Olefin epoxidation by hydrogen peroxide catalysed by molybdenum complexes in ionic liquids and structural characterisation of the proposed intermediate dioxoperoxomolybdenum species†

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The complex [MoO4(dmpz)2]1+ (1) has been isolated as part of a study of oxodiperoxomolybdenum catalysed epoxidation of olefin substrates with hydrogen peroxide in ionic liquids. Notably, 1 is the first dioxoperoxomolybdenum species to be structurally characterised.

Over the past few decades important advances have been made in understanding the mechanisms of peroxomolybdenum catalysed epoxidation reactions, a topic which has given rise to some controversy.1 Different mechanisms, particularly those described by Mimoun2 and Sharpless,3 have been proposed, though more recent studies have highlighted the fine relationship between the mechanism and the specific experimental conditions.4 The chemical nature of the oxidant reagent is a particularly important determinant. Industrially, molybdenum catalysed epoxidations used in fine chemical synthesis typically employ tert-butylhydroperoxide (TBHP).5 The substitution of the organoperoxo oxidants used in such processes for more environmentally friendly oxidants such as molecular oxygen6 or hydrogen peroxide7 would be beneficial for obvious reasons.

We have recently conducted several investigations of olefin epoxidation by hydrogen peroxide catalysed by simple molybdenum compounds in ionic liquids (ILs).8 As part of this work we reported on the oxidation of cis-cyclooctene and other olefin substrates to their corresponding epoxides using the oxidant-catalyst precursor combination UHP–MoO3 (UHP = urea-hydrogen peroxide adduct) in the ionic liquid C8mim-PF6.9 Developing upon this preliminary system, we have subsequently investigated means of controlling the undesired hydrolytic side reaction, allowing the use of aqueous hydrogen peroxide as the oxidant, and the influence of coordinating species on the catalysis.10 Table 1 displays some preliminary results illustrating the effect of some N-donor ligand additives.

The epoxidation reaction clearly proceeded more quickly in the IL media than in chloroform (entries 1, 4 and 7). Additionally, in the IL media, pyrazoles were found to induce complete selectivity for the epoxide and significantly enhance catalytic activity with respect to both our previously reported system with UHP6 and systems testing other N-donor species.10 Whilst unsubstituted pyrazole (pz) gave enhanced conversions, 3,5-dimethylpyrazole (dmpz) gave an even more markedly activated system. With the addition of dmpz, complete conversion to the epoxide was observed in C12mim-PF6 within the two hours, the optimum result encountered in the study.10 Furthermore, the system was easily recyclable and ten subsequent catalytic cycles were run with no decline in catalytic activity observable if the base species was replenished between cycles (see ESI† for details). The use of oxodiperoxopyrazolyl(molybdenum complexes as catalysts for oxidation reactions has a limited number of precedents, though apparently not in olefin epoxidation. Supported [Mo(O)(O2)2(H2O)(pz)] has been used to catalyse the heterogeneous oxidation of sulfides,11 and [Mo(O)(O2)2(dmpz)]2+ has been previously described as a homogeneous alkylbenzene oxidation catalyst.12

To further understand the mechanism of the oxygen atom transfer to the olefin substrate, [Mo(O)(O2)2(pz)]2+ (2) (X-ray characterised, Fig. 1) and [Mo(O)(O2)2(dmpz)]2+ (3) were investigated as stoichiometric epoxidising reagents, reacting the complexes with cis-cyclooctene in C8mim-PF6 at a 1:2 complex:olefin ratio in the absence of oxidant. Yields of ca. 50% epoxide were obtained, suggesting that these oxodiperoxomolybdenum complexes are capable of epoxidising only 1 equivalent of olefin despite possessing two peroxo ligands.13,14 After the stoichiometric oxidation of the cis-cyclooctene, completion of the catalytic cycle can be demonstrated by reoxidising the metal complex with a small amount of hydrogen peroxide: complete conversion was observed within 2 h. Extraction with pentane (3 × 3 mL) yields 50% epoxide in both cases.

Table 1 Molybdenum catalysed epoxidations of cis-cyclooctene in the presence of selected N-donor base additivesa

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base additive</th>
<th>Solvent</th>
<th>Conversion</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>C12CH</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Pyrazole</td>
<td>C8mim-PF6</td>
<td>38</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>Pyrazole</td>
<td>C12mim-PF6</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Pyrazole</td>
<td>C8mim-PF6</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
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<td>C12mim-PF6</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>Pyrazole</td>
<td>C12mim-PF6</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>3,5-Dimethylpyrazole</td>
<td>C12CH</td>
<td>23</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>3,5-Dimethylpyrazole</td>
<td>C8mim-PF6</td>
<td>84</td>
<td>84</td>
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<tr>
<td>9</td>
<td>3,5-Dimethylpyrazole</td>
<td>C12mim-PF6</td>
<td>99</td>
<td>99</td>
</tr>
</tbody>
</table>

a Aqueous [MoO(O2)2(H2O)2] 0.025 mmol, base additive 0.10 mmol, 30% H2O2 (aq) 3.0 mmol, cis-cyclooctene 1.0 mmol, solvent 2.0 mL, T = 60 °C, t = 2 h. Extraction with pentane (3 × 3 mL), yields and conversions calculated by GC.

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excess (1.2 equiv.) of aqueous H₂O₂ under appropriate reaction conditions. The oxodiperoxo complex is regenerated and after eliminating any excess H₂O₂ further addition of cis-cyclooctene yields the same result (ca. 50% conversion). Visually, clear colour changes were apparent both when the complex reacted with the olefin and when it was regenerated with H₂O₂ (ESI†).

The reaction profile for the stoichiometric epoxidation of the model olefin substrate ethylene by 3 calculated through DFT calculations carried out at the B3LYP level is shown by Fig. 2. The reaction is exergonic, in common with related studies.¹⁵ The transition structure TS₁ adopts the spirocyclic form proposed by Sharpless³ and theoretically analysed for [Mo(O)(O₂)(L)] models by several groups.¹⁶ The structural parameters of TS₁ agree well with those of similar species as previously reported (ESI†). The first intermediate after oxygen abstraction by the olefin, A, is a dioxoperoxo complex with the two dmpz ligands occupying approximately cis positions, as calculated for the parent oxodiperoxo complex 3. Complex A then isomerises to the second intermediate B, where the two dmpz ligands are in mutually trans positions, via an energetically favourable transition.

All efforts to isolate the metal complex remaining following stoichiometric oxidation, presumably the dioxoperoxo B, have so far been unsuccessful. However, in attempting to crystallise the oxodiperoxo complex 3 a small quantity of yellow crystals of compound 1 were isolated and characterised by X-ray diffraction (Fig. 3†). Complex 1, [Mo₄O₁₆(dmpz)₆], is a tetranuclear complex consisting of a symmetrical dimer species A to which two [Mo₂O₆(dmpz)₃] units are coordinated. The latter are dioxoperoxomolybdenum species which are stabilised by their coordination to the neighbouring Mo1 atom via one of the oxo ligands. The two Mo–O₅ bonds of the dioxoperoxo species, Mo2–O5 and Mo2–O8, are found to be similar (1.763(2) and 1.707(2) Å, respectively) whilst being considerably shorter than the Mo1–O5 bond (2.346(2) Å). The dioxoperoxo species has been proposed as intermediate in several oxidation reactions catalysed by molybdenum and has been theoretically analysed in several studies,¹⁵,¹⁷ but 1 is, to our knowledge, the first dioxoperoxomolybdenum molecular species to be isolated in the solid state and experimentally characterised.¹⁸,¹⁹ Interestingly, the structural parameters of the computed complex B fit reasonably well with the experimentally determined values of the [Mo₄O₁₆(dmpz)₆] units in 1 (ESI†), strongly supporting the dioxoperoxo formation hypothesis.

The possible mechanism by which 1 had formed was also investigated by DFT (Fig. 4). The first step involves the reduction of one of the peroxy ligands of [Mo(O)(O₂)(dmpz)] to an oxo, as in complexes A and B. This reaction is energetically favourable for 3, but not for the mono-dmpz complex, [Mo(O)(O₂)(dmpz)]. Subsequently, dissociation of a dmpz ligand from A or B affords the intermediate dioxoperoxo C. Due to the unsaturation of species C, formation of the dimer species D is consequently favourable, thus forming the symmetrical core observed in the experimentally synthesised complex 1. The structural parameters computed for D agree well with the experimental values of 1, with the exception of the pyramidalisation observed at the Mo centre which results from the absence of any ligand trans to the oxo group. In the final step compound D coordinates to Mo atom of F, forming complex 1.

In summary, the [Mo₄O₁₆(dmpz)₆] (1) complex, which possesses coordinated dioxoperoxomolybdenum units, was isolated and structurally characterised during an investigation into the use of coordinating N-heterocyclic bases to enhance the oxodiperoxomolybdenum catalysed epoxidation of olefins with H₂O₂ in ILs. Dioxoperoxomolybdenum complexes have been proposed as reduced intermediate species in several Mo catalysed oxidation processes, but this is the first time that a complex of this type has been isolated in solid state and characterised.

Fig. 1 Molecular structure of [Mo(O)(O₂)(pz)]₂ (2) (30% probability thermal ellipsoids; H atoms have been omitted for clarity). For selected structural data see ESI†

Fig. 2 Energy profile of the model epoxidation reaction with [Mo(O)(O₂)(dmpz)] (3) showing the formation of the intermediate dioxoperoxo B, with zero point corrected electronic energies and Gibbs free energies (italics) (kcal mol⁻¹).

Fig. 3 Actual molecular structure (left, 30% probability thermal ellipsoids) and optimised structure (right) of [Mo₂O₆(dmpz)₃] (1). H atoms have been omitted for clarity. For selected structural data see ESI†.

\[ \text{[Mo(O)(O₂)(dmpz)]}_2 \] binuclear core to which two \[ \text{[Mo₂O₆(dmpz)₃]} \] units are coordinated. The latter are dioxoperoxomolybdenum species which are stabilised by their coordination to the neighbouring Mo1 atom via one of the oxo ligands. The two Mo–O₅ bonds of the dioxoperoxo species, Mo2–O₅ and Mo2–O₈, are found to be similar (1.763(2) and 1.707(2) Å, respectively) whilst being considerably shorter than the Mo1–O₅ bond (2.346(2) Å). The dioxoperoxo species has been proposed as intermediate in several oxidation reactions catalysed by molybdenum and has been theoretically analysed in several studies,¹⁵,¹⁷ but 1 is, to our knowledge, the first dioxoperoxomolybdenum molecular species to be isolated in the solid state and experimentally characterised.¹⁸,¹⁹ Interestingly, the structural parameters of the computed complex B fit reasonably well with the experimentally determined values of the [Mo₄O₁₆(dmpz)₆] units in 1 (ESI†), strongly supporting the dioxoperoxo formation hypothesis.

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Notes and references

10 (a) M. Herbert, PhD Thesis, Universidad de Sevilla, 2010; (b) M. Herbert, F. Montilla and A. Galindo, manuscript in preparation.
18 Dioxoperoxo Mo structures have previously been proposed but X-ray analysis of such a complex has not yet been reported: (a) C. L. Bianchi and F. Porta, Vacuum, 1996, 47, 179; (b) S. Tollart, S. Bruni, C. L. Bianchi, M. Rainoni and F. Porta, J. Mol. Catal. A: Chem., 1993, 83, 311.

Fig. 4 Energy profiles in the formation of the binuclear intermediate \([\text{Mo(O)(O}_2\text{(dmpz)}\])\] complex, which has only one dmpz ligand (see ESI).