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Oxidation of $[CpMo(CO)_3R]$ olefin epoxidation precatalysts with *tert*-butylhydroperoxide

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ABSTRACT

NMR study of the oxidation of several Mo(II) precatalysts $[CpMo(CO)_3R]$ ($R = CH_2COOC_2H_5$ **1**, $CH_2COOBornyl$ **5**, CH_3 **6**, $CH_2C_6H_5$ **7**, $CH_2C_6F_5$ **8**) with *tert*-butylhydroperoxide (TBHP) in $CDCl_3$ at 22 °C shows the formation of complexes $[CpMoO_2R]$ (**I**), $[CpMo(O)(\eta^2\text{-}O_2)R]$ (**II**) and transient species assigned as **A** and **B**. ν(Mo—O—Mo) at 678 and 655 cm^{-1} are identified during oxidation of **5** monitored by *in situ* IR. DFT calculations for $R = CH_2COOCH_3$ indicate that the involvement of $[CpMo^{IV}(O)R]$, $\mathbf{I_0}$ and $[(CpMo^{V}(O)R)_2(\mu\text{-}O)_{1,2}]$, ($\mathbf{M_{ox1,2}}$) species in various oxidative transformations is energetically feasible. Oxidative decarbonylation of **5** at different reaction temperatures and oxidant and precatalyst concentrations has also been studied. IR and mass spectroscopic analysis of the precipitate obtained from oxidation of **5** suggests that it is an oxomolybdenum species without ligand R. NMR study of catalytic epoxidation of *cis*-cyclooctene using **1** illustrates the inhibitory effect of the substrate on oxidative transformations of the precatalyst.

1. Introduction

The catalytic activities and mechanisms of homogeneous olefin epoxidation with organomolybdenum complexes containing *cis*-MoO_2^{2+} [1–5], $Mo(O)(\eta^2\text{-}O_2)_2$ [6], MoO_3 [7–9], and $(MoO)_2(\mu\text{-}O)$ [10,11] oxo units have been extensively addressed in the literature in the last half century [12–14]. Such dedicated effort is a testament to the importance of epoxides in both industry and academia, and to the necessity of developing suitable catalytic systems to obtain these valuable products [15–17]. The catalytic activity of the piano stool oxomolybdenum complex $[Cp^*MoO_2Cl]$ ($Cp^* = C_5Me_5$) was first described by Trost and Bergman for the epoxidation of several unfunctionalized alkenes with different peroxidic oxidants [18]. Later, Kühn, Romão and co-workers showed that oxidative decarbonylation of the tricarbonyl complexes $[Cp'Mo(CO)_3Cl]$ ($Cp' = C_5H_5$, C_5Me_5, $C_5(CH_2Ph)_5$) with alkyl hydroperoxides such as *tert*-butylhydroperoxide (TBHP) gives dioxo complexes $[Cp'Mo(O)_2Cl]$ in better yields than other synthetic methods [19]. The oxomolybdenum complexes are highly selective catalysts for the epoxidation of unfunctionalized olefins, but in general, more sensitive to air and moisture than their tricarbonyl precursors. Therefore it seems more practical to oxidize the precatalyst *in situ* since alkene epoxidation also utilizes the same oxidant TBHP, and loss in yield during isolation of the active oxomolybdenum(VI) catalyst can be avoided [19]. Due to the advantages of this reaction methodology, numerous $[Cp^{\neq}Mo(CO)_3R]$ ($Cp^{\neq}$ = unsubstituted or substituted cyclopentadienyl, R = halide, alkyl, *N*-heterocyclic carbene, alkylester, *ansa* bridged alkyl or cycloalkyl group, etc.) complexes have been synthesized and applied *in situ* as precatalysts for epoxidation with hydroperoxide oxidants [20]. Subsequent kinetic and mechanistic work has shown that the dioxo complexes are further oxidized to oxo-peroxo species $[CpMo(O)(\eta^2\text{-}O_2)R]$ with TBHP and the latter are also active catalysts in some cases [21–25].

The technique of *in situ* precatalyst oxidation using TBHP and H_2O_2 has also been used to obtain oxo complexes of several organo-molybdenum and -tungsten dicarbonyl and tetracarbonyl compounds for their application in olefin epoxidation [26–29]. Thus, it is necessary to evaluate the efficiency and selectivity of this oxidation process. The objective of this work is to study the oxidation of several different $[CpMo(CO)_3R]$ complexes with TBHP, and determine whether there are general modes of activation and reactivity of these complexes. Knowing these modes would be helpful

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in outlining principles for rational molecular catalyst design. In addition, the exothermic nature of the oxidative decarbonylation reaction needs to be explained and the stability of oxo complexes obtained from these precatalysts has to be assessed.

Therefore ^1H, ^{13}C, ^{95}Mo NMR and *in situ* IR techniques have been used to study the oxidative transformation of tricarbonyl precatalysts **1**, **5–8** (Fig. 1) into oxidized complexes such as **I** and **II**. A detailed NMR study was performed primarily with complex **5** since its oxidation is less exothermic (compared to **2**, **3**, **6** and [$CpMo(CO)_3Cl$]) at room temperature and slow enough to be followed on the time scale of NMR measurement. NMR profiles of the oxidation of precatalysts **1**, **7** and **8** (at 22 °C) and **6** (at 5 °C), with TBHP (in *n*-decane) are given in the Supporting Information (SI). Computational studies assist in explaining experimental observations and have been utilized to support the hypotheses for the existence of different oxomolybdenum complexes discussed in this work. Although several possible mechanistic pathways have been calculated by us and other groups, for this system the "precise" mechanism is – not really surprisingly – still unknown. As with most published reaction mechanisms, particularly those that are largely based on calculations, other reaction pathways that have not yet been considered might exist and operate in addition to the suggested ones.

2. Experimental

2.1. Theoretical calculations

All computations have been performed by using Gaussian09 C.02. For all atoms excluding Mo, the optimizations, transition state searches (Berny algorithm) [30] and frequency/thermochemistry determinations have been conducted using the density functional method B3LYP [31–33] together with the basis set 6-31G** [34,35]. For Mo, effective-core potential (ECP) basis set was used (Stuttgart 1997) [36,37]. All obtained geometries have been identified *via* the number of negative frequencies as minima (NImag = 0) or transition states (NImag = 1) and are singlet, unless indicated otherwise as triplet, ^3T. The energies are reported in kcal mol^{-1} relative to a zero point that corresponds to all the reactants. Similarly the energy of all the products is considered together at the end of a scheme. All free energy differences have been calculated for the gas phase at 298.15 K and 1.0 atm.

2.2. Materials and methods

Complexes **1–5** [38,39], **6** [40,41], **7** and **8** [39,41] were prepared by known methods. All NMR experiments were carried out in $CDCl_3$ solvent under ambient conditions. TBHP (5.5 M solution in *n*-decane stored over molecular sieves, <4% H_2O) was purchased from Sigma Aldrich and used as such. Known amounts of mesitylene or naphthalene (Sigma Aldrich) were utilized as internal standards for quantitative NMR experiments. Process analytics monitoring by *in situ* IR spectroscopy was carried out using the Mettler-Toledo ReactIR™ 15 instrument at 25 °C under air.

2.3. Typical reaction conditions and data acquisition in ^1H and ^{13}C NMR study for precatalyst oxidation

0.1 mmol of **5** (1 equiv.) was dissolved in 0.4 mL $CDCl_3$ in an NMR tube with a known amount of mesitylene as an internal standard and its ^1H and ^{13}C spectra were recorded at 298 K. 10 equiv. of TBHP (5.5 M *n*-decane solution) was added to the NMR tube and the solution was mixed properly before the start of reaction progress monitoring by *multizg* acquisition programme of Bruker Topspin spectrometer. To obtain a good resolution of signals after addition of TBHP, shimming was required and the first ^1H spectrum (16 scans) was measured after 5 min and ^{13}C (164 scans) spectrum after 15 min of initiating the reaction. Subsequently, in an alternating manner, ^1H and ^{13}C NMR spectra were obtained at intervals of 10 min for a total duration of 4 h. To obtain data at shorter intervals, the scans for ^{13}C NMR were reduced. In experiments for varying substrate, oxidant and catalyst concentrations, only ^1H NMR spectra were measured.

2.4. Effect of temperature on precatalyst oxidation

An NMR tube containing a mixture of *ca.* 0.1 mmol of precatalyst **5**, mesitylene and 0.4 mL $CDCl_3$ was maintained at the desired temperature (10 °C or 30 °C) in the 400 MHz Bruker spectrometer using *edte* GUI. 10 equiv. of TBHP (5.5 M *n*-decane solution) was then added and the solution was mixed properly. Shimming was necessary after addition of TBHP and ^1H NMR spectrum was first recorded at 5 min, ^{13}C NMR spectrum first after 15 min and thereafter at 10 min intervals for a total duration of 4 or 6 h. Data acquisition was automated by using the *multizg* programme of the spectrometer.

2.5. Data analysis for all quantitative ^1H NMR experiments

Using NMR software MestReNova©, the characteristic signals at 6.65 ppm (mesitylene) and 7.8–8.0 ppm (naphthalene) for the internal standards were integrated to 3 H and 4 H respectively in all ^1H NMR. The concentration of different oxidized species was determined by integrating the area of Cp signals for these species as equivalent to 5 H (in case of **I** and **II**) and correlating with the known concentration of the internal standard.

2.6. Oxidation of 5 with 10 equiv. TBHP at reflux conditions

0.678 mg (1.53 mmol) of precatalyst **5** was dissolved in 30 mL dry dichloromethane. 10 equiv. TBHP (15.3 mmol, 2.78 mL of 5.5 M *n*-decane solution) was then added to the solution which was brought to reflux (45 °C). Within 35 min, formation of a yellow–white precipitate **5a** occurred. The bright yellow solution changed in colour to pale yellow at this time. After 3 h under reflux, the mixture was cooled to room temperature. The precipitate **5a** was separated from the light yellow supernatant by cannular filtration, washed with dry DCM (3 × 10 mL) and dried under vacuum. The collected supernatant and washings were treated with a small amount of activated MnO_2. When effervescence ceased, the solution was dried with $MgSO_4$ and then filtered again under argon. This was then concentrated under vacuum to obtain the air and moisture sensitive, light yellow oil **5b**.

2.7. Analytical data for precipitate ***5a***

IR (ν_{max}/cm^{-1}) 1364 *w*, 1301 *vw*, 1241 *br*, 1150 *w*, 1125 *br*, 1044 *w*, 949 *vs* 885 *vs* 814 *vs* 655 *vs* 618 *s*, 586 *w*, 561 *w*, 531 *w*, 437 *vw*. Analysis (1): Found: C, 24.59; H, 3.12; Mo, 34.33; *m/z* 288.9 (MI$^+$, CI), 136.9 (base). Analysis (2): Found: C, 17.13; H, 3.60; Mo, 34.12%; *m/z* 289.6 (MI$^+$, CI), 137.5 (Base).

2.8. Analytical data for ***5b***

^{95}Mo ($CDCl_3$, 2 M Na_2MoO_4 in D_2O) δ −628. IR (cm^{-1}) 3394 *br*, 2923 *vs* 2854 *w*, 2158 *vw*, 1735 *w*, 1691 *w*, 1455 *w*, 1363 *w*, 1247 *vs* 1195, 1153, 1080, 1026 *s*, 951 *s*, 884 *s*, 818 *w*, 668 *w*, 571 *s*, 481 *vw*.