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$CpMo(CO)_3Cl$ as a precatalyst for the epoxidation of olefins

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The tricarbonyl complex $CpMo(CO)_3Cl$ was found to act as a precatalyst for the reaction of *tert*-butyl hydroperoxide and olefins to yield the corresponding epoxides and diols. Under the reaction conditions, oxidative decarbonylation leads to the formation of the dioxo complex $CpMoO_2Cl$. The catalytic recyclability and the effect of temperature on the catalytic results have been examined, and a reaction mechanism proposed, supported by kinetic modelling.

KEY WORDS: molybdenum; organometallic oxides; oxidative decarbonylation; olefin epoxidation; *tert*-butyl hydroperoxide.

1. Introduction

High oxidation state organometallic oxides have found numerous applications as catalysts for oxidation reactions [1]. Perhaps the most famous example, methyltrioxorhenium(VII) (MTO), is an efficient catalyst for olefin epoxidation (using H_2O_2 as the oxidant), Baeyer Villiger oxidation, aromatic oxidation and metal carbonyl oxidation [2–4]. Dioxomolybdenum(VI) complexes of the type $MoO_2R_2L_2$ (R = Me, Et; L = Lewis base ligand) have also been shown to be active catalysts for olefin epoxidation using *tert*-butyl hydroperoxide (TBHP) as the oxidising agent [4–7]. Surprisingly, complexes of the type $(\eta^5\text{-}C_5R_5)MoO_2X$ (X = Cl, Br) have been less well studied as oxidation catalysts, despite the fact that they are among the earliest examples of organometallic oxides [8–10]. Nevertheless it has been known for some time that the pentamethylcyclopentadienyl analogue Cp^*MoO_2Cl is able to catalyse the olefin epoxidation reaction with TBHP [11]. More detailed studies have perhaps been held back by the lack of a convenient synthetic route to $(\eta^5\text{-}C_5R_5)MoO_2X$ complexes. The Cp^* derivative was prepared in 61% yield by irradiation of $Cp^*Mo(CO)_3Cl$ under oxygen [11]. However, a similar approach for the synthesis of the cyclopentadienyl derivative $CpMoO_2Cl$ (starting from the dimer $[CpMo(CO)_3]_2$) only results in a 25% yield [9]. A step forward in this chemistry came with the discovery that the complexes $(\eta^5\text{-}C_5R_5)MoO_2Cl$ (R = H, CH_3, CH_2Ph) are easily prepared from their corresponding and readily available $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ precursors by reaction with TBHP in *n*-decane [12]. It was found that the dioxomolybdenum(VI) complexes catalyse the epoxidation of cyclooctene, styrene, and 1-octene with TBHP as the oxidising agent. Turnover frequencies (TOF) of up to 21,000 mol $mol_{Mo}^{-1} \cdot h^{-1}$ were found that even surpass that of the well-known $MeReO_3/H_2O_2$ system. Preliminary results also indicated that the parent tricarbonyl complexes can be applied directly as catalyst precursors in the olefin epoxidation, without isolation of the dioxo complexes prior to use. Herein we report a detailed study of the catalytic behaviour of $CpMoO_2Cl$ generated *in situ*, i.e. using the $CpMo(CO)_3Cl$ precursor and an excess of TBHP. The catalytic recyclability and the effect of temperature on the catalytic results have been examined, and a reaction mechanism proposed, supported by kinetic modelling. In addition, the reaction of the tricarbonyl complex with TBHP has been followed by monitoring the evolution of CO and CO_2.

2. Experimental

$CpMo(CO)_3Cl$ (**1**) was synthesised according to slightly modified literature procedures [12–14]. The liquid-phase catalytic epoxidations were carried out under air (atmospheric pressure) in a reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath. A 2% molar ratio of $CpMo(CO)_3Cl$/substrate and a substrate/oxidant molar ratio of 0.5 (TBHP, 5.5 M in decane) were used. Samples were withdrawn periodically and analysed using a gas chromatograph (Varian 3800) equipped with a capillary column (SPB-5, 20 m × 0.25 mm) and a flame ionisation 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.

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The oxidative decarbonylation of **1** was studied in more detail by analysing the gaseous mixture produced during reaction of **1** with TBHP in a vessel specially designed for this purpose. The tests were performed under inert gas atmosphere with catalyst concentrations varying between 0.004 and 0.022 M and a catalyst/oxidant ratio of 0.1. For the presented results, CH_2Cl_2 (2 mL) and TBHP (15 μL of a 5.0–6.0 M solution in decane) were added to $CpMo(CO)_3Cl$ (**1**) (0.0024 g, 8.56 μmol), and the mixture was stirred at room temperature. Samples were taken after 1, 2, 3, 4 and 69 h, and analysed in a gas chromatograph (Thermofinnigam Trace GC) equipped with a CTR1 column from Alltech^{TM} and a thermal conductivity detector (TCD). CO and CO_2 were quantified using a calibration curve recorded prior to the reaction course. Blank reactions performed in the absence of the oxidant TBHP showed that no significant amounts of CO and CO_2 were liberated.

3. Results and discussion

The olefins used in this study were *cis*-cyclooctene, cyclododecene, *trans*-2-octene, 1-octene, (*R*)-(+)-limonene and α-pinene. When using the precatalyst $CpMo(CO)_3Cl$ (**1**) with TBHP at 55 °C, relatively high initial reaction rates were observed for all linear and cyclic substituted olefins (figure 1). Blank experiments showed that the non-catalytic contribution to olefin epoxidation was negligible. The conversion of cyclooctene reached 100% within 4 h. On the other hand, when aqueous H_2O_2 was used as oxygen donor instead of TBHP, no cyclooctene conversion was observed after this time, possibly due to the rapid formation of a peroxo compound $CpMo(O_2)OCl$ (the corresponding Cp* derivative $Cp^*Mo(O_2)OCl$ was previously shown to be inactive as a catalyst for olefin epoxidation [11]). Outstanding results were obtained particularly for the oxidation of (*R*)-(+)-limonene, which was completely transformed with TBHP in 30 min. Excellent selectivity to the corresponding epoxide (>98% at 6 h conversion) was observed for all substrates except for the monoterpenes, which are more sensitive towards epoxide ring opening originating the diol, a secondary product (figure 2). The oxidation of (*R*)-(+)-limonene originates limonene oxide and 1-methyl-4-(1-methylethenyl)-1,2-cyclohexanediol as the main products, obtained with 21 and 45% yield, respectively, at 100% conversion. The other products formed were not identified. In the case of α-pinene oxidation, 8% α-pinene oxide was yielded after 6 h, which undergoes Lewis acid catalysed rearrangement to give campholenic aldehyde (ca. 7% yield), an intermediate for the sandalwood fragrance santalol [15,16]. The relative rate of epoxidation of an unsubstituted olefin such as 1-octene is much lower than that observed for the substituted olefins.

We assume that, under the applied reaction conditions, complex **1** is transformed into the dioxo complex $CpMoO_2Cl$ (**2**), which then catalyses the epoxidation of the olefins with TBHP. Doubts remain about the "destiny" of the leaving carbonyl ligands. The ligands could leave the molecule unchanged or already as CO_2. On the other hand, the carbonyl groups could leave unchanged and be oxidised subsequently to CO_2 over time, since a large excess of oxidant is used. The liberation of CO and CO_2 has previously been studied for the oxidative decarbonylation of $Cp^*Re(CO)_3$ with O_2 and light [17] and H_2O_2 [18]. In the first case the CO/CO_2 ratio was 3:1 and in the second case 1:2. In the present work the

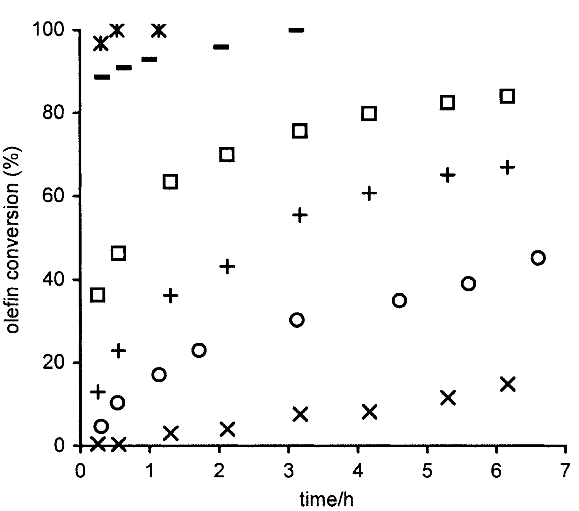

Figure 1. Conversion profiles for the epoxidation of olefins with TBHP at 55 °C using $CpMo(CO)_3Cl$ (**1**) as a precatalyst: (*) – (*R*)-(+)-limonene; (–) – *cis*-cyclooctene; (□) – cyclododecene; (+) – *trans*-2-octene; (○) – α-pinene; (×) – 1-octene.

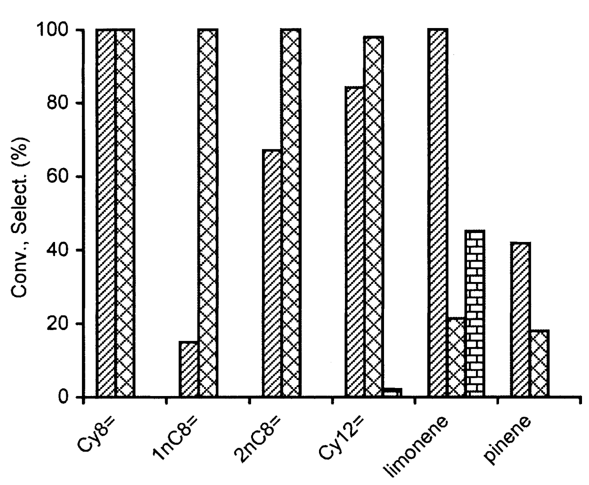

Figure 2. Olefin conversion at 6 h (hashed bars) and selectivity to the corresponding epoxide (diamonds) and diol (bricks) obtained with TBHP at 55 °C using $CpMO(CO)_3Cl$ (**1**) as a precatalyst: (Cy8=) – *cis*-cyclooctene; (lnC8=) – 1-octene (2nC8=) – *trans*-2 octene; (Cy12=) – cyclododecene; (*R*)-(+)-limonene and α-pinene.

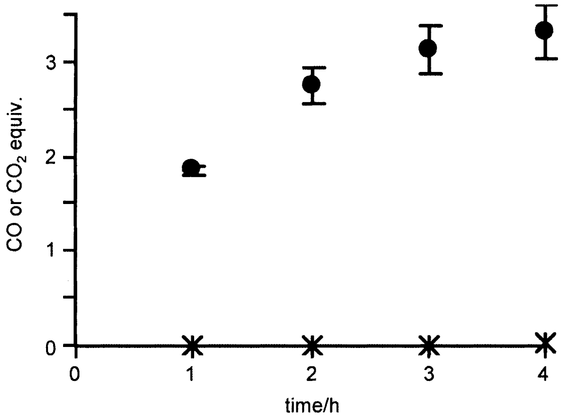

Figure 3. CO (●) and CO$_2$ (*) liberation versus time for oxidative decarbonylation of CpMo(CO)$_3$Cl (**1**) with TBHP in CH$_2$Cl$_2$ at room temperature (molar ratio **1**:TBHP = 1:10).

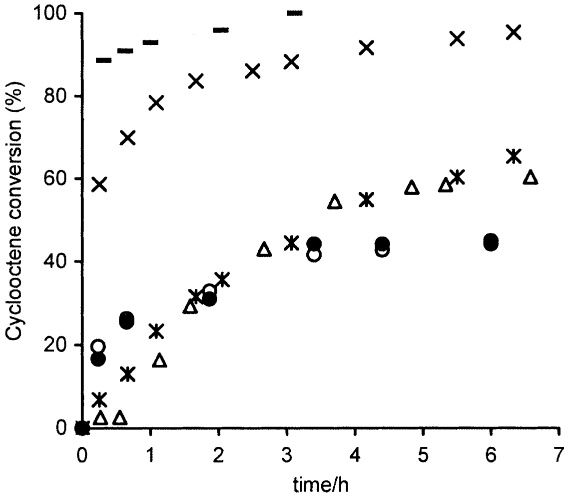

Figure 4. Conversion profiles for the epoxidation of cyclooctene with TBHP at 55 °C (run 1 (–); run 2 (*)), 43 °C (×), 30 °C (△) using CpMo(CO)$_3$Cl (**1**) directly or after treatment with TBHP at 30 °C (○ – determined experimentally; ● – calculated for the proposed kinetic model).

reaction of CpMo(CO)$_3$Cl (**1**) with TBHP was studied in more detail by monitoring the evolution of CO and CO$_2$. After 4 h of reaction at room temperature, about 3 equiv. of CO were released with a minor amount of CO$_2$ (CO/CO$_2$ $\approx$ 80) (figure 3). Differences in the concentration of **1** seemed to change the rate of decarbonylation but not the CO/CO$_2$ ratio since the amount of CO$_2$ liberated continued to be very low. Measurements made after 69 h of reaction gave the same results as those obtained after 4 h, indicating that there was no significant conversion of CO into CO$_2$. The reaction can therefore be written as shown in equation (1) in which the carbonyl groups are released unchanged and are not oxidised to CO$_2$.

The epoxdation of cyclooctene using the precatalyst **1** and TBHP was also studied at different temperatures. When the reaction temperature was lowered from 55 to 43 °C the kinetic profile was similar, i.e. initially the reaction is quite fast, but then the reaction rate progressively decreases (figure 4). No induction periods were observed, suggesting that complex **1** was readily transformed into the dioxo complex **2** under the applied oxidising conditions. A further temperature decrease to 30 °C gave rise to an induction period of ca. 30 min after which the reaction proceeded to 60% cyclooctene conversion at 6 h. An induction period was also observed for limonene oxidation after which ca. 72% conversion was achieved at 6 h. These induction periods are most likely due to the slower oxidative decarbonylation of the catalyst precursor at 30 °C. In fact, when the mixture of complex **1** and oxidant was left to stir for 2 h before the addition of the substrate, no induction period was detected and the kinetic profile was similar to that observed at higher temperatures (figure 4).

The reusability of the catalyst was examined by two different methods. In one experiment, a solid was separated from the liquid medium after 4 h reaction by precipitation with *n*-hne followed by agitation and centrifugation. After washing and drying the solid at room temperature it was reused at 55 °C. The reaction was slower and 100% cyclooctene conversion was only achieved after 24 h, compared with 3.5 h for the first run (figure 4). In another test, a second cycle was initiated (without catalyst separation) by the addition of a new charge of cyclooctene and TBHP (in equimolar amounts) to the reaction mixture after 3.5 h. It was found that the reaction proceeded at a slower rate giving ca. 60% conversion after another 3.5 h (figure 5). The gradual deactivation of the catalyst in these experiments was probably caused by catalyst decomposition and/or the formation of the peroxo complex CpMo(O$_2$)OCl [11]. Turnover frequencies of 21,000 mol $\text{mol}_{\text{Mo}}^{-1} \cdot h^{-1}$

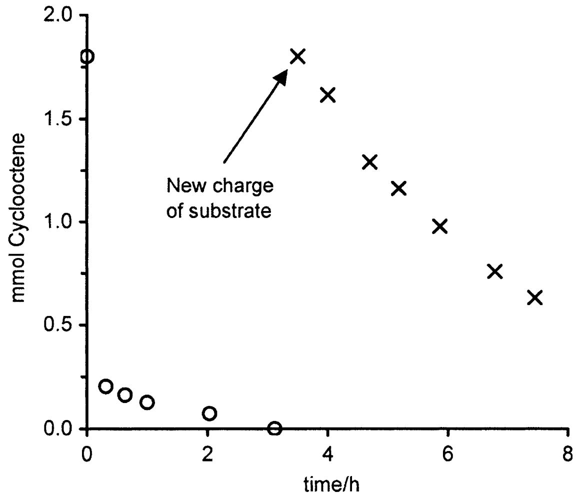

Figure 5. Kinetics of the epoxidation of cyclooctene with TBHP using CpMo(CO)$_3$Cl (**1**) as a precatalyst for the first (○) and second (×) runs, at 55 °C.

were reported for cyclooctene epoxidation catalysed by (η^5-C_5Bz_5)MoO_2Cl, using catalyst:substrate molar ratios as low as 1:10,000 [12]. Hence, the reaction proceeds smoothly even in the presence of very small amounts of complex, explaining why cyclooctene oxide can still be obtained quantitavely in a second reaction run despite the partial deactivation of the catalyst.

It is likely that the catalytic activity of the system studied in the present work is due to the formation of an intermediate complex bearing an alkyl peroxo group, as proposed previously for complexes of the type Cp^*MoO_2Cl and $MoO_2X_2L_2$ [6,11,12]. For the latter it was reported that the reaction proceeds via the initial coordination of the Lewis basic hydroperoxide to the Lewis acidic metal center of the complex (designated as MoLx) via the terminal oxygen, leading to the formation of an intermediate Mo^{VI} alkyl peroxide species where the hydroperoxide proton is transferred to one of the terminal oxygen ligands (designated as MoLy, equation (2)). In this way the peroxide is activated for oxygen transfer to the olefin resulting in the formation of the epoxide (equation (3)) and *tert*-butanol (tBuOH), a by-product which competes with TBHP for coordination to the metal center (leading to the formation of MoLz, equation (4)), thus retarding the reaction, Assuming a similar reaction mechanism for the epoxidation of cyclooctene to the corresponding epoxide (Cy8 > O) using TBHP in the presence of $CpMoO_2Cl$ and no significant catalyst deactivation at 30 °C during 6 h, we have applied the kinetic model that was built in Ref. 19 for a homogeneous batch reactor to the $CpMoO_2Cl$ catalytic system. A fairly good fitting was obtained suggesting that the referred mechanism is consistent with the observed kinetics and the assumptions made are valid and reasonable for complexes of the type (η^5-C_5R_5)MoO_2Cl under the applied reaction conditions (figure 4).

$$\mathrm{MoLx + TBHP} \rightleftarrows \mathrm{MoLy} \quad (2)$$

$$\mathrm{MoLy + Cy8} = \longrightarrow \mathrm{Cy8 > O + tBuOH + MoLx} \quad (3)$$

$$\mathrm{MoLx + tBuOH} \rightleftarrows \mathrm{MoLz} \quad (4)$$

Conclusion

This work has shown that the readily available tricarbonyl complex $CpMo(CO)_3C1$ can be used as a precatalyst for the oxidation of olefins by TBHP. Under the reaction conditions, the tricarbonyl complex is rapidly transformed to the active catalyst $CpMoO_2C1$. The catalytic behaviour for the epoxidation of cyclooctene is comparable with that obtained if the previously prepared and isolated dioxo complex $CpMoO_2Cl$ is used rather than the tricarbonyl precursor.

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