Do (pentaarylcyclopentadienyl)molybdenum(VI) dioxo species catalyse alkene epoxidations? Insights from kinetics data

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Supplementary Information

Materials. Cyclooctene and *tert*-butylhydroperoxide (TBHP, 5.5 M in decane) were purchased from Aldrich and were stored over freshly-activated 4 Å molecular sieves. $Cp^{\ddagger}MoO_2Br$ was prepared by direct oxidation of $Cp^{\ddagger}Mo(CO)_3Br$ with dioxygen as previously reported.[S1]

Instrumentation. ^{1}H NMR spectra were recorded on 300 MHz or 500 MHz Bruker Avance spectrometers. A 2 s delay between pulses was used to ensure accurate integration of the signals.

Catalyses. In all catalytic studies, reaction progress was monitored *in-situ* by ^{1}H NMR spectroscopy. The ratio of $Cp^{\ddagger}MoO_2Br$ catalyst to cyclooctene substrate to TBHP oxidising agent used was 1:100:200. These conditions were deliberately chosen to mirror those employed in previous studies reported in the literature.[S2] Dichloromethane was used as an internal standard because the ^{1}H NMR singlet due to it at δ 5.35 was well clear from interferring signals such as the cyclooctene alkene C-H muliplet at δ 5.57 and the cyclooctene epoxide C-H muliplet at δ 2.87 that were used to monitor reaction progress (e.g., see Fig. S1).

In a typical catalysis run, cyclooctene (15.5 mg, 140 μmol) was added to $Cp^{\ddagger}MoO_2Br$ (1.0 mg, 1.5 μmol) in $CDCl_3$ (1.5 g) in a NMR tube that was sealed with a septum. The solution was warmed to 305 K and kept at this temperature until the conclusion of the experiment. An initial background spectrum was collected prior to the addition of the oxidising agent, TBHP. TBHP (0.053 cm^3, 5.5 M in decane, 290 μmol) was then added and a ^{1}H NMR spectrum collected every 611 seconds over a period of 20 hours (e.g., see Figs. S1 and S2).

Analysis of the kinetics. Microsoft Excel was used to simulate the kinetics data and to extract the distribution of species versus time information.[S3] The simplest model that provides a satisfactory fit to the complete bimodal kinetic data for the epoxidation reactions is that shown in Scheme 1 (in the communication). To simplify the simulations, steps $Cp^{\ddagger}MoO_2Br \rightarrow A \rightarrow B \rightarrow C$ were treated as

irreversible; to treat them as reversible would complicate the calculations, but not alter the results. An expansion of the best fit is shown in Figure S3.

Using only two catalyst species, **A** and **C** as in Scheme S1, gave unsatisfactory fits to the experimental kinetic data. The two best two-catalyst fits are shown in Figures S4 and S5. Figure S4 shows one extreme, slow catalyst **A** degradation. Note that this is not supported by the NMR results (e.g., see Figure S2). The fit is poor and can only be improved (and then only slightly) by slowing the catalyst degradation — which goes against NMR evidence. Figure S5 shows a more sensible (intermediate) degradation of catalyst **A**. Again, however, the fit is poor and improvement is only made by (a) slowing the catalyst degradation down (which goes against the NMR evidence) or (b) making the first rate constant negative (non-sensical). And going the other way, increasing the rate of catalyst **A** degradation, simply pushes the simulation curve further towards a simple exponential — and a worse fit. Hence, the bottom line is the observed slow degradation of catalyst **A** and the epoxidation rate data cannot be correlated if a two species only model is used. Two species (**A** and **B** in Scheme 1 and Figure 1(b) in the communication), which are present to a significant extent for the first 10,000 s, are required to properly account for the initial lag time in rapid catalysis (due to catalyst **C**) as in Scheme 1 (in the communication).
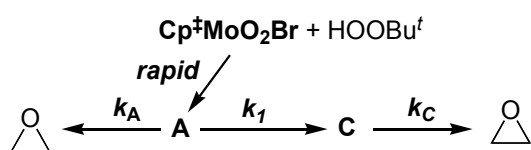
Supplementary Scheme S1.
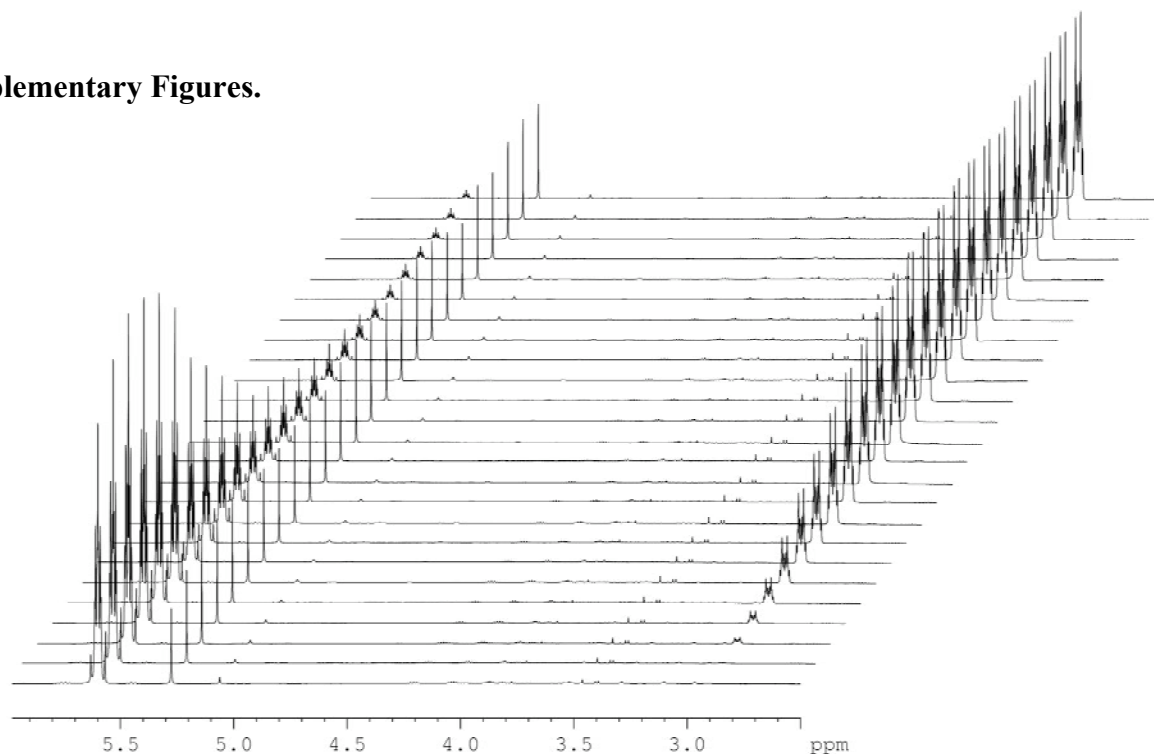
Supplementary Figures.

Figure S1. Progress of epoxidation of cyclooctene by TBHP monitored by 500 MHz ^{1}H NMR spectroscopy. The signals at δ 5.57, 5.35, and 2.87 correspond to the cyclooctene (reactant) alkene C-H muliplet, dichloromethane (standard), and the cyclooctene epoxide (product) C-H muliplet, respectively. Conditions: Cp‡MoO₂Br, cyclooctene and TBHP (1:100:200) in CDCl₃ at 305 K; every sixth spectrum acquired is shown, so there is 3666 s between the adjacent spectra in the figure, and the total elapsed time is 20 hours.
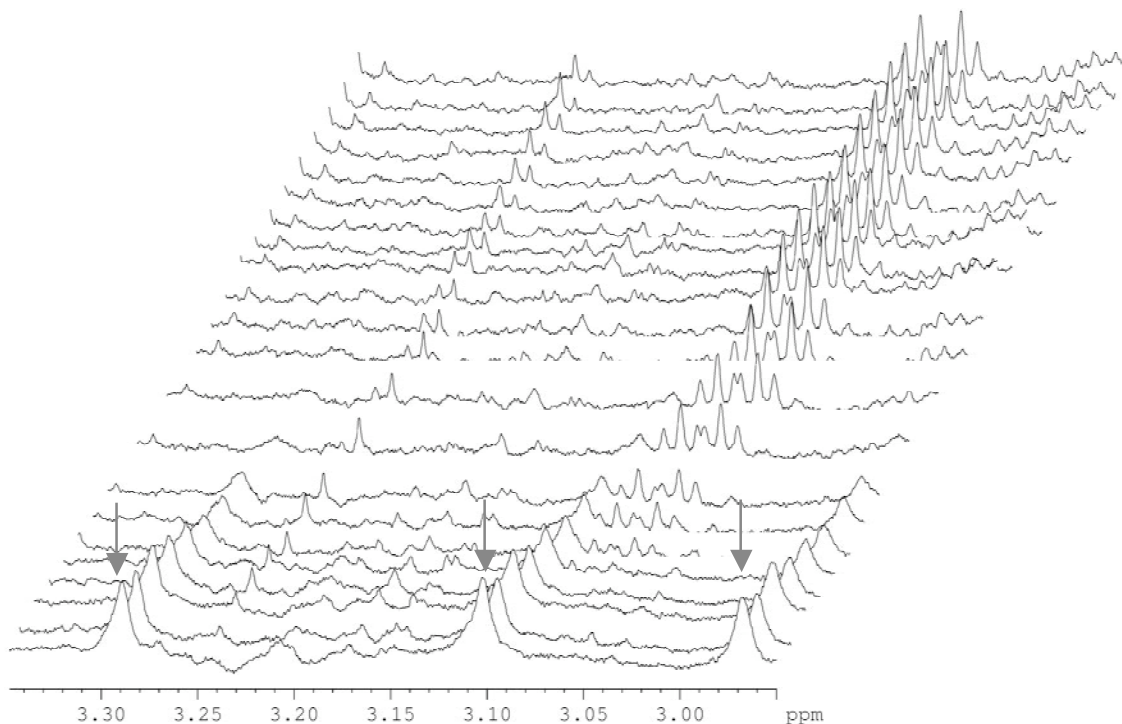

Figure S2. Expansions of selected 500 MHz ^{1}H NMR spectra over the methoxy (= catalyst dimethoxyphenyl peak) region during epoxidation cyclooctene by TBHP using Cp‡MoO₂Br as the catalyst. The arrows indicate three of the four methoxy proton signals for a Cp‡Mo species[S1] (= 'A' in text), which disappear as the catalysis

proceeds. The multiplet at δ 3.07 corresponds to the ^{13}C satellite of the cyclooctene oxide (R-CH-^{13}CH-CH$_2$-R) C-H signal that was used to monitor the reaction progress. Conditions: as for Figure S1.
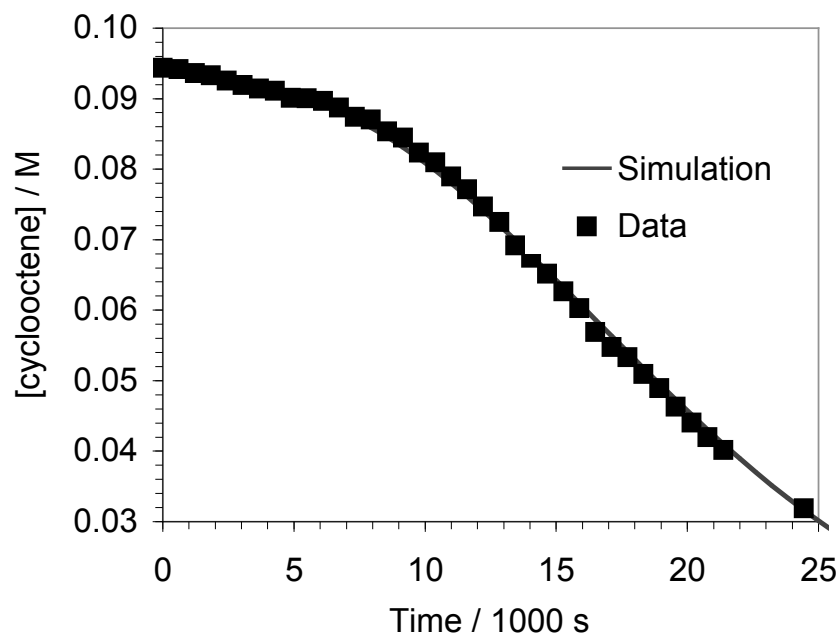

Figure S3. Cyclooctene epoxidation by TBHP catalysed by Cp‡MoO$_2$Br. Expansion over the "slow phase" of the same data as in Figure 1(a) (in the communication) for consumption of cyclooctene (but here plotted as its concentration) and the simulated fit to this data using the kinetic scheme discussed in the text (Scheme 1).
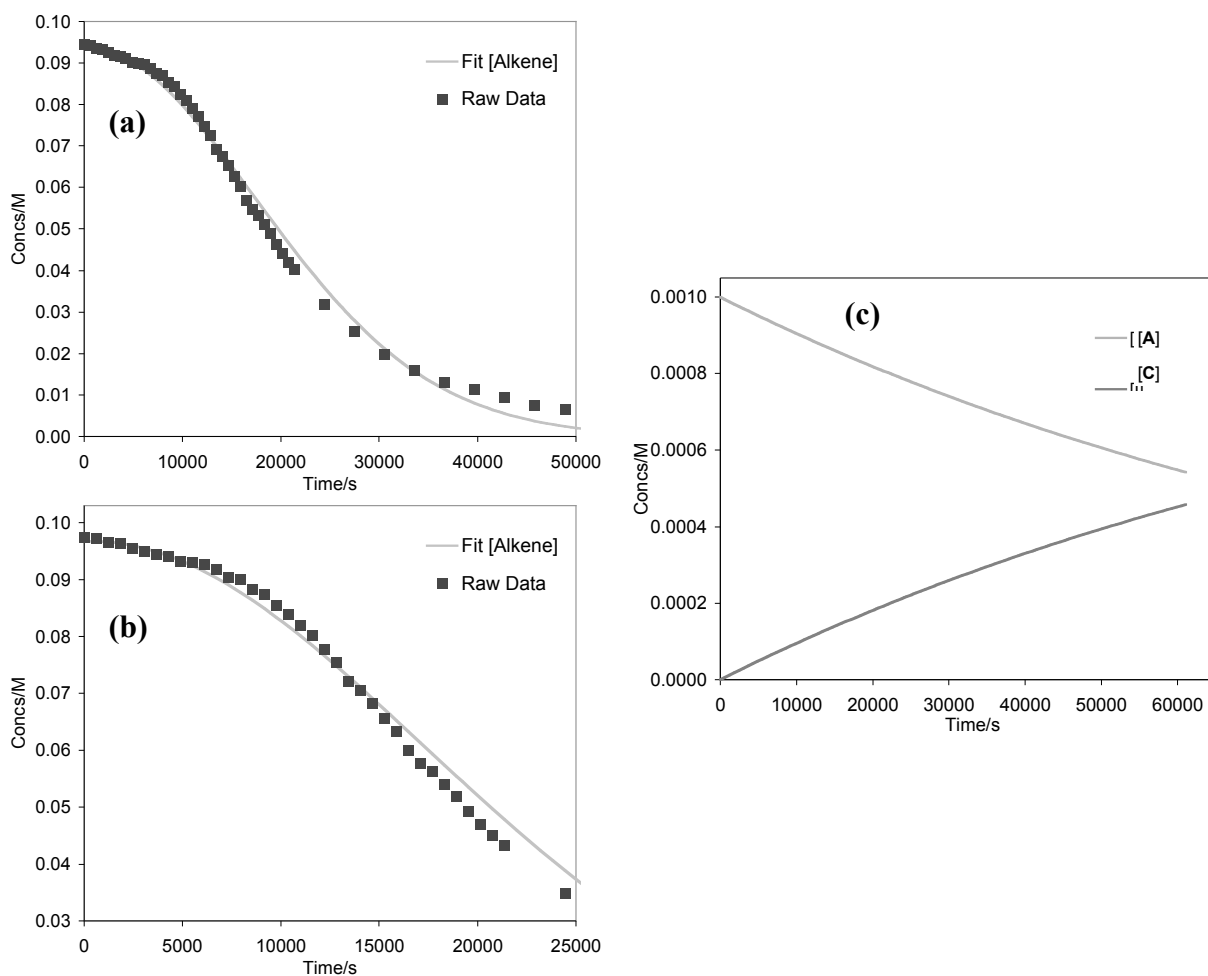
Figure S4. Cyclooctene epoxidation by TBHP catalysed by $Cp^{\ddagger}MoO_2Br$. (***a, b***) Comparison of experimental data for the consumption of cyclooctene and a simulated fit using two catalyst species (**A** and **C**, Supplementary Scheme S1) and the following kinetic parameters: $k_1 = 10^{-5}$ s^{-1}, $k_A = 5 \times 10^{-5}$ s^{-1}, $k_B = 0.35$ s^{-1}. (***c***) Concentration profiles of Mo species **A** and **C** obtained from this fit to the data.
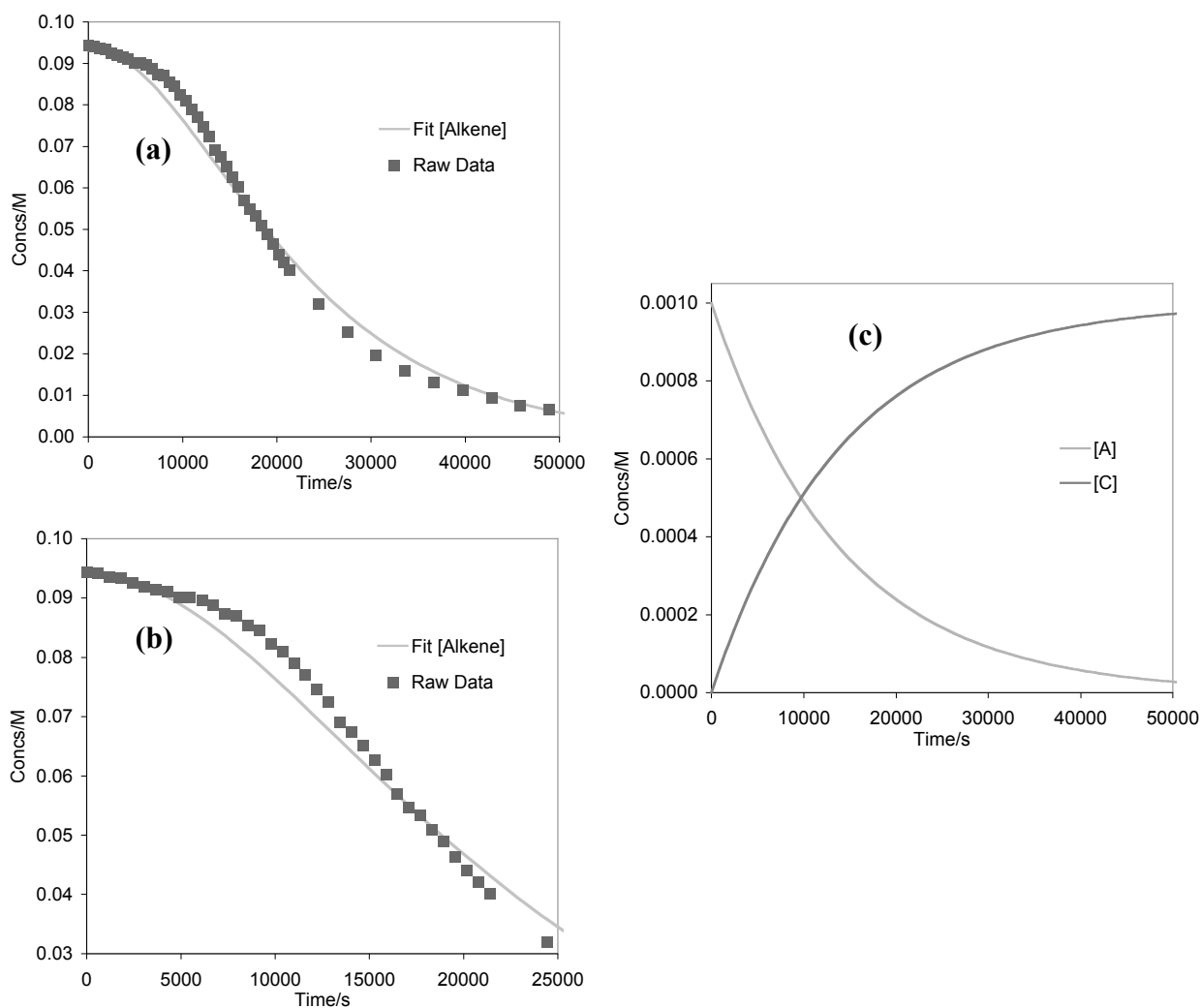
Figure S5. Cyclooctene epoxidation by TBHP catalysed by Cp‡MoO$_2$Br. (***a, b***) Comparison of experimental data for the consumption of cyclooctene and a simulated fit using two catalyst species (**A** and **C**, Supplementary Scheme S1) and the following kinetic parameters: $k_1 = 7 \times 10^{-5}$ s^{-1}, $k_A = 10^{-4}$ s^{-1}, $k_B = 0.075$ s^{-1}. (***c***) Concentration profiles of Mo species **A** and **C** obtained from this fit to the data.

References for the Supplementary Information.

S1.   W. M. Harrison, C. Saadeh, S. B. Colbran and D. C. Craig, *J. Chem. Soc., Dalton Trans.* 1997, 3785.

S2.   See refs. 3–5 in the communication.

S3.   E. J. Billo, *Analysis of Biphasic Kinetics Data,* pages 379–385 in *Analysis of Kinetics Data*, Chapter 23 in *Excel for Chemists: A Comprehensive Guide. 2nd Ed.* John Wiley & Sons, Inc., New York, 2001. ISBNs: 0-471-39462-9; (Paperback): 0-471-22058-2 (Electronic).