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Molybdenum vs. Tungsten for the epoxidation of cyclooctene catalyzed by $[\text{Cp}^*_2\text{M}_2\text{O}_5]$

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The catalytic activity of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ (M = Mo, W) for the homogeneous epoxidation of cyclooctene in a MeCN/toluene solvent mixture follows the order Mo \gg W when using TBHP/decane as oxidant, in contrast to the inverse order (W \gg Mo) when using aqueous H_2O_2 as oxidant. The catalytic activity for the Mo system strongly depends on the solvent used to deliver the oxidant (TBHP/decane \gg TBHP/ H_2O). The low activity of the W system is also decreased when using TBHP/water in place of TBHP/decane. For both metals, $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ is a better oxidant than

TBHP/ H_2O . However, while the Mo-based catalyst is much more active for the TBHP/decane epoxidation in spite of the lower TBHP oxidizing power (TBHP/decane $>$ $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ $>$ TBHP/ H_2O), the W-based system is much more active for the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ epoxidation in spite of the negative effect of water ($\text{H}_2\text{O}_2/\text{H}_2\text{O}$ $>$ TBHP/decane $>$ TBHP/ H_2O). The kinetic profile of the TBHP/decane epoxidation process is affected by product inhibition. Initial rate measurements show that the rate law is first order in substrate and has saturation behaviour in oxidant.

Introduction

Epoxidation catalysis continues to attract a lot of attention in the academic^[1] and industrial^[2] research laboratories in view of the versatility of the epoxide products as reaction intermediates in the fine chemical and polymer industries. New emphasis on this process comes from the conversion of new substrates obtained from biomass^[3] and from the desire of greener catalytic protocols for the transformation of traditional fossil resources.^[4]

In recent years, the catalytic performance of half-sandwich Group 6 (mostly Mo) complexes has been of particular interest in a few laboratories, including ours. The catalytic activity of $[\text{Cp}^*\text{MoO}_2\text{Cl}]$ in olefin epoxidation by *tert*-butylhydroperoxide (TBHP) was first described by Bergman *et al.*^[5] Many investigations were then reported by the groups of Romão, Kühn, Gonçalves and Abrantes,^[1c, 6] notable features being the very high initial activities achieved for certain systems in ionic liquid media

and the possibility to anchor the catalyst on a solid support with a certain degree of recyclability. Major problems of these systems are their deactivation, which seems to be caused at least in part by product inhibition, and their lower efficiency in the presence of water or when H_2O_2 is used as oxidant.^[6g] In many cases, however, the shortcoming of H_2O_2 could be simply related to mass transport problems in the biphasic systems.

We first observed and reported that the dinuclear compounds $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ (M = Mo, W) are excellent catalysts for the oxidation of thiophene derivatives to the corresponding sulfoxides and sulfones by aqueous H_2O_2 in MeCN. Not only was this the first report of the use of half-sandwich W^{VI} systems in catalytic oxidation, but the study also unexpectedly revealed that the W system is ca. 100 more active than the Mo system.^[7] The study further revealed, through kinetic investigations on the W system, that the catalyst does not degrade during the process and that the reaction rate is first order in substrate and zero order in H_2O_2 . Therefore, half-sandwich Mo and W systems are well capable of working with $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ as oxidant, provided the system is homogeneous, namely substrate, oxidant and catalyst are in the same phase. However, additional experiments run with the more active W catalyst have revealed that water has a negative effect on the reaction rate when added in large amounts to the catalytic mixture.


Encouraged by these results, the same catalytic system ($[\text{Cp}^*_2\text{M}_2\text{O}_5]$ in MeCN) was investigated for the epoxidation of cyclooctene by aqueous H_2O_2 . The only difference relative to the thiophene oxidation study was the need to add toluene as an inert co-solvent (1:3 relative to MeCN) in order to maintain the solution homogeneous (cyclooctene is not fully miscible in MeCN at the concentration needed for the experiments). The results paralleled those of the oxidation of the thiophene derivatives: the oxidation was efficient, selective (no product other than cyclooctene oxide were detected) and must be faster for the W system, a factor of ~ 50

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being measured in this case.^[8] Once again, the kinetics investigation indicated a first order dependence on the oxidized substrate (cyclooctene in this case) and zero order dependence in H₂O₂. Further investigations confirmed the expected first order dependence in catalyst, as well as the stability of the catalytic system against deactivation. Like in the thiophene oxidation study, the addition of large amounts of water revealed a negative effect on the catalytic activity. Finally, a study at variable temperature in the 25-55°C range for the W system allowed the derivation of the activation parameters ($\Delta H^\ddagger = 10.2(6)$ kcal/mol; $\Delta S^\ddagger = -32(2)$ e.u.) for the catalytic cycle. This study also included a comparative computational investigation of the catalytic cycle for the Mo and W systems, on the basis of the hypothesis that the reaction follows a pathway involving oxidant activation by protonation of a M=O function to yield a {M(OH)(O^αO^βH)} intermediate, followed by transfer of the O^α atom to the substrate. This pathway had already been previously calculated for the Mo system,^[9] with only small changes relative to a proposition made by Thiel^[10] and inspired by the original hypothesis formulated by Sharpless.^[11] The calculations indeed showed that the barrier of the catalytic cycle is slightly smaller for the W system. The explanation for the better catalytic activity of the W system was attributed to the greater oxophilicity and Lewis acidity of the W center, which interacts more strongly with the O^β atom in the transition state of the O^α transfer process.

The above mentioned comparative calculations^[8] were run only for H₂O₂ as the oxidant, whereas those previously published for the Mo system were also run for MeOOH as a computational model for TBHP. The profiles are essentially identical, although the barrier for the MeOOH system is marginally higher. The validity of these calculations and of the mechanistic hypothesis would lead us to predict that [Cp*₂W₂O₅] should also be a better catalyst than [Cp*₂Mo₂O₅] when using TBHP as oxidant. We have therefore investigated the relative activity of the two compounds for the epoxidation with TBHP/decane and found, contrary to the above prediction, that the Mo system is a much better catalyst under these conditions. Along this investigation, we have observed dramatic effects on the rate of the catalytic process depending on the nature of the metal (Mo vs. W), of the oxidant (TBHP vs. H₂O₂) and of the solvent that delivers the oxidant to the substrate solution (decane vs. H₂O). We report here the results of this investigation.

Results and Discussion

(a) Solvent effect

A preliminary investigation of catalytic activity for the cyclooctene epoxidation by TBHP/decane with ¹H NMR monitoring was carried out at room temperature with 1% precatalyst (or 2% metal) in order to screen solvents. The investigation included chloroform, acetone, acetonitrile and methanol and the results are shown in Table 1.

The immediate striking observation is the much greater efficiency of the dinuclear Mo^{VI} compound than the W^{VI} analogue, which is in the inverse order relative to the use of aqueous H₂O₂ epoxidation in MeCN/toluene (see Introduction). Chloroform is the best solvent for this reaction, giving a very high yield in the shortest time (84.5% in 20.5 h), but only for the Mo compound. The W analogue proves very inefficient under the same conditions with only trace amounts of product measured after 14 days. The result for [Cp*₂Mo₂O₅] in this solvent reproduces that reported in a previous contribution,^[6g] including the observed formation of a white precipitate, the nature of which is unknown. Thus, although

this reaction is initially very fast and homogeneous, it rapidly turns to a heterogeneous system. Yield and conversion are in good correspondence and the mass balance is excellent (see details in Figure S1). The catalytic mixtures in all other investigated solvents, on the other hand, remained homogeneous.

Table 1. Cyclooctene oxide yield for the cyclooctene epoxidation by TBHP catalyzed by 1% [Cp*₂M₂O₅] (M = Mo or W) at room temperature in different solvents.^[a]

Solvent	M	Time	Cyclooctene oxide yield, %
CDCl ₃	Mo	20.5 h	84.5
CDCl ₃	W	14 days	0.02
(CD ₃) ₂ CO	Mo	7 days	-
(CD ₃) ₂ CO	W	7days	-
MeOD	Mo	5 days	47.1
MeOD	W	6 days	-
CD ₃ CN	Mo	8 days	89.0
CD ₃ CN	W	2 days	-

[a] Conditions: 0.1 mL of cyclooctene (0.78 mmol), 0.28 mL of TBHP (5.5 M in decane; 1.56 mmol), [Cp*₂M₂O₅] (4.2 mg for Mo; 5.6 mg for W; 7.8 · 10⁻³ mmol), 0.3 mL of deuterated solvent.

There was no conversion at all in (CD₃)₂CO for both catalysts. A negative effect of solvent coordination through the carbonyl oxygen atom, blocking the Lewis acidic sites of the catalyst, does not seem a reasonable rationalization for this lack of catalytic activity, because the same phenomenon should then occur also in MeCN and MeOH. On the other hand, the reaction takes place in these solvents, although more slowly than in chloroform, but once again much more rapidly for the Mo containing catalyst (no significant conversion was measured for the W-based catalyst under these conditions). Plots of yield and conversion vs. time for the Mo-based catalyst in these two solvents, obtained from ¹H NMR monitoring, are given in the Supporting Information (Figures S2 and S3). Amongst these two solvents, CD₃CN affords the most efficient catalytic system, with nearly complete conversion after 8 days and very high selectivity, cyclooctene epoxide being the only observed product.

(b) Kinetics study

All subsequent catalytic experiments were carried out in a 3:1 CH₃CN/toluene combination in order to maintain the reaction mixture homogeneous at high substrate concentrations. The catalytic runs were carried out at 55°C and the reactions were followed by gas-chromatography with detection and quantification of the cyclooctene and cyclooctene oxide peaks. The conditions used are identical to those of the previous study with the H₂O₂ oxidant,^[8] except for the presence of the toluene co-solvent. A first run was carried out under pseudo-first order conditions (TBHP/cyclooctene = 8:1), allowing in principle the determination of the reaction order in cyclooctene. The GC monitoring showed that cyclooctene oxide was the terminal product with no additional visible peaks of by-products. There was a good mass balance (> 90%), the amount of produced cyclooctene oxide at each time being nearly the same as the amount of consumed cyclooctene.

Under these conditions, essentially all the cyclooctene was completely converted to the oxide product in ca. 3 hours, see Figure 1.

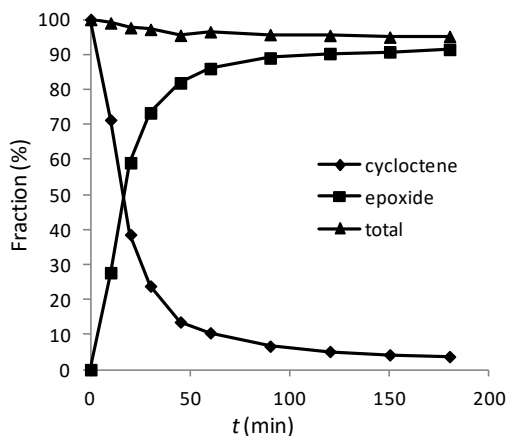
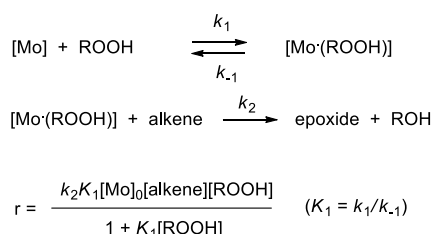


Figure 1. GC monitoring of the epoxidation of cyclooctene by TBHP (5.5 M in decane) in CD_3CN /toluene catalyzed by 1% $[\text{Cp}^*\text{Mo}_2\text{O}_5]$. Conditions: 6.4 mg of catalyst (0.0119 mmol); 0.16 mL of cyclooctene (1.19 mmol); 1.72 mL of TBHP (5.5 M in decane; 9.50 mmol), 6.05 mL (3:1 CH_3CN /Toluene) at 55°C.

The kinetic analysis shows that the cyclooctene decay does not fit as expected a first-order rate law (SI figures S4). It fits better a second order decay law (figure S5). However, such rate law dependence is unexpected and unreasonable, because it would indicate that two molecules of cyclooctene must be involved at the level of the rate-determining transition state. The generally accepted kinetic scheme for this process and the corresponding rate law are as shown in Scheme 1, predicting that the reaction should always be first order in alkene and with an order between zero and one for the oxidant, depending on the position of the catalyst-oxidant association equilibrium (saturation kinetics).^[12] We believe that the kinetics is affected by an interfering phenomenon that makes the olefin consumption look like a second order decay. One possibility is a dampening effect of the catalytic activity by the produced *tert*-butanol, namely a product inhibition phenomenon. Indeed, it has been previously highlighted that certain Mo-catalyzed epoxidations are product-inhibited, with a slow-down of the catalytic activity as the epoxide product accumulates.^[13]



Scheme 1. Kinetic scheme and rate law for the Mo-catalyzed olefin epoxidation.^[12]

In order to avoid the complication of product inhibition, we have carried out an investigation of initial rates: (a) on one hand, with variable concentration of cyclooctene at constant TBHP

concentration in order to determine the reaction order in cyclooctene; (b) on the other hand, with variable concentrations of TBHP at constant cyclooctene concentration in order to determine the reaction order in TBHP. All experiments were carried out with excess TBHP and the initial rates were measured on the basis of the cyclooctene consumption (see details in SI, Figures S6-S11), during a time interval where the TBHP concentration can be assumed to remain approximately constant, even for the experiments run with a low $[\text{TBHP}]/[\text{cyclooctene}]$ ratio. The initial rate values are reported in Table 2 and represented graphically in Figure 2. Once again, the reaction selectivity was excellent, with a good mass balance, and product inhibition was observed from the first-order kinetic analyses. From part (a) of the study, it is clear that the data are in better agreement, as expected, with a first order dependence of the reaction rate on the olefin concentration and not with a second order dependence as suggested by the kinetic analysis of the entire oxidation process. From part (b), the rates show a dependence on TBHP between zero and one, suggesting balance in the substrate-oxidant adduct formation equilibrium, in agreement with saturation behavior (Scheme 1; $K_1[\text{TBHP}]$ not too different from 1). A fit of these data to the rate equation of Scheme 1 for the independent determination of k_2 and K_1 is prevented by the limited number of points and by the approximate values of the measured initial rates.

Table 2. Initial rates of cyclooctene oxidation by TBHP catalyzed by 1% $[\text{Cp}^*\text{Mo}_2\text{O}_5]$ at different cyclooctene and TBHP concentrations.^[a]

Run	$[\text{TBHP}]_0 = 1.5 \text{ M};$ $[\text{Cp}^*\text{Mo}_2\text{O}_5] = 2.0 \cdot 10^{-3} \text{ M}$		Run	$[\text{cyclooctene}]_0 = 0.25 \text{ M};$ $[\text{Cp}^*\text{Mo}_2\text{O}_5] = 2.5 \cdot 10^{-3} \text{ M}$	
	$[\text{cyclooctene}]_0/\text{M}$	$v_0/\text{M}\cdot\text{s}^{-1}$ [b]		$[\text{TBHP}]_0/\text{M}$	$v_0/\text{M}\cdot\text{s}^{-1}$ [b]
1	0.199	$4.61 \cdot 10^{-4}$	4	0.496	$9.39 \cdot 10^{-5}$
2	0.412	$10.6 \cdot 10^{-4}$	5	0.911	$12.6 \cdot 10^{-5}$
3	0.769	$14.7 \cdot 10^{-4}$	6	1.563	$15.0 \cdot 10^{-5}$

[a] Solvent = 3:1 CH_3CN /Toluene, $T = 55^\circ\text{C}$. [b] Rates measured from the initial slope (5 min) of the [epoxide] vs. time plot.

Figure 3 shows a qualitatively energy profile that fits the above determined trends. Previously reported DFT calculations run on the $[\text{Cp}^*\text{MoO}_2\text{Cl}]$ catalyst first used by Bergman^[5] (which can also be considered as a model of the $[\text{Cp}^*\text{Mo}_2\text{O}_5]$ catalyst) have shown that the adduct with MeOOH (used as a model of *t*BuOOH), $[\text{Cp}^*\text{MoO}(\text{OH})(\text{OOMe})\text{Cl}]$, lies at higher energy than the corresponding adduct with H_2O_2 , $[\text{Cp}^*\text{MoO}(\text{OH})(\text{OOH})\text{Cl}]$.^[9] Therefore, the adduct formation equilibrium is expected to lie less extensively on the right hand side for TBHP (Figure 3, case A) and lead to the observed behavior in Figure 2(b), whereas H_2O_2 is able to displace further the adduct formation equilibrium (Figure 3, case B) and give an observed zero order dependence on H_2O_2 . This difference can be easily understood in terms of steric bulk, the bigger *t*-Bu group destabilizing the catalyst-oxidant adduct.

Another interesting question is why there is product inhibition when using TBHP, whereas the cyclooctene concentration follows clean first-order decay when using H_2O_2 .^[8] In the TBHP system, product inhibition can be related to coordination of the *tert*-butanol, the reaction by-product generated from TBHP, to a catalyst

coordination site, making it less available to operate the catalytic cycle, or to formation of a catalyst-*tert*-butanol adduct that has greater stability than the catalyst resting state. In each case, an energetically more stable off-loop species would form after the beginning of the reaction, gradually increasing the energy span of the catalytic cycle. When the oxidant is aqueous H₂O₂, on the other hand, the by-product of the reaction is water, which is already present in the medium from the beginning of the reaction. Therefore, a retardation effect is not expected.

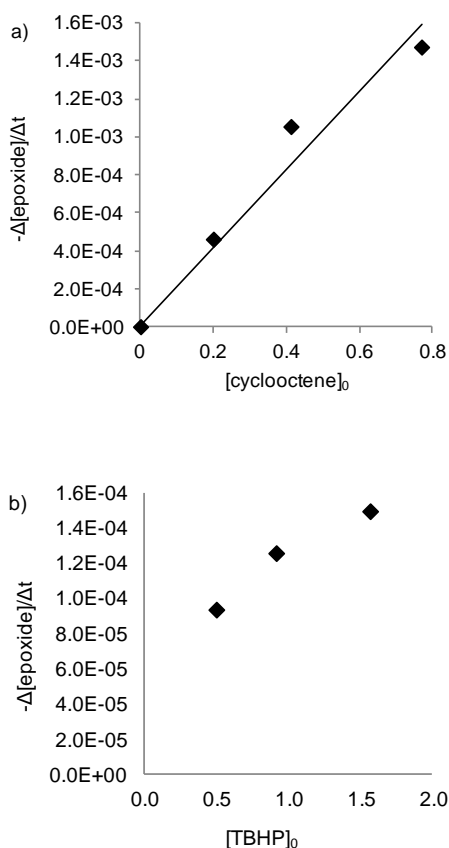


Figure 2. Dependence of the initial rate of cyclooctene oxidation by TBHP catalyzed by 1% [Cp*₂Mo₂O₅] on: (a) [cyclooctene] at constant [TBHP] and [Cp*₂Mo₂O₅]; (b) [TBHP] at constant [cyclooctene] and [Cp*₂Mo₂O₅].

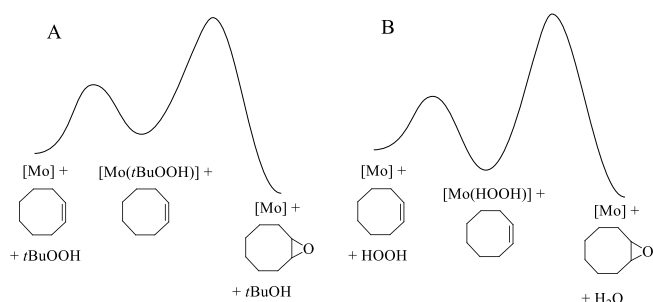


Figure 3. Energy profiles of two limiting rate laws for the kinetic scheme shown in Scheme 1.

The temperature dependence of the catalytic reaction was investigated in the temperature range 35–65°C under standard conditions, namely with 1% catalyst and with a [TBHP]/[cyclooctene] ratio of 10, in order to insure pseudo-first order conditions. The kinetic profiles are given in Figure S12. The cyclooctene

decay was again affected by retardation at high conversions. Hence, the observed pseudo-first order rate constants were obtained from the first-order decay analysis restricted to the initial phase of the reaction (< 40 min), see Figure S13. The observed rate constants are collected in Table 3.

Table 3. Rate constants for the [Cp*₂Mo₂O₅] catalyzed epoxidation of cyclooctene by TBHP at different temperatures.^[a]

T (°C)	k_{obs} (s ⁻¹)	$k_{\text{obs}}/[\text{cat}]$ (s ⁻¹ ·M ⁻²)
35	1.17·10 ⁻⁴	0.468
45	3.57·10 ⁻⁴	1.43
55	6.16·10 ⁻⁴	2.46
65	1.22·10 ⁻³	4.88

[a] Reaction conditions: [Cp*₂Mo₂O₅] = 4.8·10⁻⁴ M; [cyclooctene] = 0.048 M; [TBHP] = 0.48 M. Solvent = MeCN/toluene (2:1).

The subsequent Eyring analysis of the data is not straightforward because of the saturation behaviour. The obtained $k_{\text{obs}}/[\text{cat}]$ values reported in Table 3 correspond to the expression ($k_2K_1[\text{TBHP}]/(1+K_1[\text{TBHP}])$). According to transition state theory, the rate constant k of a bimolecular collision can be expressed as in equation 1. For the reaction analyzed here, this would be appropriate for the second step of the process in Scheme 1 (k_2), the reaction between the catalyst-oxidant adduct and cyclooctene. However, the measured $k_{\text{obs}}/[\text{cat}]$ also incorporates the temperature dependence of the term $K_1[\text{TBHP}]/(1+K_1[\text{TBHP}])$, which depends on the equilibrium of the first step. This term could be eliminated under saturation conditions ($K_1[\text{TBHP}] \gg 1$), where $k_{\text{obs}}/[\text{cat}]$ simplifies to k_2 . Under the opposite limiting conditions ($K_1[\text{TBHP}] \ll 1$), $k_{\text{obs}}/[\text{cat}]$ would simplify to (k_2K_1) and a modified Eyring expression may be written for the resulting (k_2K_1) values as equation 2, where the $\ln K_1$ term has been developed according to van't Hoff's expression of the equilibrium constant temperature dependence. Under these conditions, the measured thermodynamic parameters would correspond to the difference between the rate determining transition state and the (cyclooctene + catalyst + TBHP) mixture. In an intermediate situation, as is experimentally observed, the thermodynamic ΔH_1° and ΔS_1° values of the pre-equilibrium give an intermediate contribution to the measured activation parameters from the Eyring analysis. Unfortunately, under our experimentally accessible conditions of solvent and reagent concentrations it was not possible to access either limiting situation of the rate law. The Eyring plot (shown in Figure 4), yields a good linear correlation and the values determined from the slope (ΔH^*) and intercept (ΔS^*) are 15.1 kcal/mol and 37.4 cal (mol·K)⁻¹, respectively.

$$\ln[(kh)/(k_B T)] = -\Delta G^\ddagger/RT = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R \quad (1)$$

$$\ln[(k_2K_1h)/(k_B T)] = \ln[(k_2h)/(k_B T)] + \ln K_1 = -\Delta G_2^\ddagger/RT - \Delta G_1^\circ/RT = -(\Delta H_2^\ddagger + \Delta H_1^\circ)/RT + (\Delta S_2^\ddagger + \Delta S_1^\circ)/R \quad (2)$$

Whereas the ΔH^* value (essentially equivalent to ΔH_2^\ddagger with some contribution from ΔH_1°) can be easily interpreted as the enthalpic barrier from the pre-equilibrium situation to the rate-determining transition state, the large positive value of ΔS^* (ΔS_2^\ddagger with some contribution from ΔS_1°) contrasts with the large negative ΔS^\ddagger value that was previously determined for the [Cp*₂W₂O₅] catalyzed cyclooctene epoxidation by H₂O₂ (-32

cal·mol⁻¹·K⁻¹).^[8] The latter is consistent with the associative nature of the transition state relative to the catalyst-oxidant adduct and H₂O₂ (Figure 3, case B). Therefore, under the reasonable hypothesis that ΔS_2^\ddagger for the oxidation by TBHP is also negative, the observed positive value of ΔS^* must originate from a large positive contribution of the ΔS° term. This could result, for instance, from the presence of several interacting solvent molecules, e.g. by hydrogen bonding, in the initial reagent mixture (cyclooctene + TBHP + catalyst) that need to dissociate in order to allow activation of the oxidant molecule.

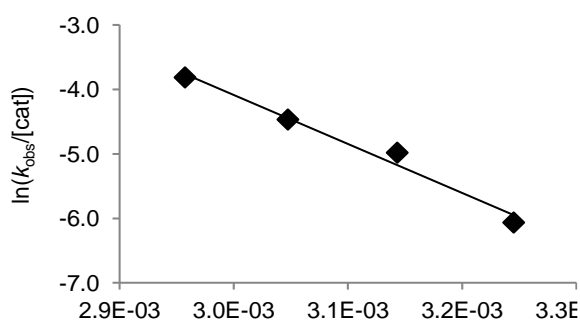


Figure 4. Eyring plot of the kinetic data in Table 3.

(c) Effect of water

The observed opposite relative order of catalytic activity, under the same experimental conditions (MeCN/toluene solvent mixture), for the epoxidation of cyclooctene by TBHP/decane in the present study (Mo \gg W) and by H₂O₂/H₂O in the previous study^[8] (Mo \ll W) is an interesting puzzle, motivating us to run additional experiments in order to arrive at a mechanistic interpretation. Before wondering about a possible specific mechanistic difference induced by the nature of R in the oxidant ROOH (R = H or *t*Bu), it is necessary to examine the possible effect of the solvent that delivers ROOH to the olefin solution. H₂O₂ was delivered as an aqueous solution, whereas TBHP was delivered as the commercially available solution in decane. It is therefore possible that the presence of water negatively affects the catalytic activity of the Mo system to a greater extent relative to the W system.

Since TBHP is also commercially available as an aqueous solution, we have carried out a comparative study of the cyclooctene epoxidation by TBHP/H₂O under analogous experimental conditions used for the previous studies. The result of this investigation (see Figure 5) clearly shows that water has a dramatic negative effect on the catalytic activity. The selectivity in epoxide remains high for the TBHP/H₂O epoxidation (excellent mass balance). Therefore, the lower epoxide yield must be the result of a reduced catalyst activity in the presence of water. The activity for the oxidation by TBHP/H₂O seems even lower (ca. 12% conversion after 30 h, see Figure 5) than that of the oxidation by H₂O₂/H₂O, (ca. 60% conversion after 25 h under the same conditions of temperature, reagents, catalyst concentrations and solvent except for the absence of toluene).⁴⁷ This comparison clearly shows that H₂O₂ is the better oxidant. In fact, there is even more water in the system for the faster oxidation with H₂O₂ (30%

in H₂O) than in the slower oxidation with TBHP (70% in water). Use of TBHP/H₂O also slightly reduces the catalytic activity of [Cp*₂W₂O₅] relative to TBHP/decane, for which the activity is already quite low (see Figure S14). Therefore, the much lower activity of the W-based catalyst in the epoxidation by TBHP/decane vs. H₂O₂/H₂O is attributable to the nature of the oxidant (TBHP \ll H₂O₂), the nature of the solvent being expected to give a positive contribution (decane $>$ water), which is however insufficient for this catalyst to inverse the effect. The negative effect of water was already pointed out for the [Cp*₂W₂O₅] catalyst in the epoxidation by H₂O₂.^[8]

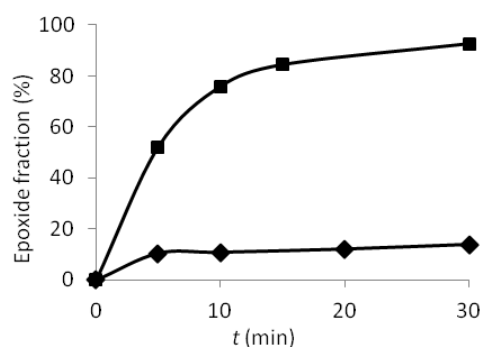


Figure 5. Cyclooctene epoxide yield vs. time for the [Cp*₂Mo₂O₅]-catalyzed epoxidation with TBHP/decane (squares) and TBHP/water (diamonds) in 3:1 MeCN/toluene at T = 55°C. Concentrations for the TBHP/decane run: [Cp*₂Mo₂O₅] = 1.83·10⁻³ M; [cyclooctene] = 0.734 M; [TBHP] = 1.457 M. Concentrations for the TBHP/water run: [Cp*₂Mo₂O₅] = 1.99·10⁻³ M; [cyclooctene] = 0.798 M; [TBHP] = 4.13 M.

(d) Activity comparisons

The [Cp*₂Mo₂O₅]-catalyzed cyclooctene epoxidation shows complex behavior under identical conditions except for the nature of R in the ROOH oxidant and the small amount of solvent (decane vs. water) that delivers ROOH to the substrate solution in MeCN/toluene. The present study shows that the Mo system is a much more efficient catalyst than the W system when using TBHP/decane, whereas previous studies have shown that the opposite is true when using H₂O₂/H₂O.^[8] Under comparable conditions (solvent, temperature, concentrations, oxidant/substrate ratio), the rate in the presence of the Mo catalyst follows the order TBHP/decane \gg H₂O₂/H₂O. On the basis of the result of the last experiment (Results, section c), this trend can be easily rationalized as a consequence of the presence of water in the oxidant solution, since a dramatic loss of activity is observed on going from TBHP/decane to TBHP/water. This trend can be quite simply rationalized on the basis of the catalyst inhibition by water, similar to the product inhibition observed in the TBHP reaction. As pointed out above, the H₂O₂ epoxidation does not show product inhibition because the by-product water is already present in the system from the very beginning of the reaction, but this presence is reflected dramatically on the reaction rate.

The opposite trend, however, is observed for the W system. Under comparable conditions (solvent, temperature, concentrations, oxidant/substrate ratio), the rate in the presence of the W catalyst follows the order H₂O₂/H₂O \gg TBHP/decane. It has been shown here for the TBHP oxidation (Figure S14) and earlier for the H₂O₂ oxidation^[8] that water has a negative effect for the W catalyzed

process just like for the Mo catalyzed process. However, whereas the negative effect of replacing decane with water overrules the positive effect of replacing TBHP with H₂O₂ when using the Mo-based catalyst, the opposite is true for the W-based catalyst. This opposite behaviour may simply be related to a different inhibiting effect of water for the two catalysts (much stronger for Mo than for W), or to a different rate enhancement factor on going from TBHP to H₂O (much stronger for W than for Mo) or to the combination of both effects. It is also possible, however, that competing reaction mechanisms also affect the system. The possibility of a new catalytic epoxidation pathway, which is specific for H₂O₂, has been presented in recent computational studies.^[9, 14] This pathway still requires a first step of oxidant activation to form the same activated M(OH)(O^αO^βH) intermediate, but then involves transfer of the O^β atom to the incoming olefin substrate, concomitant with a 1,2 shift of the proton from O^β to O^α, instead of the commonly proposed^[10] transfer of the O^α atom. This new mechanism obviously cannot take place for the corresponding M(OH)(O^αO^βtBu) intermediate. The calculations have shown that this mechanism has a much lower activation barrier for the W catalyst.

Conclusions

In the present investigation of the [Cp*₂Mo₂O₅] catalyzed olefin epoxidation using the model cyclooctene substrate, we have reported new experimental results revealing that dramatic effects are induced by the nature of the oxidant (H₂O₂ vs. TBHP), of the solvent that delivers the oxidant (decane vs. H₂O), and of the metal in the pre-catalyst (Mo vs. W). Under identical experimental conditions, the process is much faster for Mo than for W when using TBHP/decane as oxidant. Use of TBHP/water reduces the activity dramatically. On the other hand, as previously reported,^[8] the W system is much more active than the Mo analogue when using H₂O₂/H₂O, while water still negatively affects the catalytic activity. The negative effect of water is easily rationalized as an inhibiting effect and is qualitatively common to both metals, though quantitative differences may exist. A comparison of activity shows that H₂O₂ is a better oxidant than TBHP and this result is also qualitatively common to both metal catalysts. However, whereas the oxidant change is more important for the W-based catalyst (H₂O₂/H₂O >> TBHP/decane > TBHP/H₂O), the nature of the solvent that delivers the oxidant is more important for the Mo-based catalyst (TBHP/decane >> H₂O₂/H₂O > TBHP/H₂O). The intervention of a new mechanism, which is possible only for H₂O₂ and that seems much more favoured for the W-based catalyst, possibly contributes to yield the observed effect. The rate dependence on the oxidant (intermediate saturation behaviour for TBHP) is consistent with the generally accepted mechanistic proposals requiring oxidant activation in the first step to yield a catalyst-oxidant adduct as intermediate and with equilibrium for this activation step (Figure 3).

Experimental Section

General. All preparations and manipulations were carried out with Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures and distilled under argon prior to use. ¹H NMR spectra were recorded on a Bruker AM 250, operating at 250 MHz. Chemical shifts are expressed in ppm downfield from Me₄Si. Coupling constants are given in Hertz. The gas chromatographic analyses were completed by using an Agilent 7890 A instrument equipped with an SPB-5 capillary column (30 m x 0,25 mm x 0,25 μm) and with a flame ionization detector. Compounds [Cp*₂Mo₂O₅] (M = Mo, W) were prepared as described in the literature.^[15]

Cyclooctene (Fluka), dodecane (Aldrich) and *t*BuOOH solutions in decane (5.5.M) or in water (70%, ca. 19 M) (Aldrich) were used as received.

Catalytic epoxidation experiments monitored by ¹H NMR. The catalytic reactions were carried out in an NMR tube at room temperature. For each experiment, the NMR tube was charged with cyclooctene (0.086 g, 0.78 mmol) and 0.3 mL of the deuterated solvent (CDCl₃, MeOD, CH₃CN, (CD₃)₂CO). Subsequently the catalyst ([Cp*₂Mo₂O₅]; 7.8 μmol) was added and finally the catalytic reaction was started by the addition of TBHP (283 μL of a 5.5 M solution in decane, 1.56 mmol) and monitored by NMR. After 15 minutes, formation of a precipitate in considerable quantities was observed in all solvents except in acetonitrile. All attempts to isolate the precipitate (which is soluble only in DMSO and acetonitrile) were unsuccessful. The % yield of cyclooctene oxide was calculated from the NMR intensity.

Catalytic epoxidation experiments monitored by gas chromatography.

The epoxidations were carried out under an argon atmosphere in Schlenk tubes equipped with a magnetic stirrer and immersed in a thermostatic bath set at the desired temperature. In a typical experiment (corresponding to run 4 in Table 2), the tube was charged with cyclooctene (132.7 mg, 1.204 mmol), the internal standard dodecane (134.9 mg, 0.792 mmol), the [Cp*₂Mo₂O₅] catalyst (6.5 mg, 12.0 μmol), and TBHP (as a 5.5 M solution in decane, 0.43 mL, 2.36 mmol) in 4 mL of acetonitrile/toluene (3:1). Aliquots of the reaction mixture (0.2 mL) were withdrawn at predetermined times, quenched by addition of manganese dioxide, diluted with 2 mL of diethyl ether and filtered through a Pasteur pipette filled up with silica to eliminate the residual MnO₂. The silica was washed by 3 mL diethyl ether. The resulting organic phase was analyzed by gas chromatography.

Supporting Information (see footnote on the first page of this article):

Plots of all kinetic runs (9 pages).

Acknowledgments

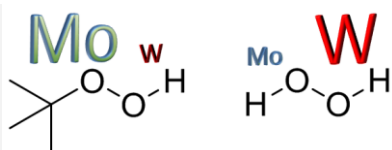
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Entry for the Table of Contents

Mo vs. W oxidation catalyst



The [Cp*₂M₂O₅]-catalyzed cyclooctene epoxidation is more efficient for M = Mo when the oxidant is TBHP/decane, whereas it is more efficient for M = W when using H₂O₂/H₂O. Water has a

negative effect with both oxidants and H₂O₂ is a better oxidant than TBHP for both metals, but the relative effects are system specific.

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Molybdenum vs. Tungsten for the epoxidation of cyclooctene catalyzed by [Cp*₂M₂O₅]

Keywords: Molybdenum / Tungsten / Epoxidation / Homogeneous Catalysis / *tert*-butylhydroperoxide