Kinetics of Cyclooctene Epoxidation with *tert*-Butyl Hydroperoxide in the Presence of [MoO_2X_2L]-Type Catalysts (L = Bidentate Lewis Base)

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Mo^{VI} complexes with the general formula [MoO_2X_2L] [X = Cl, Br; L = 4,4′-dimethyl-2,2′-bipyridine (dmbp) or 4-hexyl-4′-methyl-2,2′-bipyridine (hmbp)] have been prepared and characterized by IR and solution NMR (^{1}H, ^{13}C, ^{17}O and ^{95}Mo) spectroscopy. The complexes were applied as catalysts in the homogeneous phase for the epoxidation of cyclooctene, with *tert*-butyl hydroperoxide (TBHP) as the oxygen source. The desired epoxide was the only product and turnover frequencies of up to about 9000 h^{-1} could be reached. The catalytic activities increased in the order [MoO_2Br_2(dmbp)] < [MoO_2Br_2(hmbp)] < [MoO_2Cl_2(dmbp)] < [MoO_2Cl_2(hmbp)]. A kinetic model was built up for a homogeneous batch reactor based on a simplified mechanism involving three steps: (i) reversible coordination of TBHP to the starting Mo^{VI} complex to give a Mo^{VI} alkylperoxide; (ii) irreversible oxidation of cyclooctene to cyclooctene oxide by the species formed in step 1, with formation of the starting complex and *tert*-butyl alcohol; (iii) reversible coordination of *tert*-butyl alcohol to the starting complex. This model is consistent with the observed kinetics. The first step in this reaction mechanism was characterized in more detail by studying the kinetics of the reaction of the starting complexes with TBHP in the absence of any reductant by UV/Vis spectroscopy. Rate constants, equilibrium constants, and activation parameters were determined. All $\Delta S^{‡}$ values were negative and therefore support an associative mechanism in which a seven-coordinate intermediate is formed. The results also suggest that the first step is not always the rate-limiting step of cyclooctene epoxidation with these complexes.

Introduction

Dioxomolybdenum(VI) complexes are important catalysts or catalyst precursors for oxygen-atom transfer reactions in industrial and biological systems.[1] Polymeric compounds of the composition MoO_2X_2 and WO_2X_2 have been known for many years.[2a] With Lewis bases, such as 2,2′-bipyridine, and with donor solvents, such as THF, adducts of the composition [MO_2X_2L] (M = Mo, W) are formed.[2b,2c] A particular interest in complexes of this type arose in the late 1960s when ARCO and Halcon were granted patents on olefin epoxidation catalyzed by Mo^{VI} compounds in the homogeneous phase.[2d,2e] In the following years different mechanisms were suggested to explain the reactivity of these complexes, most notably those by Mimoun et al.[2f] and by Sharpless et al.[2g] The debate has not been settled to date, despite the fact that a lot of information has been derived from NMR studies and catalytic reactivity patterns;[2h] several theoretical and mechanistic studies have also been presented.[2i–2l] It is generally agreed, however, that formation of a Mo^{VI} alkyl peroxide occurs followed by transfer of the distal oxygen atom of the alkyl peroxide rather than an oxo ligand.[2m] It is also becoming clear from the results published during the last decades on Mo^{VI} and W^{VI} complexes that the different catalyst types do not all follow the same mechanism,[2n–2p] as some authors assumed in the early days of this chemistry.[2q,2r]

We have recently published a series of papers focusing on complexes of the type [MO_2X_2L], which are excellent catalyst precursors for olefin epoxidation in the presence of *tert*-butyl hydroperoxide (TBHP).[3] Already in the early 1980s Mimoun et al. assumed that the [MO_2X_2L] complexes are transformed into [$Mo(O_2)_2OL_2$] in the presence of excess H_2O_2,[4] while the reaction of [MoO_2X_2L] with excess TBHP remained unclear. It has to be noted, however, that the industrially applied oxidation agent in the ARCO/Halcon process is TBHP. It is therefore of significant interest to

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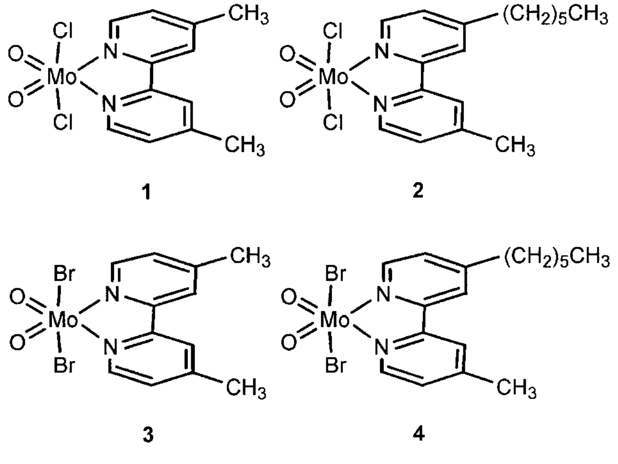
gain a deeper insight into the mechanism of the epoxidation catalysis with [MoO$_2$X$_2$L] as the catalyst precursor and TBHP as oxidizing agent. In this paper we present a kinetic model of the epoxidation reaction supported by NMR and UV/Vis spectroscopy, GC/MS, and calculations using the program Kinsim.[5]

Results and Discussion

Preparation and Characterization of the Dioxomolybdenum(VI) Complexes

The dioxomolybdenum(VI) complexes **1**–**4** (Scheme 1) were obtained as pale-yellow, microcrystalline powders in good yields by previously described routes.[3b] In general, the spectroscopic data for these four complexes present no surprises compared with other Lewis-base adducts of bis(halogeno)dioxomolybdenum(VI) prepared using the same method.[3b] Thus, the complexes display their symmetric and asymmetric IR stretching vibrations for the *cis*-dioxo unit in the expected range (905–940 cm^{-1}).[3] ^{17}O NMR solution spectra were obtained for ^{17}O labeled complexes **5**–**8**. The chemical shifts for the dichloro derivatives **5** and **6** are $\delta(^{17}O)$ = 1005 and 993 ppm, respectively, and these are identical within the error range to those of the corresponding dibromo complexes [$\delta(^{17}O)$ = 1003 and 994 ppm]. The related 2,2′-bipyrimidine adducts [MoO$_2$X$_2$(bpym)] were also found to exhibit a minimal ^{17}O shift difference between the chloro and bromo derivatives [$\delta(^{17}O)$ = 997 (Cl) and 996 ppm (Br)].[5] For complexes **5** and **6**, and **7** and **8**, the 9–12 ppm ^{17}O NMR shift difference reflects a slightly higher electron density in the complexes containing the unsymmetrical 4-hexyl-4′-methyl-2,2′-bipyridine ligand. ^{95}Mo NMR solution spectra were also recorded for complexes **5**–**8**. The differences in the ^{95}Mo shift between the symmetrical and the unsymmetrical bipyridine ligand is comparatively small, only a few ppm in each case. The chemical shift difference between Cl and Br is about 50 ppm. These results parallel those observed for adducts of the type [MoO$_2$X$_2$L] (X = Cl, Br; L = 2,2′-bipyridine, 2,2′-bipyrimidine).[6]



Scheme 1.

Kinetics of Catalytic Olefin Epoxidation With Complexes 1–4

Certain dioxomolybdenum(VI) complexes are able to catalyze the epoxidation of olefins with molecular oxygen as an oxygen source at atmospheric pressure.[7–9] However, preliminary experiments showed that the complexes [MoO$_2$Cl$_2$(4,4′-dimethyl-2,2′-bipyridine)] (**1**) and [MoO$_2$Cl$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (**2**) are not active for the epoxidation of cyclooctene with molecular oxygen at atmospheric pressure under any of the conditions applied previously in the literature.

The dioxomolybdenum(VI) complexes **1**–**4** are active in the epoxidation of cyclooctene with TBHP as oxidant, at 55 °C, yielding cyclooctene oxide as the only product. The catalytic activity of the complexes depends strongly on the substituent pattern of the donor ligand, in agreement with previous studies on oxomolybdenum complexes.[2p,3d,3e,6,9–11] Cyclooctene conversion is higher in the presence of **2** than **1** (initial activities at a catalyst:substrate ratio of 1:100 are 248 mol mol$_{Mo}^{-1}$ h^{-1} and 25 mol mol$_{Mo}^{-1}$ h^{-1}, respectively), and the yield of cyclooctene oxide reaches about 97% after 24 h in the case of **2** compared to about 76% for **1** (Figure 1). A similar trend is observed for complexes **3** and **4**. As discussed below, it is possible that the presence of a large organic group on the bipyridine ligand leads to the formation of a more hindered (reactive) oxidizing Mo^{VI} intermediate. The Br catalysts possess lower activity towards cyclooctene epoxidation than the corresponding Cl analogs, in agreement with the results reported in the literature for complexes of this type.[6]

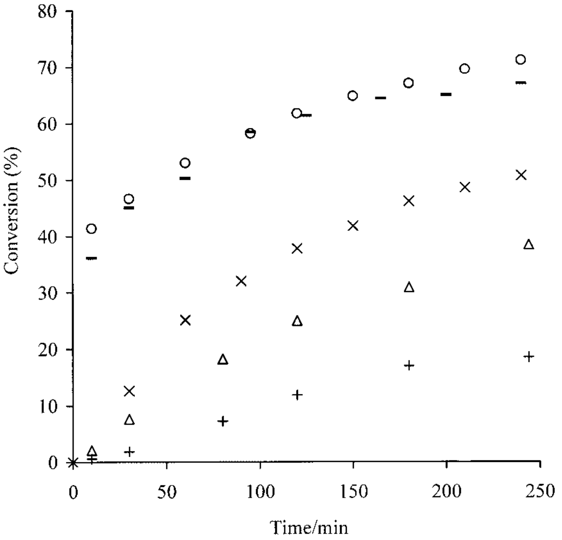


Figure 1. Conversion vs. time profiles for cyclooctene epoxidation using TBHP at 55 °C in the presence of [MoO$_2$Cl$_2$(4,4′-dimethyl-2,2′-bipyridine)] (**1**; ×), [MoO$_2$Cl$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (**2**; ○), [MoO$_2$Br$_2$(4,4′-dimethyl-2,2′-bipyridine)] (**3**; +), [MoO$_2$Br$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (**4**; Δ), and a radical scavenger plus **2** (–).

As has already been confirmed with related compounds, such as [CpMoO$_2$Cl] and derivatives,[12] a catalyst-to-substrate ratio of 1:100 is far from being optimal. Reducing the catalyst-to-substrate ratio to 1:10 000 leads to the highest turnover frequencies (TOFs). The highest activities have been observed with [MoO_2X_2(4,4′-bis(*tert*-butyl)-2,2′-bipyridine)] and cyclooctene as substrate. The TOF of that system with a 1:10 000:15 000 catalyst:substrate:oxidant ratio is 9360 h^{-1} after five minutes. With compound **2** a TOF of about 8800 h^{-1} is reached under the same reaction conditions. With [$CpMoO_2Cl$] systems TOFs as high as 20 000 h^{-1} can be obtained,[12] while with the very active catalyst methyltrioxorhenium[13] (utilizing H_2O_2 instead of TBHP) TOFs of up to 14 000 have been reported.[13c] Nevertheless, the TOFs reached with some of the [MoO_2X_2L] systems reported here are still impressive and show the potential of these compounds as oxidation catalysts.

In this section a mechanism is proposed based on our experimental results and other studies for similar systems,[14] and a kinetic model is developed for a homogeneous batch reactor. In order to exclude solvent effects on the reaction no additional solvent was used. The fact that complexes **1**–**4** do not oxidize cyclooctene with O_2 at atmospheric pressure makes it unlikely that noncatalytic "olefin autoxidation" operates when the epoxidation is carried out with TBHP, at 55 °C, in air. Furthermore, no induction periods were detected (Figure 1) and without catalyst no conversion was observed (under otherwise identical reaction conditions).

Herrmann et al. have reported that for complexes of the type [MoO_2L_2] (L = pyridyl alcohol) a radical-type mechanism could be involved in olefin epoxidation with elemental oxygen (atmospheric pressure).[9] In the present work, the existence or otherwise of a mechanism involving radical pathways was investigated by carrying out an experiment with complex **2** in the presence of a radical scavenger added at the beginning of the reaction (equimolar amounts of cyclooctene and 2,6-di-*tert*-butyl-4-methylphenol, under identical reaction conditions to those described in the Experimental Section). As shown in Figure 1 the reaction rate was not significantly affected, which suggests that a nonradical reaction mechanism is involved.

According to some authors, the mechanism of molybdenum(VI)-catalyzed epoxidation may be similar to those involving titanium(IV) and vanadium(V).[10,15] The reaction mechanisms suggest that the first step in the epoxidation of an alkene is the coordination of the Lewis basic hydroperoxide to the Lewis acidic metal center by the terminal oxygen, thereby activating the peroxide for oxygen transfer.[2p,6,11,15,16] As expected, in the absence of oxidant no reaction took place. There is a consensus that the nature of the reactive intermediate formed by coordination of TBHP to molybdenum complexes is of the alkylperoxidic type.[4,6,11] We have generalized this to the case of complexes **1**–**4** ([MoL^x], L^x = ligand set) for cyclooctene epoxidation (under the reaction conditions used), in which the oxidizing agent is [$MoL^y(O_2R)$] (R = *tert*-butyl), formed in Equation (1). The incoming TBHP molecule can affect the ligands such that L^x becomes L^y. In a previous study with the complexes [MoO_2X_2(4,4′-dihexyl-2,2′-bipyridine)] (X = Cl, Me) and TBHP we were able to re-isolate the unchanged starting complexes, in quantitative yield, after the catalytic reactions.[6,17] There is no indication that η^2-bisperoxo species of the type [$MoO(O_2)_2L$] are formed and then "recycled" to the starting materials. We can therefore conclude that the Mo–X bonds are not cleaved during the reaction with TBHP and that the catalytically active species exists in an equilibrium with the starting complex in solution.

$$\mathrm{TBHP} + [\mathrm{MoL^x}] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{MoL^y(O_2R)}] \tag{1}$$

Many studies have reported that molybdenum(VI) centers favor heterolytic peroxometal pathways (Mo^{VI} alkyl peroxide intermediate), leading to electrophilic attack on the olefinic double bond.[11,18] It has been reported for molybdenum peroxo complexes that oxygen transfer to the olefin takes place irreversibly.[15,16] We will therefore assume that cyclooctene is irreversibly oxidized to cyclooctene oxide (CyO) by [$MoL^y(O_2R)$], with formation of the starting complex [MoL^x] and *tert*-butyl alcohol [TBOH, Equation (2)]. It is known that molybdenum catalysts are active for the conversion of TBHP to TBOH.[10,11,16,19]

$$[\mathrm{MoL^y(O_2R)}] + \mathrm{Cy} \xrightarrow{k_3} [\mathrm{MoL^x}] + \mathrm{CyO} + \mathrm{TBOH} \tag{2}$$

Molybdenum-catalyzed epoxidations with TBHP can be prone to autoretardation by the co-product TBOH, the extent of which would be related to the equilibrium constants for the formation of catalyst–alkylperoxide and catalyst–alkoxide complexes.[3f,3h,20] Such autoretardation effects would explain the decrease of the observed reaction rate, which is more rapid in the case of the more active complex **2** (Figure 1). When TBOH was added at the beginning of the reaction (equimolar amounts of cyclooctene and TBOH, under identical reaction conditions to those described in the Experimental Section), the initial activity of **2** for cyclooctene epoxidation decreased by about 44%. On the other hand, TBHP efficiency for cyclooctene conversion (determined by iodometric titration at 240 min) was around 95% (TBHP consumed in cyclooctene epoxidation/total conversion of TBHP). It is assumed that TBOH can react reversibly with [MoL^x] to give a complex designated as [$MoL^z(OR)$] [Equation (3)].

$$[\mathrm{MoL^x}] + \mathrm{TBOH} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} [\mathrm{MoL^z(OR)}] \tag{3}$$

The overall rates of formation of cyclooctene, cyclooctene oxide, TBHP, TBOH, and molybdenum species can be written for the above elementary reactions as follows [Equations (4), (5), (6), (7), (8), (9) and (10)].

$$r_{\mathrm{Cy}} = -k_3[\mathrm{MoL}^y(\mathrm{O_2R})][\mathrm{Cy}] \quad (4)$$

$$r_{\mathrm{CyO}} = k_3[\mathrm{MoL}^y(\mathrm{O_2R})][\mathrm{Cy}] \quad (5)$$

$$r_{\mathrm{TBHP}} = -k_1[\mathrm{TBHP}][\mathrm{MoL}^x] + k_2[\mathrm{MoL}^y(\mathrm{O_2R})] \quad (6)$$

$$r_{\mathrm{TBOH}} = k_3[\mathrm{MoL}^y(\mathrm{O_2R})][\mathrm{Cy}] - k_4[\mathrm{MoL}^x][\mathrm{TBOH}] + k_5[\mathrm{MoL}^z(\mathrm{OR})] \quad (7)$$

$$r_{[\mathrm{MoL}^x]} = -k_1[\mathrm{TBHP}][\mathrm{MoL}^x] + k_2[\mathrm{MoL}^y(\mathrm{O_2R})] + k_3[\mathrm{MoL}^y(\mathrm{O_2R})][\mathrm{Cy}] - k_4[\mathrm{MoL}^x][\mathrm{TBOH}] + k_5[\mathrm{MoL}^z(\mathrm{OR})] \quad (8)$$

$$r_{[\mathrm{MoL}^y(\mathrm{O_2R})]} = k_1[\mathrm{TBHP}][\mathrm{MoL}^x] - k_2[\mathrm{MoL}^y(\mathrm{O_2R})] - k_3[\mathrm{MoL}^y(\mathrm{O_2R})][\mathrm{Cy}] \quad (9)$$

$$r_{[\mathrm{MoL}^z(\mathrm{OR})]} = k_4[\mathrm{MoL}^x][\mathrm{TBOH}] - k_5[\mathrm{MoL}^z(\mathrm{OR})] \quad (10)$$

Assuming that $[\mathrm{MoL}^x]$, $[\mathrm{MoL}^y(\mathrm{O_2R})]$, and $[\mathrm{MoL}^z(\mathrm{OR})]$ are the only metal species formed, and that their total concentration at any instant is equal to the initial concentration of complex $[\mathrm{MoLx}]_0$, we get [Equation (11)]

$$[\mathrm{MoL}^x]_0 = [\mathrm{MoL}^x] + [\mathrm{MoL}^y(\mathrm{O_2R})] + [\mathrm{MoL}^z(\mathrm{OR})] \quad (11)$$

Applying a mole balance to a homogeneous liquid-phase batch reactor (constant-volume reaction process under isothermal operation) the following differential equation can be written with respect to each chemical species [Equation (12)]

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = r_{\mathrm{P}} \quad (12)$$

where P is cyclooctene, cyclooctene oxide, TBHP, TBOH, or a molybdenum species. Figure 2 shows the model fitting to data points for the experiments of cyclooctene epoxidation with TBHP in the presence of **1**–**4**. In all cases the predicted kinetic curves fit the experimental data points. The fairly good fitting achieved indicates that the above mechanism of cyclooctene oxidation is consistent with the experimental data and that the assumptions made are valid and reasonable.

UV/Vis Studies of Catalyst Formation

The kinetics of the reaction of $[\mathrm{MoL}^x]$ with TBHP in the absence of any reductant was studied by UV/Vis spectroscopy, thereby allowing equilibrium constants and rate constants to be determined for this step.

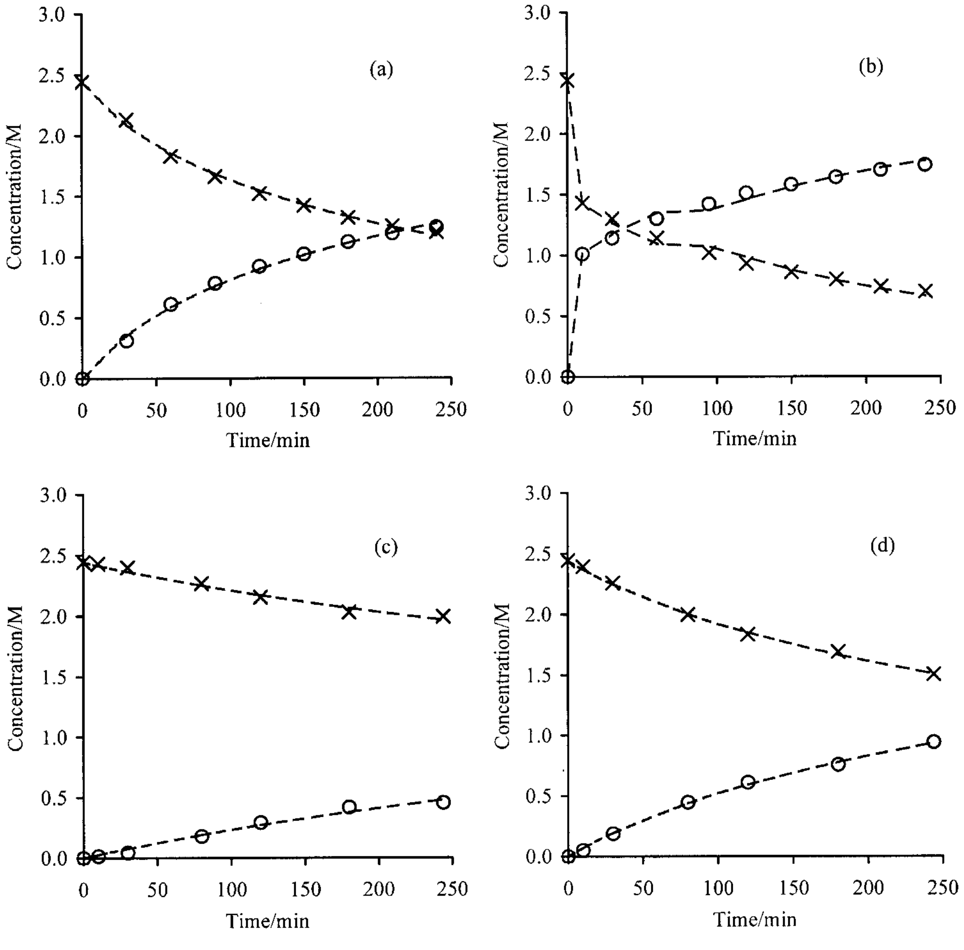


Figure 2. Concentration vs. time profiles of cyclooctene and cyclooctene oxide for (a) **1**, (b) **2**, (c) **3** and (d) **4** determined experimentally (points) and calculated for the proposed model (dashed lines).

The Equilibrium Constants of Catalyst Formation

The absorbance vs. concentration diagram of solutions of complex **3** and **4** with TBHP is not like a titration curve (see Figure 3 for complex **3**). It continues, however, to build up as more TBHP is added, until finally a plateau is reached. This reaction was assumed to form a 1:1 adduct, $[MoL^y(O_2R)]$, in equilibrium with the original $[MoL^x]$ and TBHP [Equation (1)]. The changes in absorbance (at 300 nm) due to the loss of $[MoL^x]$ and formation of $[MoL^y(O_2R)]$ can be expressed by Equation (13) (assuming a 1.0-cm path-length)

$$\mathrm{Abs} = \varepsilon_1[\mathrm{MoL}^x] + \varepsilon_2[\mathrm{MoL}^y(\mathrm{O_2R})] \tag{13}$$

where ε_1 and ε_2 are the molar absortivities for $[MoL^x]$ and $[MoL^y(O_2R)]$ adducts, respectively. Substituting the equilibrium constant (K_{eq}) for the formation of the $[MoL^y(O_2R)]$ adduct in Equation (13), and using the molar balance $[Mo]_T = [MoL^x] + [MoL^y(O_2R)]$, we obtain Equation (14):

$$\frac{\mathrm{Abs}}{[\mathrm{Mo}]_\mathrm{T}} = \frac{\varepsilon_1 + \varepsilon_2 K_\mathrm{eq}[\mathrm{TBHP}]}{1 + K_\mathrm{eq}[\mathrm{TBHP}]} \tag{14}$$

The data were obtained with a constant initial concentration of MoL^x and over a range of concentrations of TBHP of 5.0–50 mM. The fitting of Equation (14) to the experimental data of absorbance (at equilibrium) as a function of TBHP allowed values for the equilibrium constants to be calculated (Figure 3, Table 1).

The thermodynamic parameters for the reaction of **3** with TBHP to form the catalyst were estimated from the equilibrium constants at 25 °C and 55 °C, determined as 123 ± 19 and 482 ± 34 M^{-1}, respectively (Table 1). The values of ΔG (at 25 °C), ΔH, and ΔS are -12 kJ mol^{-1}, $+28.6$ kJ mol^{-1} and $+136$ J mol^{-1} K^{-1}, respectively, indicating that the formation of the catalyst is an endothermic and spontaneous process. The positive enthalpy value may also indicate that the Mo–OOR bond is weaker than the Mo–X bond. The equilibrium constant for the reaction of **3** with TBHP is seven to eight times greater than that for the reaction of **4** with TBHP. It seems therefore that the presence of the large hexyl substituent (compared with the methyl for **3**) reduces the stability of the catalyst relative to the starting complex. This would explain the observed higher reactivity (lower stability) of the Mo^{VI} oxidizing species bearing a hexyl group towards cyclooctene epoxidation.

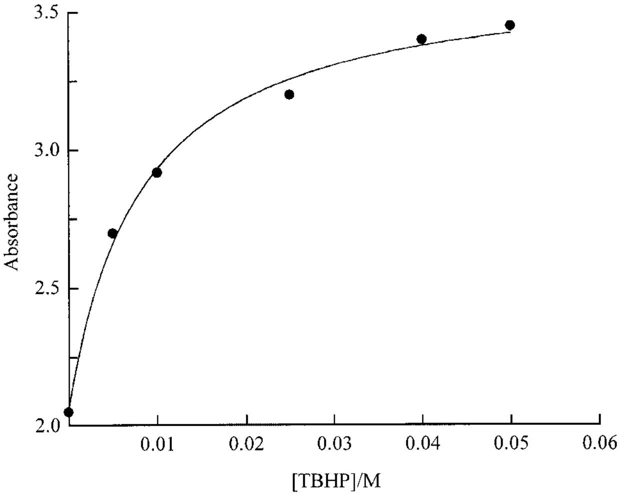


Figure 3. A plot of the absorbance at 300 nm of equilibrium mixtures of TBHP and **3** as a function of [TBHP] at $[Mo]_T = 0.5$ mM in acetonitrile at 25 °C. The solid line is the absorbance calculated from Equation (14) with the values of $K_{eq} = 123$ M^{-1}, $\varepsilon_1 = 4.0 \times 10^3$ $\mathrm{M}^{-1}\mathrm{cm}^{-1}$ and $\varepsilon_2 = 7.3 \times 10^3$ $\mathrm{M}^{-1}\mathrm{cm}^{-1}$.

Kinetic Studies of Catalyst Formation

The rate constants for the reactions of complexes **2**, **3** and **4** with TBHP were determined by initial rate (method I) and pseudo-first-order (method II) methods. In both cases, the complexes were in limiting amount (0.5 mM) and TBHP in large excess (at least 10-fold).

Initial Rate (Method I)

The initial rates (v_i) were calculated from the initial absorbance change (2–5%) of the absorbance-time curves based on Equation (15),

Table 1. The equilibrium constants and the rate constants for the reactions of the Mo^{VI} complexes **2**, **3** and **4** with TBHP.

Complex	K_{eq}	k_1 [L mol^{-1} s^{-1}]	k_2 [10^{-3} s^{-1}]	$\Delta H^\ddagger$ [kJ mol^{-1}]	$\Delta S^\ddagger$ [J (mol K)$^{-1}$]
2	–[a]	$(1.5 \pm 0.3)\times10^{-4}$[b]		80 ± 2	-76 ± 32
		$(1.7 \pm 0.4)\times10^{-3}$[c]			
3	123 ± 19[b]	0.043 ± 0.005[b][d]	0.35[b]	65.7 ± 6.0	-39 ± 5
		0.061 ± 0.008[b][e]	0.50[b]		
	482 ± 34[c]	0.25 ± 0.02[c][d]	0.52[c]		
		0.36 ± 0.06[c][e]	0.75[c]		
4	16 ± 7[b]	0.059 ± 0.008[b][d]	3.7[b]	49.0 ± 4.2	-96 ± 13
		0.067 ± 0.010[b][e]	4.2[b]		
		0.47 ± 0.06[c][d]			
		0.63 ± 0.12[c][e]			

[a] Not determined. [b] At 25 °C. [c] At 55 °C. [d] Obtained by method I. [e] Obtained by method II.

$$v_i = \frac{\Delta \mathrm{Abs}_i}{\Delta t \cdot b \cdot \Delta\varepsilon} \qquad (15)$$

where $\Delta\mathrm{Abs_i}$ is the initial absorbance change observed for the reaction of complex **i** (i = **2**, **3**, **4**) with TBHP in the time interval Δt, $\Delta\varepsilon$ is the difference in the molar absortivities of the starting complex [MoL^x] and the catalyst [MoL^y(O$_2$R)], and b is the light path length. Variation of the initial rate with the initial concentration of TBHP is shown in Figure 4 for complex **3** at 55 °C. The second-order rate constants (k_1, Table 1) were calculated from the slopes based on the rate-law equation v_i = k_1[MoL^x][TBHP], where slope = k_1[MoL^x].

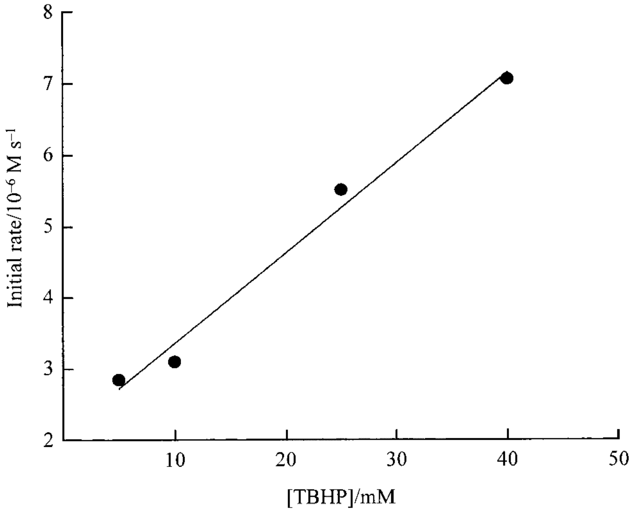


Figure 4. Variation of the initial rate with [TBHP] for the reaction of **3** (0.5 mM) and TBHP in acetonitrile at 55 °C. The solid line represents the calculated data based on a linear fit of the experimental data with slope = k_1[**3**] = 1.25×10^{-4} s^{-1}.

Pseudo-First-Order (Method II)

In this method, the pseudo-first-order rate constants (k_ψ) were determined by fitting the last 20–50% of the absorbance vs. time curves to a first-order exponential equation, in a similar fashion to that reported previously.[21] The values of k_ψ vary linearly with [TBHP] in the range 5–25 mM and the slopes give the second-order rate constants (k_1), as shown in Figure 5 for complex **4** at 25 °C. The values of the reverse rate constants k_2 [Equation (1)] were calculated from the values of the second-order rate constants k_1 for the reaction of complexes **2**, **3**, and **4** with TBHP and the equilibrium constants, $k_2 = k_1/K_\mathrm{eq}$. Methods I and II give similar values of k_1 and k_2 within the range of experimental error (Table 1).

The kinetic results show that the rate of formation of the catalyst, [MoLy(O$_2$R)], is much faster for the Br complexes than for the Cl ones (Table 1). For example, the rate constant for the formation of the catalysts from the reaction of [MoO$_2$Br$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (**4**) with TBHP is 2–3 orders of magnitude higher than that for the reaction of [MoO$_2$Cl$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (**2**) with TBHP. These results, taken together with the fact that Br catalysts of this type generally possess lower activity towards epoxidation of an olefin,[6] suggest that the first step (the catalyst formation) is not always the rate-limiting step of cyclooctene epoxidation with these complexes.

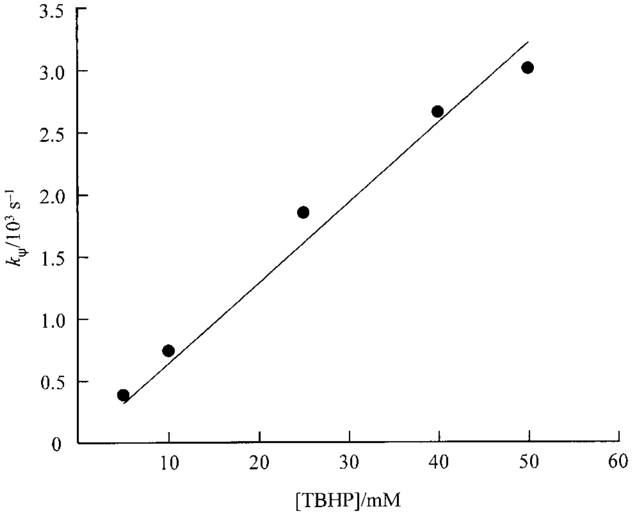


Figure 5. A plot of the pseudo-first-order rate constants as a function of [TBHP] for the reaction of **4** (0.5 mM) with TBHP in acetonitrile at 25 °C.

Experimental results on the effect of temperature variation in the range 20–60 °C on the catalyst formation from the reaction of complexes **1**–**4** with TBHP showed that the rate increases significantly with increasing temperature. Plots of ln(k_1/T) vs. $1/T$, where k_1 is the second-order rate constant for the reaction of the Mo complex with TBHP, led to the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (Figure 6,

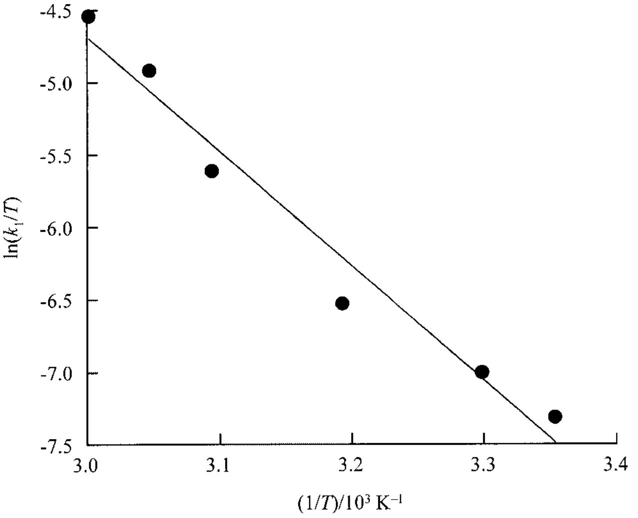


Figure 6. A plot of ln(k_1/T) vs. $1/T$ for the catalyst formation from the reaction of TBHP with **3** in acetonitrile. The activation parameters were calculated from the slope (–7.9) and the intercept (19.0) based on the equation $\ln(k_1/T) = 23.76 + \Delta S^\ddagger/R - \Delta H^\ddagger/R(1/T)$.

Table 1). All the $\Delta S^{\ddagger}$ values obtained for the catalyst formation in this study have negative values, thus indicating that the catalyst formation is associated with an entropy decrease. These results support an associative mechanism in which a seven-coordinate intermediate is formed. The trend in the $\Delta H^{\ddagger}$ values confirms the trend in the rate constants for the catalyst formation (k_1 decreases in the order **4** $>$ **3** $>$ **2**). Also, the values of $\Delta H^{\ddagger}$ are of the same order of magnitude as those obtained for similar W complexes.[21] However, in the case of the Mo complexes the values of $\Delta H^{\ddagger}$ are generally lower, which explains the higher activity of Mo catalysts in comparison with the W ones.

Concluding Remarks

Several complexes with the general formula $[MoO_2X_2L]$ (X = Cl, Br) have been synthesized and examined as catalysts for the epoxidation of cyclooctene using TBHP as the oxidant. The kinetics studies support the theory that the first step in the reaction mechanism is associative and involves the reaction of TBHP with the starting complex. It is assumed that the peroxide transfers a hydrogen to one of the Mo=O oxygens and the remaining ROO^- anion binds as a seventh ligand. In contrast to recent findings on tungsten complexes[21] and with theoretical investigations on Mo complexes, the present work indicates that the first step is not always the rate-limiting step. DFT calculations are being carried out in order to probe in more detail various aspects of the reaction mechanism.

Experimental Section

All preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures (THF, hexane, and diethyl ether over Na/benzophenone ketyl; CH_2Cl_2 and CH_3CN over CaH_2), distilled, and kept under nitrogen over molecular sieves. Microanalyses were performed at the ITQB and the Mikroanalytische Labor of the Technical University of Munich (M. Barth). IR spectra were measured on Mattson Mod 7000 and Perkin–Elmer FTIR spectrometers using KBr pellets. Solution NMR spectra were measured on Bruker CXP 300 (^{1}H, 300 MHz), Bruker Avance DPX-400 (^{1}H: 400 MHz; ^{13}C: 100.28 MHz; ^{95}Mo: 26.07 MHz) and JEOL JNM GX-400 (^{13}C: 100.28 MHz; ^{17}O: 54.14 MHz) spectrometers. 4,4′-Dimethyl-2,2′-bipyridine was purchased from Aldrich and used as received. The compounds 4-hexyl-4′-methyl-2,2′-bipyridine,[22] $[MoO_2X_2]$ (X = Cl, Br)[23] and $[MoO_2X_2(THF)_2]$ (X = Cl, Br)[2b] were prepared according to published procedures with only minor changes.

Synthesis of Complexes 1–4: The complexes $[MoO_2Cl_2(THF)_2]$ (1.37 g, 4.00 mmol) and $[MoO_2Br_2(THF)_2]$ (1.73 g, 4.00 mmol) were each dissolved in CH_2Cl_2 (20 mL) and treated with 1 equiv. of 4,4′-dimethyl-2,2′-bipyridine or 4-hexyl-4′-methyl-2,2′-bipyridine. The resulting turbid solutions were each stirred for a further 1 h. The solvent was removed under vacuum, and the product washed with diethyl ether and dried under vacuum.

[MoO$_2$Cl$_2$(4,4′-dimethyl-2,2′-bipyridine)] (1): Yield: 1.47 g (96%). Selected IR (KBr): $\tilde{\nu}$ = 1613 cm^{-1} (vs), 1025 (s), 938 (vs) (Mo=O$_{asym}$), 907 (vs) (Mo=O$_{sym}$), 832 (vs), 517 (s) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 20 °C): δ = 3.00 (s, 6 H, CH$_3$), 8.18 (d, 2 H, py-H), 9.11 (s, 2 H, py-H), 9.68 (d, 2 H, py-H) ppm. ^{95}Mo NMR (DMSO, 20 °C): δ = 205 ppm. $C_{12}H_{12}Cl_2MoN_2O_2$ (383.08): calcd. C 37.62, H 3.16, N 7.31; found C 37.48, H 2.96, N 7.29.

[MoO$_2$Cl$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (2): Yield: 1.65 g (91%). Selected IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (s), 1611 (vs), 1417 (s), 1026 (s), 938 (vs) (Mo=O$_{asym}$), 913 (vs) (Mo=O$_{sym}$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C): δ = 0.90 (t, 3 H, CH_3CH$_2$-), 1.33 [m, 6 H, (CH$_2$)$_3$], 1.75 (m, 2 H, CH$_2$), 2.60 (s, 3 H, CH$_3$), 2.86 (m, 2 H, CH$_2$), 7.54 (d, 2 H, py-H), 8.09 (s, 2 H, py-H), 9.33 (t, 2 H, py-H) ppm. ^{13}C NMR (CD$_3$Cl, 20 °C): δ = 14.4, 22.15, 22.86, 29.34, 30.49, 31.88, 36.23, 122.68 (py-C), 123.46 (py-C), 127.36 (py-C), 128.10 (py-C), 149.91 (py-C), 151.96 (py-C), 158.26 (py-C) ppm. ^{95}Mo NMR (CD$_2$Cl$_2$, 20 °C): δ = 201 ppm. $C_{17}H_{22}Cl_2MoN_2O_2$ (453.21): calcd. C 45.05, H 4.89, N 6.18; found C 45.07, H 4.75, N 6.07.

[MoO$_2$Br$_2$(4,4′-dimethyl-2,2′-bipyridine)] (3): Yield: 1.47 g (78%). Selected IR (KBr): $\tilde{\nu}$ = 1614 cm^{-1} (vs), 1025 (s), 935 (vs) (Mo=O$_{asym}$), 905 (vs) (Mo=O$_{sym}$), 830 (s), 517 (s) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 20 °C): δ = 2.57 (s, 6 H, CH$_3$), 7.72 (d, 2 H, py-H), 8.55 (s, 2 H, py-H), 8.73 (d, 2 H, py-H) ppm. ^{95}Mo NMR (DMSO, 20 °C): δ = 254 ppm. $C_{12}H_{12}Br_2MoN_2O_2$ (471.98): calcd. C 30.54, H 2.56, N 5.94; found C 30.42, H 2.40, N 5.77.

[MoO$_2$Br$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (4): Yield: 1.54 g (71%). Selected IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (s), 1611 (vs), 1417 (s), 1026 (s), 935 (vs) (Mo=O$_{asym}$), 906 (vs) (Mo=O$_{sym}$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C): δ = 0.83 (t, 3 H, CH_3CH$_2$-), 1.28 [m, 6 H, (CH$_2$)$_3$], 1.70 (m, 2 H, CH$_2$), 2.54 (s, 3 H, CH$_3$), 2.78 (m, 2 H, CH$_2$), 7.48 (d, 2 H, py-H), 8.02 (d, 2 H, py-H), 9.32 (t, 2 H, py-H) ppm. ^{13}C NMR (CD$_3$Cl, 20 °C): δ = 14.0, 21.8, 22.5, 29.0, 30.1, 31.5, 35.9, 122.4 (py-C), 123.2 (py-C), 127.0 (py-C), 127.8 (py-C), 149.6 (py-C), 151.9 (py-C), 153.2, 157.9 (py-C) ppm. ^{95}Mo NMR (CD$_2$Cl$_2$, 20 °C): δ = 251 ppm. $C_{17}H_{22}Br_2MoN_2O_2$ (542.12): calcd. C 37.66, H 4.09, N 5.17; found C 37.49, H 3.88, N 5.09.

Synthesis of ^{17}O-Labeled Complexes 5–8: The labeled complexes $[Mo^{17}O_2Cl_2(DMF)_2]$ and $[Mo^{17}O_2Br_2(DMF)_2]$ were prepared according to the published procedure using $H_2{}^{17}O$.[4] IR (KBr): $\tilde{\nu}$ = 941 cm^{-1} (s), 928 (vs), 904 (vs), 891 (s), 870 (vs), 860 (s) (Mo=O) cm^{-1}. Recrystallization of $[Mo^{17}O_2X_2(DMF)_2]$ (X = Cl, Br) from THF gave the labeled starting materials $[Mo^{17}O_2Cl_2(THF)_2]$ and $[Mo^{17}O_2Br_2(THF)_2]$, which were subsequently used to prepare the labeled Lewis-base adducts **5**–**8**.

[Mo^{17}O$_2$Cl$_2$(4,4′-dimethyl-2,2′-bipyridine)] (5): IR (KBr): $\tilde{\nu}$ = 938 cm^{-1} (vs), 924 (s), 908 (vs), 897 (s), 874 (s) (Mo=O) cm^{-1}. ^{17}O NMR (DMSO, 20 °C): δ = 1005 ppm.

[Mo^{17}O$_2$Cl$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (6): IR (KBr): $\tilde{\nu}$ = 937 cm^{-1} (vs), 928 (s), 913 (vs), 903 (s), 889 (m), 871 (s) (Mo=O) cm^{-1}. ^{17}O NMR (CD$_2$Cl$_2$, 20 °C): δ = 993 ppm.

[Mo^{17}O$_2$Br$_2$(4,4′-dimethyl-2,2′-bipyridine)] (7): IR (KBr): $\tilde{\nu}$ = 934 cm^{-1} (s), 922 (s), 904 (vs), 895 (s), 869 (s) (Mo=O) cm^{-1}. ^{17}O NMR (DMSO, 20 °C): δ = 1003 ppm.

[Mo^{17}O$_2$Br$_2$(4-hexyl-4′-methyl-2,2′-bipyridine)] (8): IR (KBr): $\tilde{\nu}$ = 934 cm^{-1} (vs), 927 (s), 903 (vs), 871 (m) (Mo=O) cm^{-1}. ^{17}O NMR (CD$_2$Cl$_2$, 20 °C): δ = 994 ppm.

Catalytic Reactions with Compounds 1–4 as Catalysts: The epoxidation of cyclooctene was carried out at 55 °C, in air, in a batch reactor equipped with a magnetic stirrer. The reactor was loaded with 73 µmol of complex, 7.3 mmol of cyclooctene (1% molar ratio of catalyst/substrate) and 11 mmol of *tert*-butyl hydroperoxide (5.5 M in decane), which was used as oxidant. Samples were withdrawn periodically and analyzed with a gas chromatograph (Varian 3800) equipped with a capillary column (SPB-5, 20 m × 0.25 mm × 0.25 µm) and a flame ionization detector. The products were identified by gas chromatography-mass spectrometry (HP, 5890 Series II GC; HP 5970 Series Mass Selective Detector) using He as carrier gas.

UV/Vis Experiments: All kinetic experiments were carried out under pseudo-first-order conditions with excess TBHP in CH_3CN at 25 and 55 °C. The reactions were carried out in quartz cuvettes with a path length of 1 cm. In a typical experiment, TBHP was added to a thermostatted UV cell containing a solution of the catalyst. The catalyst concentration was held constant at 0.5 mM and TBHP concentration was varied in the range 5.0–50 mM. The absorbance changes at 300 nm were recorded with time using a Jasco V-560 spectrophotometer equipped with a Jasco EHC-477S Peltier thermostatted single cell holder. All data analysis was carried out with the KaleidaGraph program.

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