Metal-Catalyzed Oxidations, 10[‡]

New Insights into the Mechanism of Hydroperoxide Activation by Investigation of Dynamic Processes in the Coordination Sphere of Seven-Coordinated Molybdenum Peroxo Complexes

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Dedicated to Prof. O. Nuyken on the occasion of his 60th birthday

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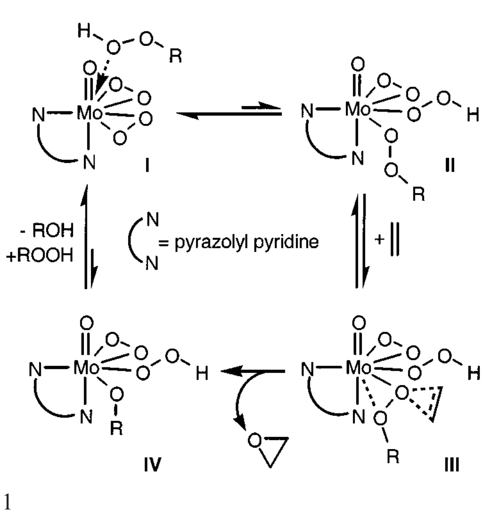
Seven-coordinated molybdenum oxobisperoxo complexes with chelate nitrogen donors like pyrazolylpyridines are catalysts for the epoxidation of olefins. An NMR spectroscopic and quantumchemical study on the fluxionality of the chelate ligand proves that during this process partial ligand dissociation takes place. This gave rise to a detailed theoretical study on the activation of CH_3OOH at the model complex $(NH_3)_2MoO(O_2)_2$ including dissociation of one of the ammonia ligands and proton transfer from the hydroperoxide to one of the peroxo ligands.

Introduction

During the last decades, a series of mechanistic studies on the olefin epoxidation with hydroperoxides catalyzed by high-valent transition metal complexes was carried out to get a deeper insight into the elementary steps of the activation of the oxidising agent,[2–5] but also to understand the transfer of chirality in the synthetically important enantio- and diastereoselective epoxidation of allylic alcohols.[6] As a result of these investigations, it is more and more accepted that the activation of alkyl hydroperoxides (ROOH) is performed by an intermediate η^2-coordination of the peroxidic agent to the Lewis acidic metal centre.[7–12] This is considered to be an "umpolung" of the electron rich alkyl peroxide allowing an electrophilic attack to the olefin. The intermediate alkyl peroxo complexes are usually generated by ligand exchange from suitable precursor complexes, but some transition metal alkyl peroxo complexes have been isolated[13–21] and a few exhibiting η^2-coordination of ROOH have been structurally characterised.[9,10,22] An analogous sequence may be postulated when hydrogen peroxide is used as the oxidising agent, but the final prove of a M–OOH structural motive is still lacking.

We investigated the mechanism of the olefin epoxidation with seven-coordinated molybdenum peroxo complexes of the type $MoO(O_2)_2(L–L)$ (L–L = pyrazolylpyridine ligand) during the last years[23–28] and were able to show that these complexes do not transfer oxygen from one of the η^2-O_2 ligands to the olefin, neither via a spirocyclic transition state nor by precoordination of the olefin to molybdenum as it was postulated in the literature. Instead, they act as activators of the oxidising agent ROOH as it is known from other high valent transition metal complexes. Based upon these results, a new mechanism for the olefin epoxidation with molybdenum peroxo complexes could be proposed (Scheme 1), wherein the oxidising agent coordinates to the Mo^{VI} centre (**I**), undergoes a proton transfer to one of the peroxo ligands (**II**) and is activated for oxygen transfer by η^2-coordination (**III**). This mechanistic idea was supported by a series of experiments especially concerning the proton transfer and kinetic aspects.[25,26]



Scheme 1

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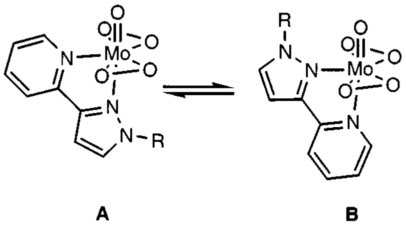
Owing to the asymmetric nature of the ligand bearing two different nitrogen donor centres, these peroxo complexes exist in two isomeric forms **A** and **B**, which differ in the orientation of the aromatic rings relative to the axial oxo ligand and which are in equilibrium in solution (Scheme 2, R = alkyl, $-CH_2COOEt$). This special feature gave us insight into the role of the Lewis acidity of the metal centre which can be tuned by the donor properties of the chelate ligands and allowed for the first time to establish a quantitative relationship between the structure of an epoxidation catalyst and its activity.[27]



Scheme 2

In the present paper, we report on the NMR spectroscopic investigation of the isomerisation process (**A** $\rightleftarrows$ **B**). In addition to the kinetic and thermodynamic data obtained herein, this investigation opens up the door to the activation of ROOH at peroxo complexes, which we elucidated by means of computational methods.

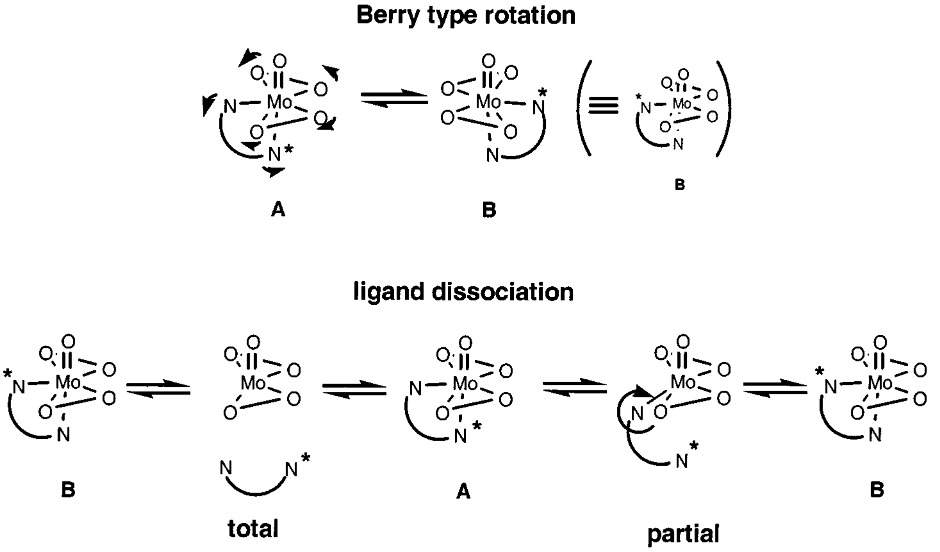
Results and Discussion

For long, the existence of the two isomers **A** and **B** was discussed as a more or less static phenomenon, since simple temperature dependent NMR experiments did not show any significant change in the spectra of the pyrazolylpyridine complexes up to a temperature of 100 °C. This simple image had to be improved when the fluxionality of these systems was preliminarily examined[29] by one dimensional spin transfer experiments, which allow the determination of slow dynamic processes.[30,31]

From a formal point of view, the isomer equilibration (**A** $\rightleftarrows$ **B**) can be achieved either by a Berry-type process of ligand fluxionality (Scheme 3, top) or by ligand dissociation (either complete or partial dissociation; Scheme 3, bottom).

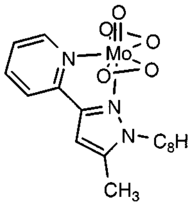
While a Berry-type rotation may be considered unfavourable due to the chelating ligands (pyrazolylpyridine, η^2-O_2-), ligand dissociation from the high valent transition metal centre Mo^{VI} will also be an endothermic process. For a more accurate and extended determination of these processes and the related kinetic and thermodynamic data, the oxobisperoxo molybdenum complexes **1–4**, bearing pyrazolylpyridine ligands with different substituents at the pyrazole moiety, were investigated by temperature-dependent two dimensional NOESY[32] experiments. A common feature of the peroxo complexes investigated are positive entropies of activation (ca. 42–76 $JK^{-1}mol^{-1}$), which prove a dissociation to take place in the rate determining step of the equilibration and therefore rule out a Berry-type rotation. The energies of activation derived from the kinetic data are found in a range of ca. 89–110 $kJmol^{-1}$ (Table 1).

Since these NMR experiments do not allow to distinguish between a partial and a complete ligand dissociation, we investigated the dissociation process by quantum chemical calculations on the model complex $MoO(\eta^2$-$O_2)_2(NH_3)_2$ using density functional theory (B3LYP-method[33–35] with LanL2DZ* basis set[36–39]) . The complex geometries resulting from these calculations are in good agreement with the bond parameters obtained from X-ray structure analysis of analogous molybdenum peroxo complexes.[23,24,28,40–42] Figure 1 shows a comparison between the calculated structural parameters and those of oxodiperoxo[3-(2-pyridyl)-1-pyrazolylacetic acid ethyl ester]molybdenum(VI).[23] All calculated bond lengths are found slightly too long, which is due to the applied method.[43] Only the distance between the apical NH_3 ligand and the

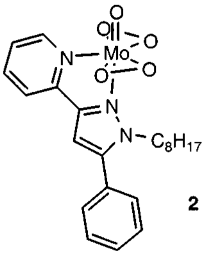


Scheme 3

Table 1. Activation parameters (from NOESY data) for the isomer equilibration of some molybdenum peroxo complexes



1



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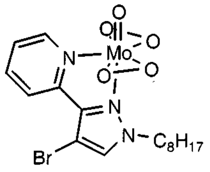

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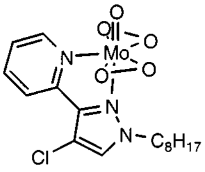


4

	1	2	3	4
E_A	111.0	108.1	97.1	89.1
$\Delta H^{\ddagger}$	108.4	105.6	94.6	86.6
$\Delta S^{\ddagger}$	76.2	77.0	71.0	42.7

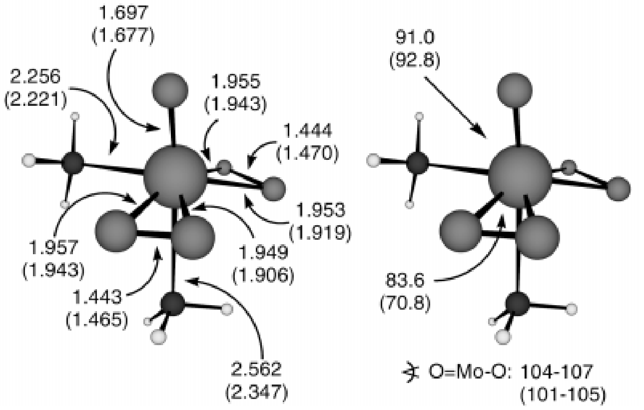


Figure 1. Calculated (DFT) bond lengths (left side) and bond angles (right side) of $MoO(\eta^2\text{-}O_2)_2(NH_3)_2$ compared with values obtained by X-ray structure analysis (in parentheses)[23]

molybdenum centre is calculated much too long, implicating a flat PES (potential energy surface). The same feature has already been described for the ligated water molecule in the rhenium peroxo complex $ReO(\eta^2\text{-}O_2)_2(CH_3)(H_2O)$ by Rösch et al.[44]

Ligand dissociation obviously is an endothermic process: we calculated 56.2 $kJmol^{-1}$ for the dissociation of the axial NH_3 ligand, about 165 $kJmol^{-1}$ for the dissociation of the equatorial NH_3 ligand, and 241.9 $kJmol^{-1}$ for the dissociation of both NH_3 ligands (Figure 2, Table 2). While calculation of $MoO(\eta^2\text{-}O_2)_2$(*ax*-NH_3)(*eq*-NH_3) (**a**), $MoO(\eta^2\text{-}O_2)_2$(*eq*-NH_3) (**c**), and $MoO(\eta^2\text{-}O_2)_2$ (**d**), resulted in stable geometries, geometry optimisation of the axially-coordinated isomer **b** lead to **c**. Therefore, the dissociation energy related to isomer **b** could just be obtained by a single point calculation.

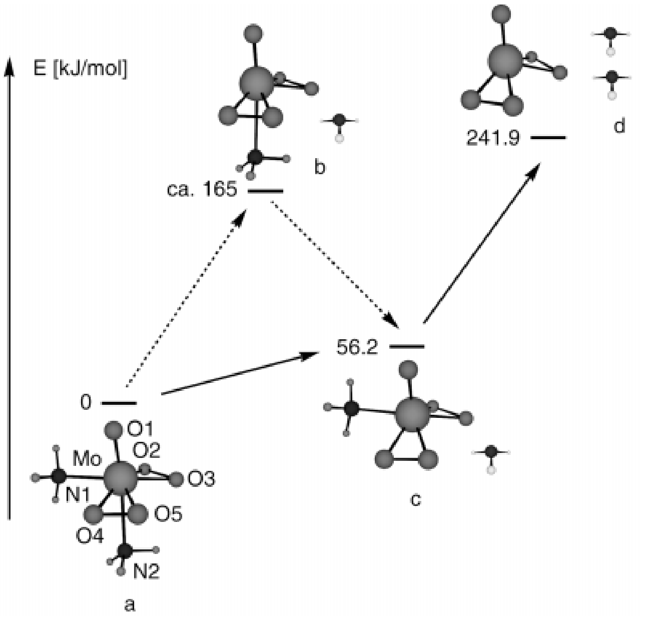


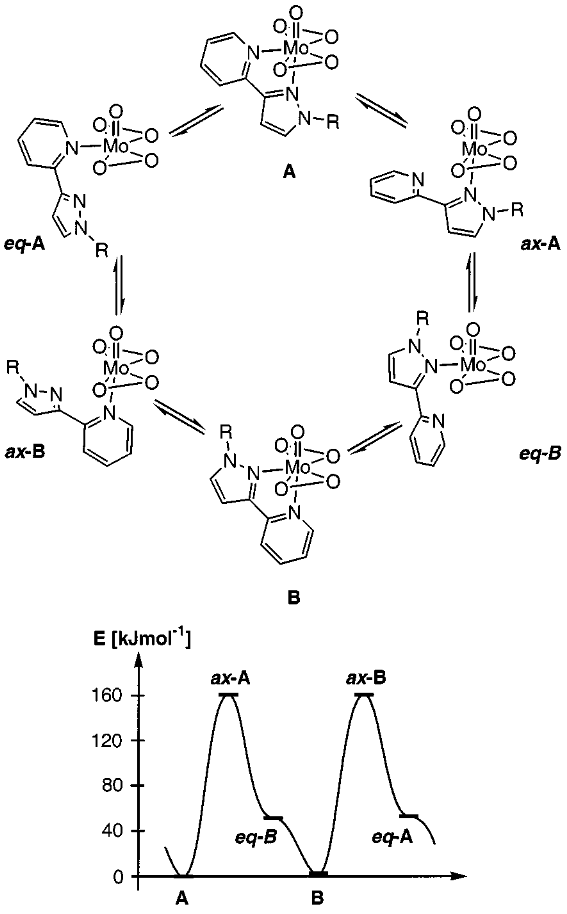
Figure 2. Energy profile (DFT) of the subsequent dissociation of NH_3 ligands from of $MoO(\eta^2\text{-}O_2)_2(NH_3)_2$

Table 2. Dissociation energies and structural features (DFT) of the complexes shown in Figure 2

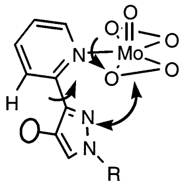
	a	b[a]	c	d
		Energy [$kJmol^{-1}$]		
	0[b]	ca. 165	56.2	241.9
		Bond lengths [Å]		
Mo–N1	2.256	–	2.242	–
Mo–N2	2.562	2.563	–	–
Mo–O1	1.697	1.697	1.692	1.683
Mo–O2	1.955	1.955	1.926	1.910
Mo–O3	1.953	1.953	1.950	1.944
Mo–O4	1.957	1.957	1.926	1.910
Mo–O5	1.949	1.949	1.949	1.944
O2–O3	1.444	1.444	1.446	1.431
O4–O5	1.443	1.443	1.446	1.431

[a] The dissociation energy to complex **b** was obtained by a single point calculation, the bond parameters were taken from compound **a**. – [b] By definition.

As the geometry of the $MoO(\eta^2\text{-}O_2)_2$ centre does not change dramatically by addition of one or two NH_3 ligands (Table 2), the energies of activation obtained from the NMR experiments should be somehow related to one of the calculated dissociation energies. Since 242 $kJmol^{-1}$ for the complete ligand dissociation is far from the experimentally found value of about 100 $kJmol^{-1}$, we propose a partial ligand dissociation as the key step in the isomerisation process. This agrees with the observation that peroxo complexes of this type undergo a relatively slow decomposition in the presence of excess trifluoroacetic acid (after 15 min about 10–15% of decomp.) in $CHCl_3$ solution.[45] A complete dissociation of the chelate ligand would give rise to a rapid protonation of the liberated ligand and precipitation of a polymeric molybdenum peroxide. Additionally the catalytic activity of the complexes strongly depends on the substituent pattern of the donor ligand, which also makes a complete ligand dissociation unfavourable. Based on the quantum chemical calculations, spectroscopic investigations and reactivity studies, the isomerisation process depicted in Scheme 4 is proposed.



Scheme 4



Scheme 5

Since we could not find a stable axially coordinated intermediate $MoO(\eta^2-O_2)_2(ax-NH_3)$ in our calculations, the compounds ***ax*-A** and ***ax*-B** may be discussed as transition states in the isomerisation sequence. The species ***eq*-A** and ***eq*-B** represent flat minima or saddle points of the PES, which correlates with the dissociative nature of the rate determining step.

While the activation energies obtained from the NOESY kinetics qualitatively reflect the strengths of the Mo–N bonds to be broken and therefore the donor potencies of the appropriate chelate ligands, the entropies of activation give an idea about the increase of ligand fluxionality after partial dissociation. They should depend on the substitution pattern of the pyrazolyl fragment: bulky substituents in 4-position (Br) as well as substituents forming H interactions with the proton in the 3-position of the pyridine ring (Cl) will hinder the free rotation around the pyrazole–pyridine bond (Scheme 5) and decrease the entropy of activation (Table 1).

Beside the clarification of the equilibration process, these investigations may open up a new insight into mechanistic details of the olefin epoxidation with seven-coordinated molybdenum peroxo catalysts. The intermediate $16e^-$ complex **II** of the postulated epoxidation mechanism (Scheme 1) still may undergo a η^2-coordination of the alkyl hydroperoxide to give the activated species **III** ($18e^-$). However, its Lewis acidity should be rather moderate and the derived eight-coordinated species **III** can be considered as sterically overcrowded, which makes the activation process unfavourable. In contrast, partial ligand dissociation would open a coordination site at the molybdenum centre for coordination/activation of the alkyl hydroperoxide, and additionally enhance its Lewis acidity. For that reason, we investigated by quantum chemical calculations the interaction of methyl hydroperoxide (CH_3OOH) with both, the seven-coordinated model system $MoO(\eta^2-O_2)_2(NH_3)_2$ (**a**) and its six-coordinated congener $MoO(\eta^2-O_2)_2(eq-NH_3)$ (**c**), which has been calculated to be just about 56 $kJmol^{-1}$ higher in energy.

A first interaction of a hydroperoxide with a seven-coordinated peroxo species of the type **I** (Scheme 1) may result either from a hydrogen bond between one or both of the peroxo ligands, an attack of one of the Lewis basic oxygen atoms of the hydroperoxide at the molybdenum center, or by a combination of both. For the first mode as a series of stable geometries were found by computational calculations ($\mathbf{e_1}$, $\mathbf{e_2}$, $\mathbf{e_3}$). Despite the well-known fact that density functional theory is not the best method for the calculation of weak interactions like hydrogen bonds,[46] we believe that the geometries and energies we found may give an impression about the first approach of a hydroperoxide to the peroxo complex. The hydrogen bonded system is stabilised by 46.6 to 67.7 $kJmol^{-1}$ compared to free $MoO(\eta^2-O_2)_2(NH_3)_2/CH_3OOH$ (Figure 3, Table 3). Taking into account that one of the ammonia ligands also forms hydrogen bonds to the hydroperoxide in all the calculated structures and that the calculations do not include any solvent effect, the calculated energies reflect quite well the energy of an intermolecular hydrogen bond in complex **5** (Scheme 6, S = solvent), which was estimated to 8–20 $kJmol^{-1}$ by NMR spectroscopic investigations.[28] **5** forms intramolecular H-bonds to an η^2-O_2 ligand in nonpolar solvents like chloroform, intermolecular H-bonds to the solvent in polar solvents like acetone and intermolecular H-bonds to an η^2-O_2 ligand of another peroxo complex in the solid state structure.[28]

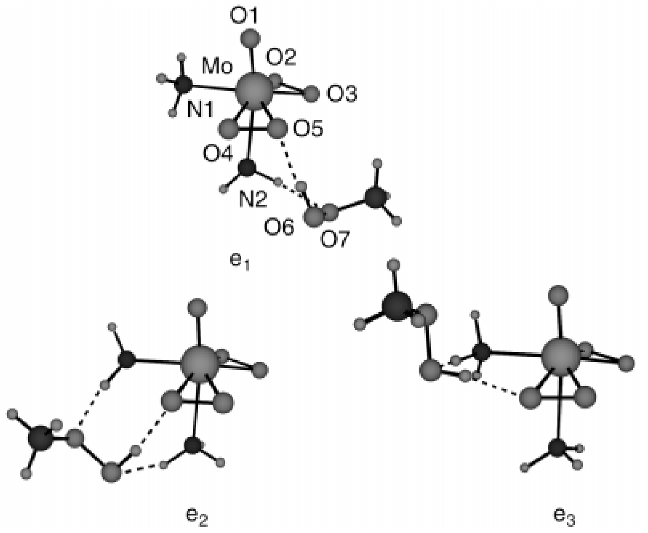
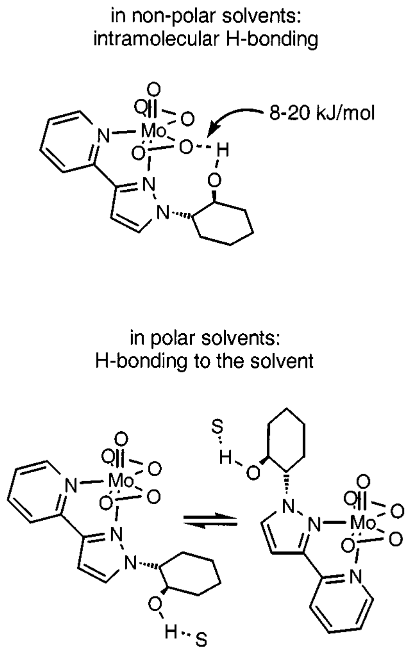


Figure 3. Different modes of H bonding between CH_3OOH and $MoO(\eta^2\text{-}O_2)_2(NH_3)_2$

Table 3. Energetic and structural features (DFT) of the complexes shown in Figure 3

	e_1	e_2	e_3
		Energy[a] [$kJmol^{-1}$]	
	–46.6	–67.7	–53.1
		Bond lengths [Å]	
Mo–N1	2.261	2.249	2.244
Mo–N2	2.505	2.512	2.538
Mo–O1	1.698	1.696	1.695
Mo–O2	1.959	1.956	1.953
Mo–O3	1.943	1.943	1.947
Mo–O4	1.963	1.985	1.971
Mo–O5	1.966	1.957	1.964
O4···HO	–	1.761	1.893
O5···HO	1.847	–	–
O6···HN	–	2.232	1.984
O7···HN	1.954	1.947	–

[a] Compared to free $MoO(\eta^2\text{-}O_2)_2(NH_3)_2$ + CH_3OOH.



Scheme 6

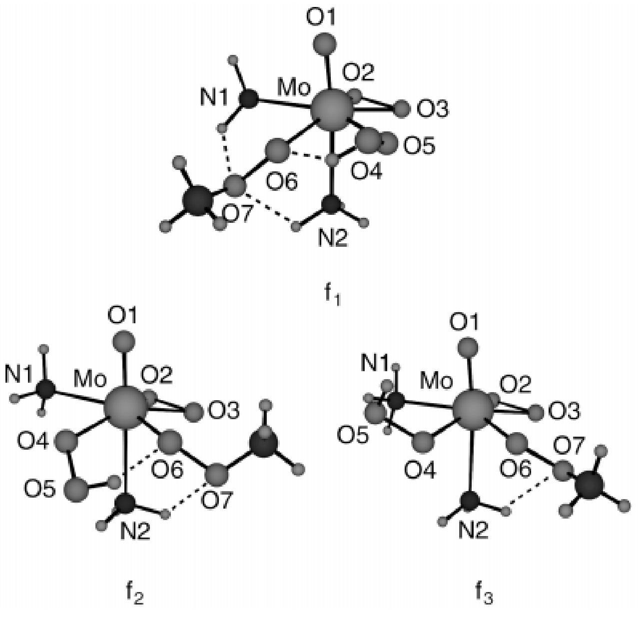


Figure 4. Isomeric species of the type $MoO(\eta^2\text{-}O_2)(OOH)(OOCH_3)(NH_3)_2$

Up to now it was not possible to find a local minimum on the PES representing a Lewis acid/base interaction between $MoO(\eta^2\text{-}O_2)_2(NH_3)_2$ (**a**) and CH_3OOH or a combination of the latter feature with hydrogen bonding.

Proton transfer from the hydroperoxide to either the rear or the front oxygen atom of one of the peroxo ligands results in the formation isomeric species of the type **II** $MoO(\eta^2\text{-}O_2)(OOH)(OOCH_3)(NH_3)_2$ (**f**$_1$, **f**$_2$, **f**$_3$), all lower in energy than the starting materials (Figure 4, Table 4).

They are stabilised by intramolecular hydrogen bonding (**f**$_1$, **f**$_2$) between the proton of the hydroperoxo ligand and the α-oxygen atom of the alkyl peroxo ligand, forming a five-membered ring system and hydrogen bonds to one or both of the ammonia ligands. Along with these theoretical studies we investigated the behaviour of oxobisperoxo(pyrazolylpyridine)molybdenum complexes in the presence of excess *t*BuOOH by NMR. NMR spectroscopy did not prove any interaction between the hydroperoxide and the molybdenum complex, which may either be explained by the different steric demand of *t*BuOOH and CH_3OOH or by a certain error related to the computational method due to the simplification of the donor ligand by NH_3 and by neglect of solvent effects. However, it is indisputable that the energies assigned to the proton transfer and the opening of one $\eta^2\text{-}O_2$ ligand to form a $Mo(OOH)(OOCH_3)$ fragment are low, which makes the existence of species of the type **II** (Scheme 1) in equilibrium with **I** feasible.

Parallel to the seven-coordinated system $MoO(\eta^2\text{-}O_2)_2(NH_3)_2$ (**a**) the interaction of CH_3OOH with the six-coordinated complex $MoO(\eta^2\text{-}O_2)_2(eq\text{-}NH_3)$ (**c**) was investigated. As shown before, dissociation of the axial donor was found to be low in energy. Although unproductive in the

Table 4. Energetic and structural features (DFT) of the complexes shown in Figure 4

	f$_1$	**f$_2$**	**f$_3$**
		Energy[a] [kJmol^{-1}]	
	–20.7	–37.1	–20.6
		Bond lengths [Å]	
Mo–N1	2.307	2.305	2.274
Mo–N2	2.458	2.479	2.457
Mo–O1	1.698	1.704	1.705
Mo–O2	1.943	1.958	1.957
Mo–O3	1.970	1.966	1.965
Mo–O4	2.838	1.995	2.044
Mo–O5	1.974	2.989	2.963
Mo–O6	2.074	2.012	1.978
O6···HO	1.853	1.821	–
O7···HN	2.249/2.020	2.374	2.241

[a] Compared to free $MoO(\eta^2\text{-}O_2)_2(NH_3)_2 + CH_3OOH$.

Table 5. Energetic and structural features (DFT) of the complexes shown in Figure 5

	g$_1$	**g$_2$**	**g$_3$**
		Energy[a] [kJmol^{-1}]	
	+7.0	+16.4	–1.5
		Bond lengths [Å]	
Mo–N1	2.232	2.230	2.226
Mo–O1	1.689	1.689	1.687
Mo–O2	1.938	1.936	1.944
Mo–O3	1.949	1.943	1.948
Mo–O4	1.952	1.950	1.943
Mo–O5	1.951	1.962	1.967
Mo–O6	2.798	2.798	2.749
Mo–O7	3.997	3.714	3.541
O4···HO	2.341	2.347	2.272
O5···HO	2.732	2.234	2.022
O6···HN	2.169	2.371	2.316

[a] Related to the reaction: **a** + CH_3OOH → **g** + NH_3.

isomerisation process of the pyrazolylpyridine complexes (Scheme 4), it may be considered as the key step in the activation of the alkyl hydroperoxide.

We therefore investigated structures of the type $MoO(\eta^2\text{-}O_2)_2(eq\text{-}NH_3)(ax\text{-}CH_3OOH)$ (**g**) by means of computational methods and found three minima on the PES (there may even be more). The energies of these compounds (Table 5), wherein the hydroperoxide can be bound to the molybdenum centre by either the protonated (**g$_1$**, **g$_2$**) or the alkylated (**g$_3$**) oxygen atom, are related to the reaction $MoO(\eta^2\text{-}O_2)_2(NH_3)_2 + CH_3OOH \rightarrow MoO(\eta^2\text{-}O_2)_2(eq\text{-}NH_3)(ax\text{-}CH_3OOH) + NH_3$. The data prove that methyl hydroperoxide is able to stabilise the molybdenum centre in the same manner as ammonia does it. This is promoted by interactions between the proton of the hydroperoxide and one or two of the oxygen atoms of an η^2-peroxo ligand and one of the NH_3 protons with the coordinating oxygen atom of the hydroperoxide, reflecting the basicity of CH_3OOH (Figure 5, Table 5).

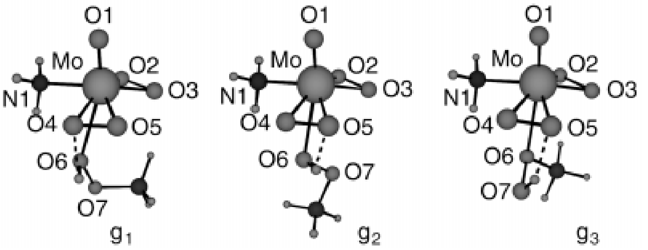


Figure 5. Structures of CH_3OOH adducts to $MoO(\eta^2\text{-}O_2)_2(eq\text{-}NH_3)$

The weak hydrogen bond between OOH and (η^2-O_2) can again be considered as the first step of a proton transfer from the hydroperoxide to the peroxo ligand as discussed before. Proton transfer leads to a series of isomeric molybdenum complexes of the type $MoO(\eta^2\text{-}O_2)(eq\text{-}NH_3)(OOH)(OOCH_3)$ (**h**) showing different ligand conformations (Figure 6 shows three examples, there may be more). The energies given in Table 6 are related to the reaction $MoO(\eta^2\text{-}O_2)_2(NH_3)_2 + CH_3OOH \rightarrow MoO(\eta^2\text{-}O_2)(\eta^1\text{-}O_2H)(eq\text{-}NH_3)(\eta^1\text{-}OOCH_3) + NH_3$.

The intramolecular proton transfer should be a rapid process with a low barrier of activation, it is only slightly endothermic. In all cases we observed, the complexes are stabilised by hydrogen bonds and by η^2-coordination of the methyl hydroperoxo and/or the hydroperoxo ligand, a feature which was not found in the complexes $MoO(\eta^2\text{-}O_2)(OOH)(OOCH_3)(NH_3)_2$ (**f$_1$**–**f$_3$**, Figure 4). This shows that previous partial dissociation of one donor ligand from a seven-coordinated peroxo complex is energetically feasible and that the activation of the hydroperoxide for oxygen transfer may start with such a dissociative process.

The calculated Mo–O–O angles lie between the data of complexes bearing η^1-coordinated (112–118°[13–21]) and η^2-coordinated alkyl peroxo ligands (59–65°[9,10,20]).

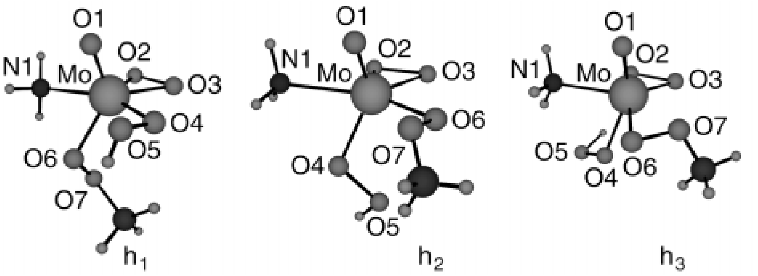
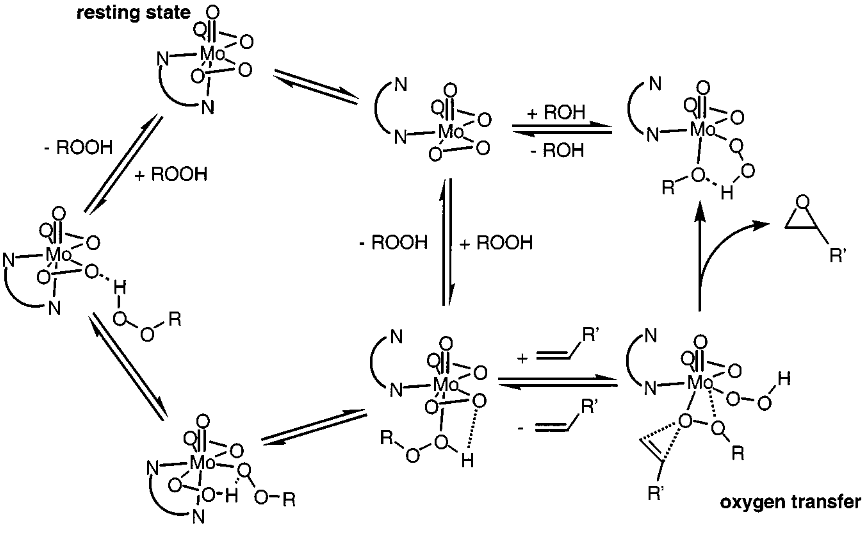


Figure 6. Calculated geometries of molybdenum complexes of the type $MoO(\eta^2\text{-}O_2)(eq\text{-}NH_3)(OOH)(OOCH_3)$

Table 6. Energetic and structural features (DFT) of the complexes shown in Figure 6

	h$_1$	**h$_2$**	**h$_3$**
		Energy[a] [kJmol^{-1}]	
	25.8	44.0	79.0
		Bond lengths [Å]	
Mo–N1	2.326	2.368	2.253
Mo–O1	1.692	1.699	1.712
Mo–O2	1.929	1.921	1.996
Mo–O3	1.952	1.954	1.923
Mo–O4	1.974	1.976	2.071
Mo–O5	2.640	2.742	3.108
Mo–O6	2.106	1.957	2.105
Mo–O7	2.492	2.597	2.150
O2···HO	–	–	2.033
O6···HO	2.193	–	–
O7···HN	2.468	–	–
		Bond angles [°]	
Mo–O4–O5	100.0	105.1	117.3
Mo–O6–O7	90.1	98.3	76.4

[a]Related to the reaction: **a** + $CH_3OOH \rightarrow$ **h** + NH_3.



Scheme 7

The overall mechanistic idea resulting from the NMR investigations and the computational calculations is shown in Scheme 7, wherein the seven-coordinated oxobisperoxo complex represents a kind of resting state in the catalytic cycle.

Thus, seven-coordinated molybdenum peroxo complexes bearing chelate pyrazolylpyridine ligands do not undergo a direct oxygen transfer from an η^2-coordinated peroxo ligand to an olefin but activate a potential oxidising agent for oxygen transfer, similar to other high valent and highly Lewis acidic transition metal centres. This includes the requirement of basic ligands to undergo a proton transfer reaction prior to the activation of the hydroperoxide. η^2-Coordinated peroxo ligands are ideal for this purpose since they are weak π donors, which preserves the Lewis acidity of the metal centre. They remain ligated to the metal in a η^1-coordination mode allowing rapid intramolecular proton transfer after the oxygen transfer to regenerate the catalyst.

Conclusion

As shown by NMR spectroscopy and quantum chemical calculations, ligand fluxionality may play an important role in the activation of the hydroperoxide. We were able to show, that the energies related with a partial ligand dissociation and intra- and intermolecular proton transfer reactions are low and that η^2-coordination of an alkylperoxo ligand stabilises six-coordinated molybdenum species.

Experimental Section

NMR spectra were recorded with a Bruker DMX 600 spectrometer and processed by Silicon Graphics workstations with the X-WIN-NMR software package. The 1D spectra and the 2D NOESY spectra were measured at different temperatures/mixing times: **1** (297.3 K/2s, 306.8 K/2 s, 316.3 K/2 s, 325.8 K/2 s), **2** (297.3 K/1 s, 306.8 K/1 s, 316.3 K/1 s), **3** (287.9 K/1 s, 297.3 K/0.5 s, 306.8 K/0.3 s, 316.3 K/0.2 s), **4** (290.0 K/1 s, 300.0 K/0.5 s, 310.0 K/0.2 s, 320 K/0.1 s). – Quantum chemical calculations were performed with the program Gaussian98W using the B3LYP gradient-corrected exchange-correlation functional[33–35] in combination with the Los Alamos effective core potentials on molybdenum atoms together with a gaussian valence basis set of double zeta quality (LanL2DZ).[36–39] The orbital basis sets of carbon, nitrogen and oxygen atoms were augmented by a single set of polarisation functions.[47] Full geometry optimisations were carried out in C_1 symmetry using analytical gradient techniques and the resulting structures were confirmed to be true minima by diagonalisation of the analytical Hessian Matrix.

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