

### Epoxidation of Propylene by Diperoxomolybdenum(VI) Complexes. Accelerating Effect of Propylene Oxide and Propene-1,2-Diol

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The diperoxomolybdenum(VI) complex of the formula  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ , where L is hexamethylphosphoramide (HMPT), has been reported by Mimoun *et al.* [1, 2] to act as a selective stoichiometric reagent for olefin epoxidation under mild conditions. Epoxidations of this type are relevant to biological oxygenation systems effecting selective oxygen atom transfer to various organic substrates *via* the intervention of 'oxenoid' species [3]. These are mostly unspecified metalloenzyme–dioxygen complexes, whose chemistry might be accessible *via* the design of simple models such as transition metal complexes with  $\text{O}_2$ -activating properties. Although many  $\text{O}_2$ -carrier complexes have been prepared, only a few are capable of acting as catalysts in oxidation reactions [4–7].  $\text{MoO}(\text{O}_2)_2\text{L}$  and  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  are remarkable because of their 'oxenoid' properties, although no direct route has been devised for their synthesis *via* dioxygen.

In this paper we report on two additional 'oxenoid' reagents that can be derived from  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  via complexation with O-donor ligands such as propylene oxide (PO) and propane 1,2-diol (PD). Both are more reactive than the parent complex and have been discovered during studies of propylene epoxidation.

The reaction of  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  with propylene in dichloroethane as solvent was followed volumetrically at constant pressure, using a gas burette. The absorption curves were independent of the stirring speed, indicating the absence of transport control. The propylene uptake curves *a* and *c* in Fig. 1 show a sigmoid shape, characteristic of autocatalytic behaviour. No rate acceleration is expected from the epoxidation mechanism suggested by Mimoun *et al.* [1, 7] involving complex formation between  $\text{MoO}(\text{O}_2)_2\text{L}$  and the olefin, followed by olefin insertion into the Mo–O bond and subsequent epoxide elimination. The observed volumetric curves (*a* and *c*) indicate acceleration due to product formation.

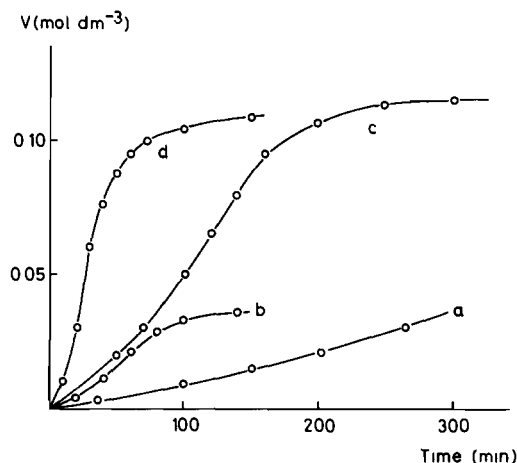


Fig. 1. Propylene absorption curves with and without added PO ( $T = 40^\circ\text{C}$ , total pressure 1 bar, solvent dichloroethane). *a* –  $0.055 \text{ mol dm}^{-3} \text{ MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ ; *b* – same as *a*, with  $0.17 \text{ mol dm}^{-3}$  PO added; *c* –  $0.163 \text{ mol dm}^{-3} \text{ MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ ; *d* – same as *c*, with  $0.17 \text{ mol dm}^{-3}$  PO added. Vertical axis: volume of propylene absorbed, in mol propylene per  $\text{dm}^3$  solution.

Indeed, addition of *ca.* 1 mol propylene oxide per mol  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  before the admission of propylene gas to the reactant solution markedly changes the propylene uptake curve: the same overall amount of propylene is absorbed much faster (curves *b* and *d*, Fig. 1) than without added propylene oxide. However, the sigmoid shape of the volumetric curves is retained. This behaviour indicates complex formation between PO and  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ , leading to a more reactive epoxidation reagent.

The nature of this new complex has been studied by following the reaction of  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  with PO by IR spectroscopy. An excess of PO was reacted with  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. Samples of the solution taken at intervals were evaporated on a NaCl plate, then their IR spectra were recorded on a Hitachi EPI-G 3 Grating Infrared Spectrophotometer. The volatility of PO excludes the presence of free PO in the samples. The  $\nu(\text{Mo}=\text{O})$  band at  $965 \text{ cm}^{-1}$  [2] decreases with reaction time and finally disappears. No epoxide ring is present in the complex as shown by the complete absence of absorption in the  $1270 \text{ cm}^{-1}$  range, associated with symmetrical ring stretching. There is a steadily growing band at  $1375 \text{ cm}^{-1}$ , unmasked by other bands in this range, assignable to  $\delta_s\text{CH}_3$  of a PD moiety. A new band appears also at  $905 \text{ cm}^{-1}$ , increasing in parallel to  $\delta_s\text{CH}_3$ , which has its analog in free PD at  $920 \text{ cm}^{-1}$ . The  $1620 \text{ cm}^{-1}$  band of coordinated water is replaced by a broad absorption at  $1640 \text{ cm}^{-1}$  due to free water.

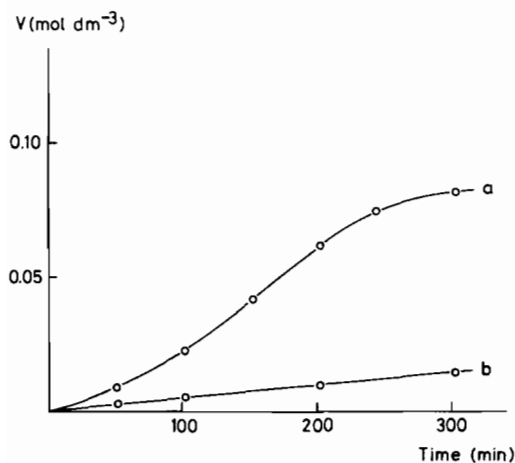
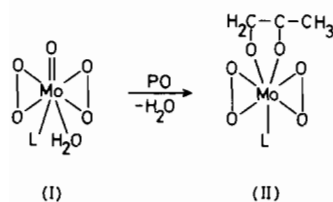


Fig. 2. Propylene absorption curves in the absence and presence of excess HMPT (for conditions, see Fig. 1). a –  $0.11 \text{ mol dm}^{-3} \text{ MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ ; b – same as a, with  $0.11 \text{ mol dm}^{-3}$  excess HMPT. Vertical axis: see Fig. 1.

The  $\nu(\text{O}-\text{O})$  band at  $865 \text{ cm}^{-1}$  decreases to some extent, indicating that PO is slowly oxidized by  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ . This reaction has also been detected by GLC analysis of the product mixtures from propylene oxidation: the PO concentration increases initially, then levels off with further oxidation products appearing. When reacting PO with  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  the active O-content of the latter decreases, pointing to a redox interaction.

The IR spectroscopic monitoring of the PO +  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  reaction indicates an initial non-redox process. As PO enters the coordination sphere with ring opening, and the  $\text{Mo}=\text{O}$  oxo ligand is lost, the following reaction scheme seems reasonable:



Reaction (1) is an insertion of PO into the  $\text{Mo}-\text{O}$  bond, resulting in the formation of a (propane-1,2-diolato)diperoxomolybdenum(VI) complex, which is a more reactive epoxidizing reagent than the starting *I*. This complex is apparently responsible for the acceleration of propylene uptake (Fig. 1) and the levelling off of the PO concentration in the product mixture. Reaction (1) is accompanied by displacement of coordinated  $\text{H}_2\text{O}$ , in line with the known coordination number of 7 for *I* [8].

Excess HMPT suppresses epoxidation by *I* as is shown in Fig. 2. There is a marked rate decrease at 1 mol added HMPT per mol *I* (curve b) and com-

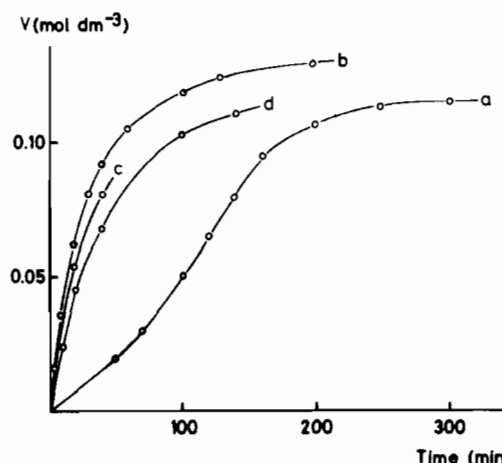


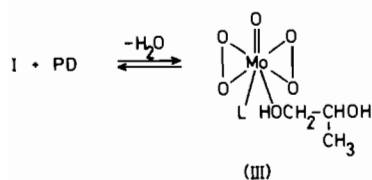
Fig. 3. Propylene absorption curves with and without added PD (for conditions, see Fig. 1). a –  $0.16 \text{ mol dm}^{-3} \text{ MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$ ; b – same as a, with  $0.08 \text{ mol dm}^{-3}$  PD added; c – same as a, with  $0.13 \text{ mol dm}^{-3}$  PD added; d – same as a, with  $0.18 \text{ mol dm}^{-3}$  PD added. Vertical axis: see Fig. 1.

plete inhibition at a 5-fold excess. Apparently, the epoxidation activity of *I* is destroyed upon its conversion to the known [2]  $\text{MoO}(\text{O}_2)_2\text{L}_2$ .

The rate of propylene epoxidation is also influenced by added propane-1,2-diol (PD). Figure 3 shows that the addition of 0.5 mol PD per  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  eliminates the sigmoid shape of the absorption curve and strongly accelerates propylene uptake (curve b). A further increase in PD concentration slightly decreases the initial rate and the total amount absorbed (curves c and d). These phenomena must be due to complex formation between *I* and PD, which is supported by the conspicuously faster dissolution of *I* in dichloromethane containing PD.

The IR spectra from evaporated solutions containing 1 mol PD per mol  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  point to displacement of the coordinated water molecule by a PD ligand. The sharp band of coordinated  $\text{H}_2\text{O}$  at  $1620 \text{ cm}^{-1}$  is replaced by a more intense, sharp band at the same wavenumber, but no changes in either the  $965 \text{ cm}^{-1} \nu(\text{Mo}=\text{O})$  or in the  $865 \text{ cm}^{-1} \nu(\text{O}-\text{O})$  band can be detected. Interestingly, when methanol was used instead of PD, the changes were similar and again the  $\text{Mo}=\text{O}$  and  $\text{O}-\text{O}$  bonds were not affected. In line with expectations, no displacement of coordinated HMPT was detectable in either case. In consequence of these facts, the interaction of  $\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})$  with PD can be described by the equation III.

In III, PD acts as a unidentate ligand when replacing the coordinated water. The epoxidizing activity of III is higher than those of either *I* or *II*, a fact that



may be utilized in epoxide syntheses with peroxo-molybdenum complexes. The kinetics and mechanism of epoxidation by these reagents will be dealt with in a forthcoming paper.

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