Metal-Catalyzed Oxidations, 4[◇]

The Reaction of Molybdenumperoxo Complexes with Brønsted and Lewis Acids

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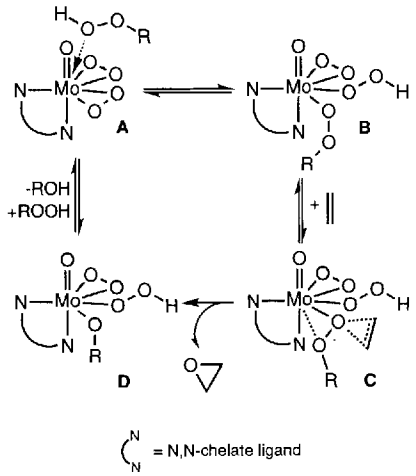
NMR studies of the reaction of complexes of the type (L-L)$MoO(O_2)_2$ (L−L = bidentate ligand) with strong Brønsted and Lewis acids prove that protons are transferred preferentially to an η^2-peroxo and not to the oxo ligand. This behavior in proton transfer reactions is one critical point of the catalytic activity of such complexes in olefin epoxidation. EH calculations on the model complex $(NH_3)_2MoO(O_2)_2$ support the spectroscopic investigations.

High valent molybdenum complexes are extensively used as catalysts in olefin epoxidations[2]. Mechanistic studies of stoichiometric reactions of molybdenum peroxo complexes of the type $(L)_2MoO(O_2)_2$ (L = monodentate ligand) showed that the oxygen atom is transferred from a peroxo ligand to the olefin[3]. In contrast, we recently found that olefin-substituted molybdenum peroxo complexes of the type (L−L)$MoO(O_2)_2$ (L−L = chelate ligand with olefinic side chain) are stable against autoepoxidation[1]. However, olefin epoxidation starts immediately after the addition of a peroxide, e.g. *tert*-butyl hydroperoxide (TBHP) or H_2O_2. The oxygen atom is transferred from the hydroperoxide to the olefin and the peroxo complex acts as an activator of the oxidizing agent. On the basis of these synthetic results we propose a mechanism (Scheme 1) related to the mechanism of catalytic epoxidations with high valent transition metal alkoxides, as it is found for example in the case of the Sharpless epoxidation[4].

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.

The pK_a values of the complexes $MO(O_2)_2 \cdot (H_2O)_2$ (M = Mo, pK_a = 1.85; W, pK_a = 0.12) reported by Thompson et al. prove the strong Lewis acidity of these compounds[5]. The activation of a hydroperoxide by η^2 coordination to a Lewis acidic metal center was the subject of theoretic and synthetic studies[6]. However, it was not yet clear whether the proton of the oxidizing agent is transferred either to a peroxo or the oxo ligand of the peroxo complex. In the case of oxoalkoxo complexes of molybdenum, tungsten, and vanadium this proton transfer is still controversially discussed[7]. NMR studies of the effects of excess TBHP on molybdenumperoxo complexes did not prove a proton transfer to the catalysts[8]. We therefore assume that only low concentrations of a highly active species, formed from the oxodiperoxo complex, are responsible for the activity of the catalytic system.

Scheme 1



Results and Discussion

In this paper we describe interactions of Brønsted and Lewis acids with 2-(1-octyl-3-pyrazolyl)pyridineoxodiperoxomolybdenum(VI) (**1**)[9], which can be considered as model reactions of the proton transfer from an alkyl hydroperoxide. We used the octyl substituted complex as it enables spectroscopic investigations in organic solvents due to its

[◇] Part 3: Ref.[1].

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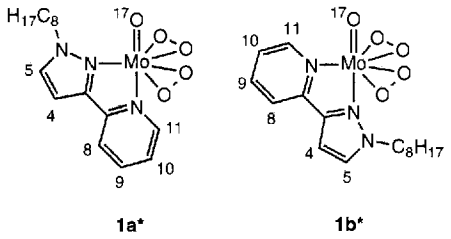
high solubility. The ^{17}O-labeled compound **1*** (10% enriched in ^{17}O) was synthesized to observe the role of the oxo ligand by ^{17}O-NMR spectroscopy. **1*** is obtained as a 2:1 mixture of the isomers[9] **1a*** and **1b*** (Scheme 2, with proton numbering), which interconvert slowly at room temperature[8].

Scheme 2



1a* **1b***

Reaction with Trifluoroacetic Acid

Perhalogenation of carboxylic acids not only leads to an increased acidity but also to an increased stability against oxidative degeneration. We therefore used trifluoroacetic acid (TFA, dried over molecular sieves, 4 Å) to examine the reactivity of **1*** against strong Brønsted acids. As shown in Figures 1 and 2, the addition of one resp. two equiv. of TFA to a solution of **1*** in $CDCl_3$ only leads to a slight low-field shift of the ^{17}O- and ^{1}H-NMR signals.

Figure 1. (a) ^{17}O-NMR spectra (δ scale) of **1***, (b) after the addition of one equiv. of TFA, (c) after the addition of two equiv. of TFA

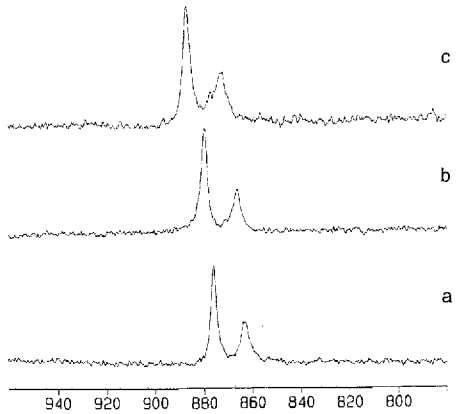
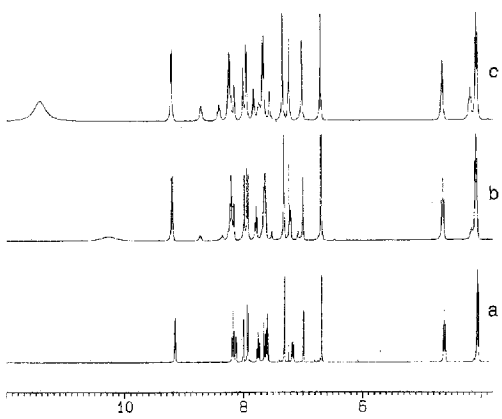
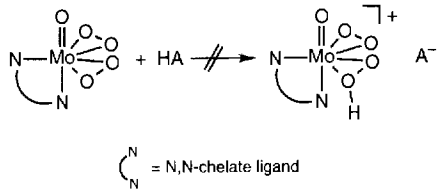


Figure 2. (a) ^{1}H-NMR spectra (δ scale) of **1***, (b) after the addition of one equiv. of TFA, (c) after the addition of two equiv. of TFA



Whether these results indicate a real protonation of **1*** at a η^2-peroxo ligand, which should be in equilibrium with unprotonated **1***, or whether they originate from the change of the solvent system due to the addition of the acid TFA, cannot be decided yet. Anyway, protonation of the oxo ligand, in equilibrium with unprotonated **1***, forming a hydroxo ligand can be excluded as it would induce a high field shift of the ^{17}O-NMR signals[10]. The protonation of low-valent Re^{III} oxo complexes clearly leads to cationic hydroxo complexes, which show a characteristic Re–OH absorption in the infrared spectra at $\tilde{\nu} \approx 600\ cm^{-1}$[10]. This absorption is not observed when **1** is treated with TFA in CH_2Cl_2. The MO=O ($\tilde{\nu} = 956\ cm^{-1}$) and the O–O absorptions ($\tilde{\nu} = 877, 866\ cm^{-1}$) are unaffected. These investigations show that the basicity of the oxo and the peroxo ligand is low due to their coordination to a high valent metal center. Therefore, a simple proton transfer from a weak Brønsted acid like TBHP cannot be the first step of the catalytic cycle (Scheme 3).

Scheme 3



Precoordination of the Lewis basic hydroperoxide to the high-valent metal center induces both, an increased acidity of the ROOH proton and an increased basicity of the peroxo ligands. Therefore, besides to presence of an acidic proton, the donor properties of the oxidizing agent play an important role in the formation of the active species. This is one possible explication for the reduced catalytic activity of complexes of the type **1** when H_2O_2 is used as oxidizing agent for olefin epoxidation instead of TBHP.

Figure 2c also shows the high coordinative stability of the chelate complex. 30 min after the addition of two equiv. of TFA only about 10% of the complex had decomposed to give the protonated ligand 2-(1-octyl-3-pyrazolyl)pyridinium trifluoroacetate [δ = 10.40 (H^+), 8.65 (H-11), 8.38 (H-9), 8.31 (H-8), 7.75 (H-9), 7.60 (H-5), 7.13 (H-10, H-4), 4.18 (N-CH_2), numbering according to Scheme 2, broad signals]. After the decomposition was going on for 2 h, the former yellow color of the solution had changed to orange and a precipitate (MoO_3) was formed. From these results (only slow decomposition of the peroxo complex) it is obvious that dissociation of the chelate ligand cannot play a role in the formation of the catalytically active species of the olefin epoxidation.

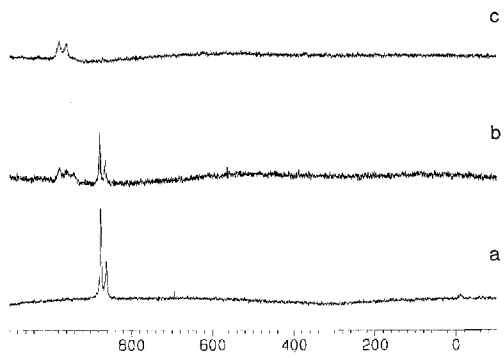
Reaction with Trifluoroacetic Anhydride

To overcome the typical NMR spectroscopic problems, which are related to the dynamics of protonation reactions, Lewis acidic reagents, such as acid anhydrides or trimethylsilyl derivatives, are commonly used instead of simple Brønsted acids. We examined different Lewis acids to gain

a deeper insight into the proton transfer process and the role of the associated attack of a Lewis base on the molybdenum center.

While the addition of one or two equivalents of acetic anhydride to a solution of **1*** in $CDCl_3$ leads to a rapid and total decomposition of the complex and formation of MoO_3, the products of the reaction with trifluoroacetic anhydride (TFAA) are stable and can be investigated spectroscopically. ^{17}O-NMR spectroscopy proves that both isomers **1a*** and **1b*** (δ = 874, 861) are consumed after the addition of two equivalents of TFAA, and several new species (δ = 980–940) are formed (Figure 3).

Figure 3. (a) ^{17}O-NMR spectra (δ scale) of **1***, (b) after the addition of one equiv. of TFAA, (c) after the addition of two equiv. of TFAA

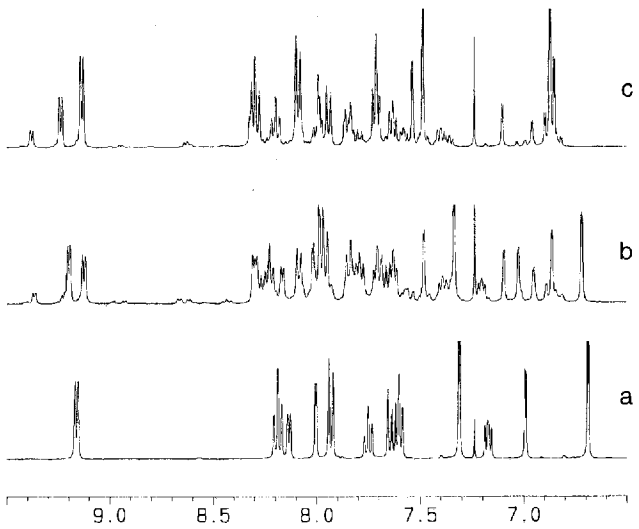


Further addition of TFAA does not cause any change in the spectrum. The low-field shift of the resonances of the labeled oxygen atoms, which are still characteristic for Mo=O-oxo ligands, indicates that TFAA attacks selectively the peroxo ligands (attacking the oxo ligand would give ^{17}O-labeled trifluoroacetate, δ = 260[11]) and that the electron density on the oxo ligands of the reaction products is decreased compared to **1***. Herrmann et al. recently showed for rhenium oxo complexes that perhalogenated carboxylic acids are only poor donor ligands. In contrast to the non-halogenated derivatives, they act as monodentate ligands (η^1 coordination)[11].

The molecular structures of the reaction products were finally elucidated by ^1H-NMR spectroscopy. After the addition of two equivalents of TFAA the resonances of **1a*** and **1b*** have disappeared. The aromatic region of the spectra shows a complex pattern due to the presence of several new species (Figure 4).

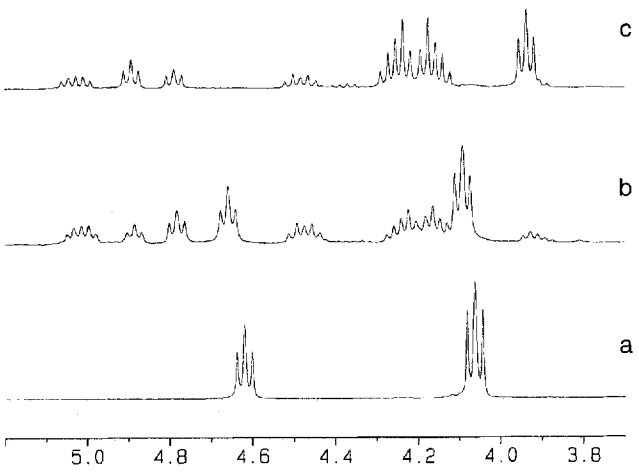
We were able to completely assign the resonances of five new compounds by H,H-COSY experiments, which are not shown here. Corresponding to the ^{17}O-NMR data, all proton resonances are more or less shifted to lower field, which also supports the higher Lewis acidity of the molybdenum center after the reaction with TFAA. In the 1D-^1H-NMR spectrum (Figure 4) three doublets (δ = 9.38, 9.25, 9.12) are observed, which, as shown by their chemical shifts, are related to protons H-11 (Scheme 2) of the pyridine ring in *trans* position to the oxo ligand. These complexes are therefore structurally related to isomer **1a***. Two other isomers can clearly be identified by two ^1H resonances of H-5 (δ = 7.15, 6.95). The chemical shifts of these protons are characteristic for a pyrazole ring in *trans* position to the oxo ligand, like in isomer **1b***.

Figure 4. (a) ^1H-NMR spectra (δ scale) (aromatic protons) of **1***, (b) after the addition of one equiv. of TFAA, (c) after the addition of two equiv. of TFAA



Further information about the molecular structures of the reaction products can be obtained from the NMR data of the α-CH_2 protons of the octyl side chain (Figure 5).

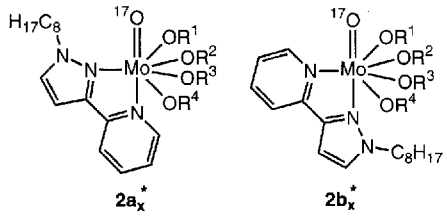
Figure 5. (a) ^1H-NMR spectra (δ scale) (NCH_2) of **1***, (b) after the addition of one equiv. of TFAA, (c) after the addition of two equiv. of TFAA



We observe two sets of signals (δ = 5.1–4.3, and δ = 4.3–3.8) with chemical shifts typical of species of type **1a*** and **1b***, respectively. Both sets are dominated by two quintuplets (δ = 5.03, 4.48, and δ = 4.25, 4.16), which can be assigned to diastereotopic NCH_2 protons. They consequently indicate a loss of C_s symmetry of the molecule due to asymmetric ligand geometry. Symmetric species give rise to two triplets (δ = 4.89, 4.79 and δ = 3.94, 3.94, respectively) in each region. Interpretation of ^{17}O- and ^1H-NMR data leads unavoidably to the molecular structure of eight isomeric reaction products $\mathbf{2a}_x$, $\mathbf{2b}_x$ (x = 1, 2, 3, 4) (Scheme 4). The pair $\mathbf{2a_2}$ and $\mathbf{2a_3}$ as well as the pair. $\mathbf{2b_2}$ and $\mathbf{2b_3}$

are enantiomers with an asymmetric ligand geometry and diastereotopic NCH_2 protons.

Scheme 4

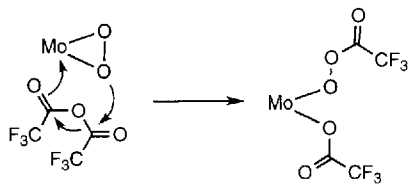


2a*x **2b*x**

x	1	2	3	4
R^1	$C(O)CF_3$	$C(O)CF_3$	$OC(O)CF_3$	$OC(O)CF_3$
R^2	$OC(O)CF_3$	$OC(O)CF_3$	$C(O)CF_3$	$C(O)CF_3$
R^3	$OC(O)CF_3$	$C(O)CF_3$	$OC(O)CF_3$	$C(O)CF_3$
R^4	$C(O)CF_3$	$OC(O)CF_3$	$C(O)CF_3$	$OC(O)CF_3$

However, permutation of two trifluoroacetato and two trifluoroperoxyacetato ligands on four coordination sites should give six species for each orientation of the oxo ligand, while only four are observed. The absence of the two isomers [$R_1 = R_2 = C(O)CF_3$ and $R_3 = R_4 = OC(O)CF_3$, resp. $R_1 = R_2 = OC(O)CF_3$ and $R_3 = R_4 = C(O)CF_3$] indicates a concerted opening of the metalladioxirane ring by the anhydride (Scheme 5) and a relatively high coordination stability of the complexes **2**. Ligand fluxionality as well as ligand dissociation/association phenomena would give rise to a statistical distribution of the ligands, which was not observed.

Scheme 5

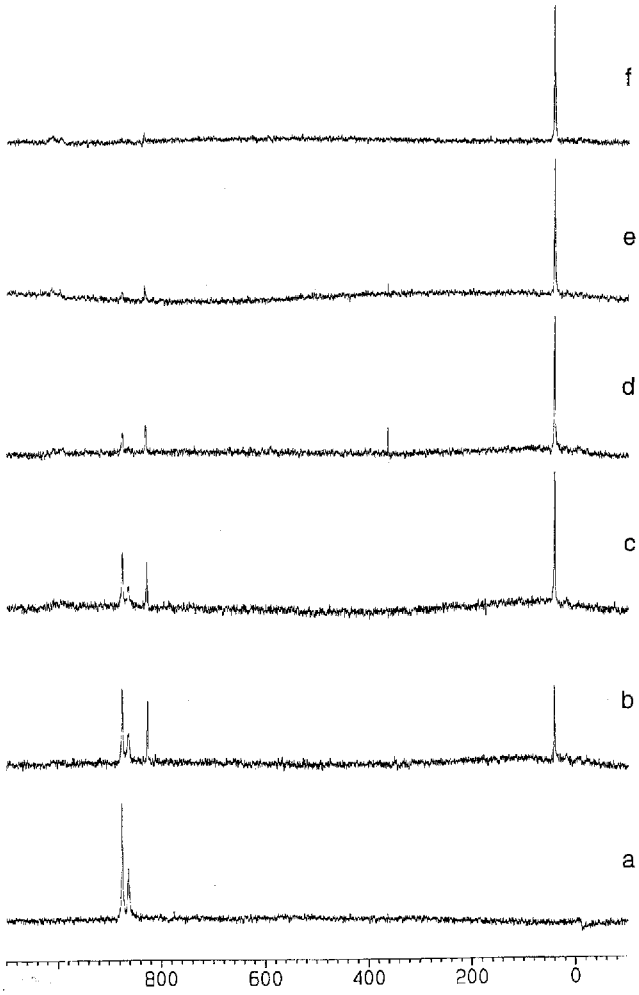


Reaction with Chlorotrimethylsilane

A different reaction takes place when freshly purified (distillation over K_2CO_3) chlorotrimethylsilane (TMSCl) is used as electrophile[12]. ^1H- and ^{17}O-NMR spectra were recorded after addition of 1–5 equiv. of TMSCl (Figures 6 and 7).

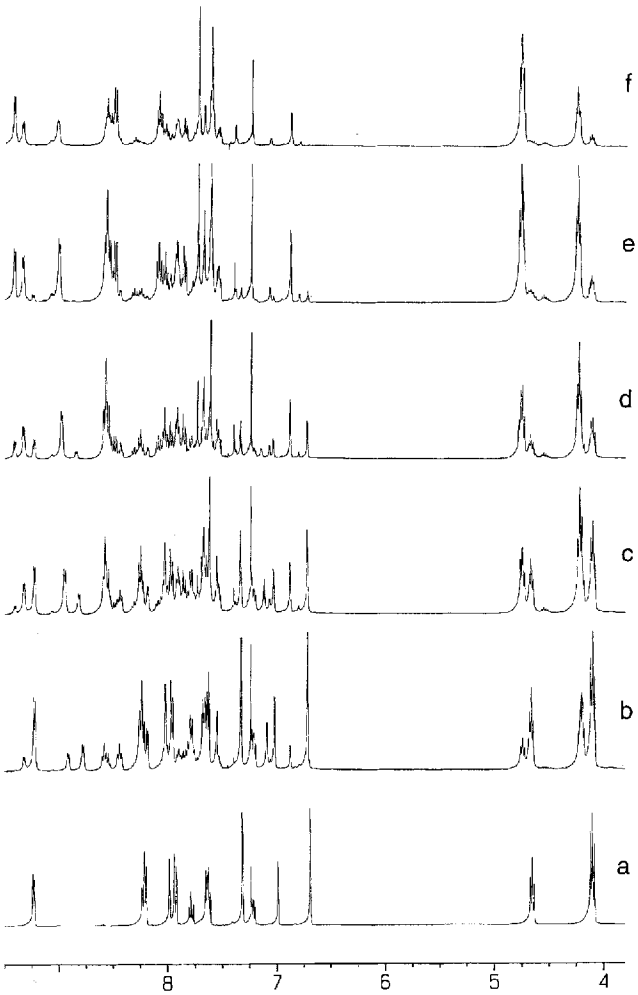
The ^{17}O-NMR spectra reveal that the electrophilic attack of TMSCl on **1*** occurs preferentially but not selectively at the peroxo ligands. While both isomers **1a*** and **1b*** are consumed simultaneously, a new resonance (δ = 827) appears (Figure 6b). It is still characteristic of a molybdenum compound with a terminal oxo ligand and therefore indicates attack at an η^2-O_2 ligand. The chemical shift of this ^{17}O-NMR signal is significant for a species with increased electron density compared to **1**. If we assume that only one η^2-O_2 ligand is attacked either one chloro and one Me_3SiOO ligand (one equiv. of TMSCl per η^2-O_2 ligand) or two chloro ligands (two equiv. of TMSCl per η^2-O_2 ligand) are formed. π Donation from these new ligands to the metal both reduces the Lewis acidity of the molybdenum center and increases the Lewis basicity of the remaining oxo ligand. From this point of view a second, consecutive reaction, which leads to ^{17}O-labeled hexamethyldisiloxane (δ = 43[13]) as the product of an attack of TMSCl at an oxo ligand, can be understood. It is obvious that a complex balance between the Lewis acidities and basicities of all involved species is responsible for the control of these reactions.

Figure 6. (a) ^{17}O-NMR spectra (δ scale) of **1***, (b–f) after the addition of 1–5 equiv. of TMSCl



After the addition of four equiv. of TMSCl the signals of molybdenum species with a terminal oxo ligand have nearly disappeared. Hexamethyldisiloxane is the only ^{17}O-labeled compound of the reaction sequence. Along with the ^{17}O-NMR data, ^1H-NMR and ^{13}C-NMR spectra indicate the complete consumption of **1*** and the formation of three new species. The cleavage of the Si–Cl bond by $Mo(O_2)$ and MoO fragments generates new chloro, trimethylsilylperoxo and/or trimethylsilanolato ligands coordinated to the molybdenum(VI) center. The exact molecular geometry of the three reaction products can therefore not be determined by NMR spectroscopy alone, but only by single-crystal X-ray diffraction experiments.

Figure 7. (a) ^{1}H-NMR spectra (δ scale) of **1***, (b–f) after the addition of 1–5 equiv. of TMSCl



Herrmann et al. recently proved the high reactivity of trimethylsilyl derivatives in the presence of terminal oxo ligands. The bistrimethylsilyl ether $Me_3SiOCMe_2CMe_2O$-$SiMe_3$ reacts with $Me_3SiOReO_3$ with cleavage of both Me_3-SiO fragments to give $(OCMe_2CMe_2O)ReO_2(OSiMe_3)$. In contrast, the monotrimethylsilyl ether $Me_3SiOCMe_2$-CMe_2OH gives the alcohol adduct $(OCMe_2CMe_2OH)ReO_3$ with the proton remaining at the oxygen atom of the alcohol function in the solid state as well as in solution[14]. We see that from the reduced selectivity of TMSCl, which we found in the reaction with **1***, a conclusion as to to the behavior of proton donors in the same context cannot be drawn.

From our spectroscopic investigations it is obvious that oxo ligands of high-valent transition-metal complexes are extremely poor proton acceptors. To obtain information about the electronic situation of both the oxo ligand and the peroxo ligands of **1**, extended Hückel (EH) calculations[15] of the model complex $(NH_3)_2MoO(O_2)_2$ were carried out. The NH_3 ligands were introduced into the positions of the nitrogen atoms of **1**[9,16]. In accordance with the results of Hoffman et al, who investigated the ligand-free system $MoO(O_2)_2$[17], 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 an η^2-peroxo ligand should therefore be more favorable than proton transfer to the oxo ligand. We are now working on calculations at a higher level of theory to gain a deeper insight into the mechanism of the interaction between hydroperoxides and peroxo complexes of the type **1**.

Conclusion

The activation of hydroperoxides against the nucleophilic attack of an olefin requires coordination to the metal center as well as a proton transfer reaction. Selectivity and reactivity of a catalytic system for epoxidation therefore should not be correlated only with the characteristics of the catalyst. Knowledge of the Lewis acidities and Lewis basicities of all components is essential for the optimization of such a system. High Lewis acidity of the metal center combined with high Lewis basicity of the hydroperoxide leads to a strong metal-ligand interaction and thus to high catalytic activity. Coordinating solvents compete with the hydroperoxide for a coordination site and therefore decrease the activity of the system. Besides, the presence of proton accepting ligands like alkoxo, peroxo, acetato, acetylacetonato, halogeno[7,18], or bridging oxo ligands is required. Lewis acidic metal oxides without these basic ligands like methyltrioxorhenium(VII)[19] show no epoxidation activity in the presence of TBHP[20].

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Experimental

2-(1-octyl-3-pyrazolyl)pyridineoxodiperoxo molybdenum(VI) (**1**) was prepared according to a literature procedure[9]. $H_2{}^{17}O$ (10% enriched) was obtained from Enritech Enrichment Technologies Ldt., Rehovot, Israel. Trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) were stored over molecular sieves (4 Å) and chlorotrimethylsilane (TMSCl) was freshly distilled from K_2CO_3 before use. – The NMR spectra were recorded at 298 K with a Bruker DPX 400 spectrometer in 5 mm NMR tubes equipped with a rubber septum for the addition of the reagents.

Synthesis of **1***: To a solution of 1.30 g (3 mmol) of **1** in 30 ml of THF 0.57 ml of $H_2{}^{17}O$ (30 mmol) was added and the mixture was stirred for 1 h at room temp. The solvent was evaporated under vacuum and the resulting yellow solid dried at 25°C/10^{-2} Torr.

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