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Molybdenum versus Tungsten for the Epoxidation of Cyclooctene Catalyzed by $[Cp*_2M_2O_5]$

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The catalytic activity of $[Cp_{2}M_{2}O_{5}]$ (M = Mo, W; Cp^{*} = pentamethylcyclopentadienyl) for the homogeneous epoxidation of a solution of cyclooctene in MeCN/toluene follows the order Mo >> W when using *tert*-butyl hydroperoxide (TBHP)/decane as oxidant, in contrast to the inverse order (W >> Mo) when using aqueous H₂O₂ as oxidant. The catalytic activity for the Mo system strongly depends on the solvent used to deliver the oxidant (TBHP/decane >> TBHP/H₂O). The low activity of the W system is also decreased when using TBHP/water in place of TBHP/decane. For both metals, H₂O₂/H₂O is a better oxidant than TBHP/H₂O. However,

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 for 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 $[Cp*MoO_2CI]$ (Cp* = pentamethylcyclopentadienyl) in olefin epoxidation by *tert*-butyl hydroperoxide (TBHP) was first described by Bergman et al.^[5] Many in-

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whereas the Mo-based catalyst is much more active for the TBHP/decane epoxidation in spite of the lower TBHP oxidizing power (TBHP/decane > H_2O_2/H_2O > TBHP/ H_2O), the W-based system is much more active for the H_2O_2/H_2O epoxidation in spite of the negative effect of water (H_2O_2/H_2O > 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 with respect to substrate and has saturation behavior with respect to the oxidant.

vestigations were then reported by the groups of Romão, Kühn, Gonçalves, and Abrantes,^[1c,6] the 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. The 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 shortcomings 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 $[Cp_{2}^{*}M_{2}O_{5}]$ (M = Mo, W) are excellent catalysts for the oxidation of thiophene derivatives to the corresponding sulfoxides and sulfones by aqueous H₂O₂ in MeCN. Not only was this the first report of the use of halfsandwich W^{VI} systems in catalytic oxidation, but the study also unexpectedly revealed that the W system is approximately 100 times 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 with respect to the substrate and zero order with respect to H₂O₂. Therefore, half-sandwich Mo and W systems are highly capable of working with H_2O_2/H_2O as oxidant, provided the system is homogeneous, that is, that 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.

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Encouraged by these results, the same catalytic system $([Cp*_2M_2O_5]$ 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 cosolvent (1:3 relative to MeCN) to maintain the solution homogeneity (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 products other than cyclooctene oxide were detected), and much faster for the W system, a factor of approximately 50 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 on the 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 $[\Delta H^{\ddagger} = 10.2(6) \text{ kcal mol}^{-1}; \Delta S^{\ddagger}]$ = -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 that involves oxidant activation by protonation of an M=O function to yield an {M(OH)($O^{\alpha}O^{\beta}H$)} 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 et al.^[10] and inspired by the original hypothesis formulated by Sharpless et al.^[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 H_2O_2 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 $[Cp*_2W_2O_5]$ should also be a better catalyst than $[Cp*_2Mo_2O_5]$ 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 versus W), of the oxidant (TBHP versus H_2O_2), and of the solvent that delivers the oxidant to the substrate solution (decane versus H₂O). We report here the results of this investigation.

Results and Discussion

Solvent Effect

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

Table 1. Cyclooctene oxide yield for the cyclooctene epoxidation by TBHP catalyzed by $1\% [Cp*_2M_2O_5] (M = Mo \text{ or } W)$ at room temperature in different solvents.^[a]

Solvent	М	t	Cyclooctene oxide yield [%]
CDCl ₃	Мо	20.5 h	84.5
CDCl ₃	W	14 d	0.02
$(CD_3)_2CO$	Mo	7 d	_
$(CD_3)_2CO$	W	7d	_
MeOD	Mo	5 d	47.1
MeOD	W	6 d	_
CD ₃ CN	Mo	8 d	89.0
CD ₃ CN	W	2 d	_

[a] Conditions: Cyclooctene (0.1 mL, 0.78 mmol), TBHP (0.28 mL; 5.5 m in decane, 1.56 mmol), $[Cp*_2M_2O_5]$ (4.2 mg for Mo; 5.6 mg for W; 7.8×10^{-3} mmol), and deuterated solvent (0.3 mL).

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 above). Chloroform is the best solvent for this reaction and gives 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 $[Cp*_2Mo_2O_5]$ 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 into a heterogeneous system. The yield and conversion are in good correspondence, and the mass balance is excellent (see details in Figure S1 of the Supporting Information). The catalytic mixtures in all other investigated solvents, on the other hand, remained homogeneous.

There was no conversion at all in $(CD_3)_2CO$ for both catalysts. A negative effect of solvent coordination through the carbonyl oxygen atom, which blocks 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 also occur 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 versus time for the Mo-based catalyst in these two solvents, obtained from ¹H NMR spectroscopic monitoring, are given in the Supporting Information (Figures S2 and S3).

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Amongst these two solvents, CD₃CN affords the most efficient catalytic system, with nearly complete conversion after eight days and very high selectivity, with cyclooctene epoxide being the only observed product.

Kinetics Study

All subsequent catalytic experiments were carried out in a 3:1 CH₃CN/toluene combination to keep 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] A first run was carried out under pseudo-first-order conditions (TBHP/cyclooctene = 8:1), which allowed 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 byproducts. There was a good mass balance (>90%), with the amount of produced cyclooctene oxide each time being nearly the same as the amount of consumed cyclooctene. Under these conditions, essentially all the cyclooctene was completely converted into the oxide product in approximately three hours (see Figure 1).



Figure 1. GC monitoring of the epoxidation of cyclooctene by TBHP (5.5 M in decane) in CD₃CN/toluene catalyzed by 1% [Cp*₂Mo₂O₅]. Conditions: catalyst (6.4 mg, 0.0119 mmol), cyclooctene (0.16 mL, 1.19 mmol), TBHP (1.72 mL; 5.5 M in decane, 9.50 mmol), and CH₃CN/toluene (6.05 mL, 3:1) at 55 °C.

Kinetic analysis shows that the cyclooctene decay does not fit a first-order rate law as expected (Figure S4 in the Supporting Information). It fits a second-order decay law better (Figure S5 in the Supporting Information). 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, which predicts 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 are 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 slowing of the catalytic activity as the epoxide product accumulates.^[13]

$$[Mo] + ROOH \xrightarrow{k_1} [Mo(ROOH)]$$
$$[Mo(ROOH)] + alkene \xrightarrow{k_2} epoxide + ROH$$
$$r = \frac{k_2 K_1 [Mo]_0 [alkene] [ROOH]}{1 + K_1 [ROOH]} \quad (K_1 = k_1/k_{-1})$$

Scheme 1. Kinetic scheme and rate law for the Mo-catalyzed olefin epoxidation. $\ensuremath{^{[12]}}$

To avoid the complication of product inhibition, we carried out an investigation of initial rates: (a) on the one hand, with variable concentration of cyclooctene at constant TBHP concentration to determine the reaction order in cyclooctene; and (b) on the other hand, with variable concentrations of TBHP at constant cyclooctene concentration to determine the reaction order in TBHP. All experiments were carried out with an excess amount of TBHP and the initial rates were measured on the basis of the cyclooctene consumption (see details in Figures S6-S11 of the Supporting Information), during a time interval in which the TBHP concentration can be assumed to remain approximately constant, even for the experiments run with a low [TBHP]/[cyclooctene] ratio. The initial rate values are reported in Table 2 and are 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, which sug-

Table 2. Initial rates of cyclooctene oxidation by TBHP catalyzed by 1% [Cp*₂Mo₂O₅] at different cyclooctene and TBHP concentrations.^[a]

[ТВНР] ₀ = 1.5 м;			$[cyclooctene]_0 = 0.25 \text{ M};$		
$[Cp*_2Mo_2O_5] = 2.0 \times 10^{-3} \text{ M}$			$[Cp*_2Mo_2O_5] = 2.5 \times 10^{-3} \text{ M}$		
Run	[cyclooctene] ₀ [M]	$v_0 [{ m M}{ m s}^{-1}]^{[b]}$	Run	[ТВНР]0 [М]	$v_0 [{\rm M}{\rm s}^{-1}]^{[b]}$
1	0.199	4.61×10^{-4}	4	0.496	9.39×10 ⁻⁵
2	0.412	10.6×10^{-4}	5	0.911	12.6×10^{-5}
3	0.769	14.7×10^{-4}	6	1.563	15.0×10^{-5}

[a] Solvent = $3:1 \text{ CH}_3\text{CN/toluene}$, $T = 55 \,^{\circ}\text{C}$. [b] Rates measured from the initial slope (5 min) of the [epoxide] versus time plot.

gests a balance in the substrate-oxidant adduct formation equilibrium and is in agreement with saturation behavior (Scheme 1; K_1 [TBHP] not varying much 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.



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], and (b) [TBHP] at constant [cyclooctene] and [Cp*₂Mo₂O₅].

Figure 3 shows a qualitative energy profile that fits the above-determined trends. Previously reported DFT calculations run on the [Cp*MoO₂Cl] catalyst first used by Bergman et al.^[5] (which can also be considered to be a model of the [Cp*₂Mo₂O₅] catalyst) have shown that the

adduct with MeOOH (used as a model of *t*BuOOH), [Cp*MoO(OH)(OOMe)Cl], lies at higher energy than the corresponding adduct with H_2O_2 , [Cp*MoO(OH)(OOH)-Cl].^[9] Therefore, the adduct formation equilibrium is expected to lie less extensively on the left-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 further displace 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, with 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 byproduct generated from TBHP, to a catalyst coordination site, thereby 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 H_2O_2 , however, the byproduct 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.

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 to insure pseudo-first-order conditions. The kinetic profiles are given in Figure S12 in the Supporting Information. 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 in the Supporting Information). The observed rate constants are collected in Table 3.

The subsequent Eyring analysis of the data is not straightforward because of the saturation behavior. The obtained k_{obsd} /[cat.] values reported in Table 3 correspond to the expression { k_2K_1 [TBHP]/(1 + K_1 [TBHP])}. According to transition-state theory, the rate constant k of a bimolecu-



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

Table 3. Rate constants for the $[Cp_2Mo_2O_5]$ -catalyzed epoxidation of cyclooctene by TBHP at different temperatures.^[a]

<i>T</i> [°C]	$k_{\mathrm{obsd.}} \mathrm{[s^{-1}]}$	$k_{\rm obsd.}/[{\rm cat.}] [{\rm s}^{-1} {\rm M}^{-2}]$
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: $[Cp*_2Mo_2O_5] = 4.8 \times 10^{-4}$ M; [cyclooctene] = 0.048 M; [TBHP] = 0.48 M; solvent: MeCN/toluene (2:1).

lar collision can be expressed as shown 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_{obsd} /[cat.] also incorporates the temperature dependence of the term K_1 [TBHP]/(1 + K_1 [TBHP]), which depends on the equilibrium of the first step. This term could be eliminated under saturation conditions (K_1 [TBHP] >> 1), in which k_{obsd} /[cat.] simplifies to k_2 . Under the opposite limiting conditions (K_1 [TBHP] << 1), k_{obsd} /[cat.] would simplify to (k_2K_1 [TBHP]), and a modified Eyring expression could be written for the resulting (k_2K_1) values as Equation (2), in which 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 kcalmol⁻¹ and $37.4 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively.

$$\ln\left[(kh)/(k_{\rm B}T)\right] = -\Delta G^{\ddagger}/RT = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R \tag{1}$$

 $\ln [(k_2 K_1 h)/(k_B T)] = \ln [(k_2 h)/(k_B T)] + \ln K_1 = -\Delta G_2^{\dagger}/RT - \Delta G_1^{\circ}/RT$ = $-(\Delta H_2^{\dagger} + \Delta H_1^{\circ})/RT + (\Delta S_2^{\dagger} + \Delta S_1^{\circ})/R$ (2)



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

Whereas the ΔH^* value (essentially equivalent to ΔH_2^{\dagger} 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^* 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 calmol⁻¹K⁻¹).^[8] The latter is consistent with the associative nature of the transition state relative to the catalyst-oxidant adduct and H_2O_2 (Figure 3, case B). Therefore, under the reasonable hypothesis that ΔS_{2}^{\dagger} 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 to allow activation of the oxidant molecule.

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 >> W) and by H_2O_2/H_2O in the previous study^[8] (Mo << W) is an interesting puzzle, which motivated us to run additional experiments to arrive at a mechanistic interpretation. Before contemplating a possible specific mechanistic difference induced by the nature of R in the oxidant ROOH (R = H or tBu), it was necessary to examine the possible effect of the solvent that delivers ROOH to the olefin solution. H_2O_2 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 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 H_2O_2/H_2O_3 (ca. 60% conversion after 25 h under the same conditions of temperature, reagents, catalyst concentrations, and solvent).^[4,7] This comparison clearly shows that H_2O_2 is the better oxidant. In fact, there is even more water in the system for the faster oxidation with H_2O_2 (30% in H_2O) than in the slower oxidation with TBHP (70% in water). Use of TBHP/H₂O also slightly reduces the catalytic activity of $[Cp*_2W_2O_5]$ relative to TBHP/decane, for which the activity is already quite low (see Figure S14 in the Supporting Information). Therefore, the much lower activity of the W-based



catalyst in the epoxidation by TBHP/decane versus H_2O_2/H_2O is attributable to the nature of the oxidant (TBHP << H_2O_2), as the nature of the solvent is 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 H_2O_2 .^[8]



Figure 5. Cyclooctene epoxide yield versus time for the $[Cp*_2Mo_2O_3]$ -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: $[Cp*_2Mo_2O_5] = 1.83 \times 10^{-3}$ M; [cyclooctene] = 0.734 M; [TBHP] = 1.457 M. Concentrations for the TBHP/water run: $[Cp*_2Mo_2O_5] = 1.99 \times 10^{-3}$ M; [cyclooctene] = 0.798 M; [TBHP] = 4.13 M.

Activity Comparisons

The [Cp*2M2O5]-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 versus 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 $>> H_2O_2/H_2O$. On the basis of the result of the last experiment (see above), 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 upon going from TBHP/decane to TBHP/water. This trend can be rationalized quite simply 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 byproduct water is already present in the system from the very beginning of the reaction, but this presence is reflected dramatically in 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 $H_2O_2/H_2O >>$ TBHP/decane. It has been shown here for the TBHP oxi-

dation (Figure S14 in the Supporting Information), and earlier for the H₂O₂ oxidation,^[8] that water has a negative effect on 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 behavior might 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 upon going from TBHP to H_2O_2 (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 $\{M(OH)(O^{\alpha}O^{\beta}H)\}$ 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 clearly cannot take place for the corresponding $\{M(OH)(O^{\alpha}O^{\beta}tBu)\}$ intermediate. The calculations have shown that this mechanism has a much lower activation barrier for the W catalyst.

Conclusion

In the present investigation of the $[Cp_2M_2O_5]$ -catalyzed olefin epoxidation using the model cyclooctene substrate, we have reported new experimental results that reveal that dramatic effects are induced by the nature of the oxidant (H₂O₂ versus TBHP), of the solvent that delivers the oxidant (decane versus H₂O), and of the metal in the precatalyst (Mo versus 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. However, as previously reported,^[8] the W system is much more active than the Mo analogue when using H₂O₂/H₂O, whereas 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, although quantitative differences might exist. A comparison of activity shows that H_2O_2 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 Wbased catalyst $(H_2O_2/H_2O >> TBHP/decane > TBHP/$ H_2O), 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 H_2O_2 and which seems much more favored for the W-based catalyst, possibly contributes to yield the observed effect. The rate dependence on the oxidant (intermediate saturation behavior for TBHP) is consistent with the generally accepted mechanistic proposals that require 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 with a Bruker AM 250 operating at 250 MHz. Chemical shifts are expressed in ppm downfield from Me₄Si. Coupling constants are given in Hertz. The gaschromatographic analyses were completed with an Agilent 7890A instrument equipped with an SPB-5 capillary column (30 m×0.25 mm×0.25 µm) and with a flame-ionization detector. Compounds [Cp*₂M₂O₅] (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 Spectroscopy: The catalytic reactions were carried out in an NMR spectroscopy tube at room temperature. For each experiment, the NMR spectroscopy tube was charged with cyclooctene (0.086 g, 0.78 mmol) and the deuterated solvent [CDCl₃, MeOD, CH₃CN, (CD₃)₂CO] (0.3 mL). Subsequently, the catalyst ([Cp*₂M₂O₅], 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 spectroscopy. After 15 min, 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 percentage yield of cyclooctene oxide was calculated from the NMR spectroscopic 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 (which corresponded 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 acetonitrile/toluene (4 mL, 3:1). Aliquots of the reaction mixture (0.2 mL) were withdrawn at predetermined times, quenched by the addition of manganese dioxide, diluted with diethyl ether (2 mL), and filtered through a Pasteur pipette filled with silica to eliminate the residual MnO₂. The silica was washed by diethyl ether (3 mL). The resulting organic phase was analyzed by gas chromatography.

Supporting Information (see footnote on the first page of this article): Plots of all kinetics runs.

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