e.g., compound B in Scheme 5) from a precursor compound (Fig. 3). We assume that this catalytically active species is a hydroperoxo, alkylperoxo complex.

One crucial point of this mechanism is the proton transfer step, which is controversially discussed for catalysts with oxo ligands. Model reactions of ^{17}O-labelled oxobisperoxo complexes with different Brønsted and Lewis acids

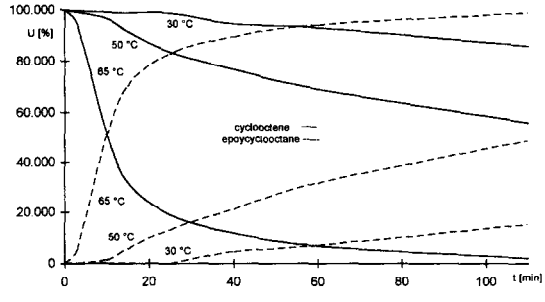
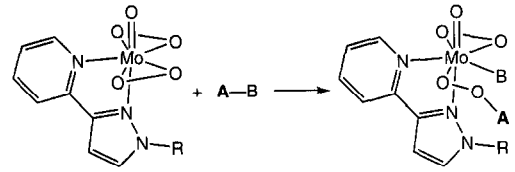


Fig. 3. Kinetics of the epoxidation of cyclooctene (with *t*-BuOOH in $CHCl_3$), catalyzed by 2-(1-octyl-3-pyrazolyl)pyridine oxodiperoxo molybdenum(VI) at different temperatures.



A—B = $CF_3C(O)$—OC(O)CF_3, Me_3Si—Cl

Scheme 6.

showed that these reagents attack preferentially at the η^2-peroxo ligands. The oxo ligand is an extremely poor proton acceptor (Scheme 6) [1].

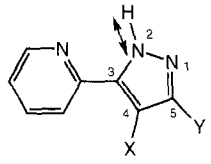
These experiments are supported by extended Hückel (EH) calculations [11] of the model complex $(NH_3)_2MoO(O_2)_2$ [1]. We found that the three highest occupied molecular orbitals, which differ only about 0.1 eV in energy, have mainly π^* character at the peroxo ligands but only very low σ^* and π^* character at the oxo ligand. Proton transfer from the oxidizing agent to a η^2-peroxo ligand should therefore be more favorable than proton transfer to the oxo ligand.

As far as we know from our studies, the Lewis acidity of the metal center is one criterion for its catalytic activity. The introduction of electron donating or withdrawing substituents at the pyrazole as well as at the pyridine ring of the ligands allows now to tune the basicity of the chelate system and therefore the Lewis acidity of the molybdenum center. For this reason we synthesized a series of substituted pyrazolypyridines and used the N–H stretching vibration as a sensor for the electronic situation of the pyrazole fragment (Table 1, Scheme 7) [12].

For 3- and 3,4-substituted pyrazoles the 1-H tautomer is usually the most stable one. How-

Table 1
N–H stretching frequencies of substituted pyrazolylpyridines

Substituent	ν(N–H)
5-CH_3	(3511), 3444, (3391)
4,5-H	3445
5-Ph	3437
4-Cl	3429
4-Br	3427
5-CF_3	3421
4-NO_2	3401



Scheme 7.

ever, for our pyrazolylpyridines the 2-H tautomer was found to be more stable than the 1-H tautomer, by computational methods (AM1 calculations) [12]. The reason for this is a strong dipole–dipole interaction between the proton at the pyrazol and the lone pair of the pyridine nitrogen atom. Correlation of the N–H stretching frequencies with the turn over frequencies, which we obtained from the catalytic epoxidation of a standard system (cyclooctene, *t*-BuOOH, $CHCl_3$) [8], proves that electron withdrawing substituents in 4- or 5-position of the pyrazole ring lead to an increase of catalytic activity (Fig. 4). The same effect is observed if we change from the octyl to the acetylester substituent at N1 or by substitution of the pyridine against a pyrazine fragment.

3. Conclusion and perspectives

The optimization of a ligand system, which is commonly carried out for the optimization of activity and/or selectivity of a known catalyst, is also a useful tool for spectroscopic investigations on mechanistic questions. We were able to show that our molybdenum oxobisperoxo complexes do not catalyze the olefin epoxidation by transferring an oxygen atom of a peroxo ligand, but by activation of a hydroperoxide (e.g. *t*-BuOOH, H_2O_2, etc.), which gave rise to a new reaction mechanism. Our spectroscopic studies and our kinetic data prove the elemental steps of this mechanism, which involves the coordination of the hydroperoxide to the metal center and a proton transfer reaction. Another important result is that the chelate ligand does not dissociate during the catalytic cycle. With this information we now work on the enantioselective catalytic epoxidation of unfunctionalized olefins with these peroxo complexes. Schurig et al. already showed that molybdenum oxobisperoxo complexes with ligands derived from (S)-lactic acid give enantiomeric excesses up to 30% and more in stoichiometric reactions [13].

4. Experimental

4.1. General

The syntheses of the catalysts were carried out as described elsewhere [7,12]. All NMR experiments were performed on a Bruker DPX

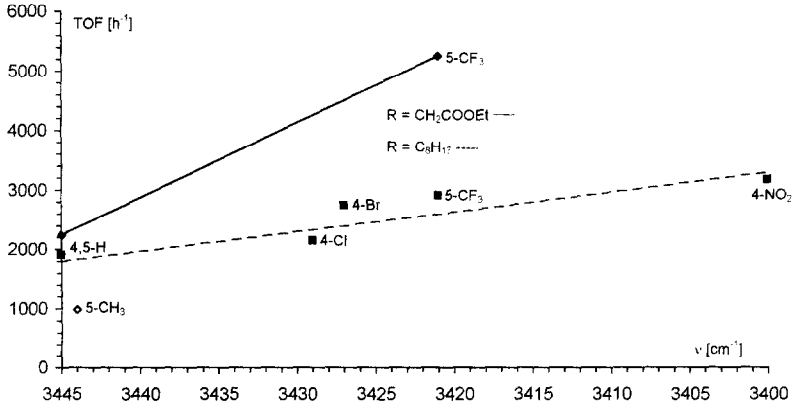


Fig. 4. Correlation of the N–H stretching frequencies of substituted pyrazolylpyridines with catalytic epoxidation activities (cyclooctene, *t*-BuOOH) of the corresponding oxobisperoxo molybdenum complexes.

400 spectrometer in 5 mm NMR tubes equipped with a rubber septum for the addition of the reagents [1]. We used a Hewlett-Packard HP 5890 gaschromatograph (capillary column: HP-1, 30 m, i.d. 0.25 mm) for kinetic investigations of catalytic epoxidation reactions. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR and AM1 calculations were carried out with the MOPAC 6.0 package under the INSIGHT II graphical user interface (Fa. Biosym) on a Silicon Graphics 4D25 workstation.

4.2. Catalytic olefin epoxidation

1.00 g (9.07 mmol) of cyclooctene, 1.00 g (7.75 mmol) of dibutylether and 25 ml of chloroform were mixed in double wall Schlenk tube (closed by a rubber septum) and heated to 65°C, using a LAUDA thermostat. After the addition of 13.0 mg of the molybdenum peroxo catalyst, 1.7 ml of a 5.35 M (9.10 mmol) solution of dry *t*-BuOOH in $CHCl_3$ were added via a syringe. Samples for GC investigations were taken with a PE-syringe without opening the reaction tube.

Acknowledgements

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