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Oxoperoxo molybdenum(VI) and tungsten(VI) and oxodiperoxo molybdate(VI) and tungstate(VI) complexes with 8-quinolinol: synthesis, structure and catalytic activity

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A solution obtained by dissolving MoO_3 in a moderate excess of H_2O_2 reacts with 8-quinolinol (QOH) to give $[MoO(O_2)(QO)_2]$ (**1**), but, when the same reaction is conducted with a large excess of H_2O_2, an anionic complex is formed, which reacts with PPh_4Cl to give the corresponding salt $[MoO(O_2)_2(QO)][PPh_4]$ (**2** · PPh_4). Freshly prepared WO_3 behaves the same way and, depending on the amount of H_2O_2 used, as above, produces either $[WO(O_2)(QO)_2]$ (**3**) or $[WO(O_2)_2(QO)][PPh_4]$ (**4** · PPh_4), respectively. Crystallographic analyses reveal the coordination geometries around the metal center in these complexes to be distorted pentagonal bipyramids. These compounds show interesting catalytic properties in the oxidation of alcohols using H_2O_2 as the terminal oxidant. In the case of aromatics, including benzylic and cinnamylic alcohols, the oxidation occurs selectively, affording aldehydes or ketones with reasonably high turnover numbers. Taking benzyl alcohol as a representative case, a probable mechanism of the alcohol-to-aldehyde conversion mediated by the prepared catalysts is suggested. The oxidation of aliphatic primary alcohols, under the same conditions, does not show the above selectivity: the reaction yields the corresponding aldehydes as well as carboxylic acids. The work was also extended to study the catalytic activity towards the oxidation of phenol and various sulfides and amines using the same oxidants.

Introduction

Molybdenum and tungsten, the 4d and 5d congeners of group 6 metals, are long known to function as potential heterogeneous catalysts for the oxidation of organic compounds, when in their higher oxidation states.[1] Homogeneous oxo-transfer chemistry of the MO_2^{2+} (M = Mo, W) core is known to be biomimetic.[2–4] Indeed, peroxo molybdenum and tungsten systems have been recognized as potential insulin mimics[5] and some oxo and oxoperoxo molybdenum and tungsten species have recently been shown to possess superior bromoperoxidase activity to that of peroxo vanadates.[6]

If much work has been done on modelling studies for Mo,[7–10] oxo-transfer modelling involving W is much less explored. The first work was reported by Holm and Yu.[11] The presence of a *cis*-$[WO_2S_4]$ group was established in an active site of ferredoxin aldehyde oxidoreductase.[12] In oxoperoxo chemistry of Mo and W an important structural motif, in which two peroxo groups and a doubly bonded oxo ligand create the median $M(O_2)_2O$ plane, is well known.[13] This core, although observed as being most stable[13] and a common motif in oxoperoxo molybdenum systems, has, in our experience, a high formation tendency without doubt but is also a rather reactive species, which readily performs substrate oxidation, converting itself into a $MO(O_2)^{2+}$ core, which gives more stable compounds than its diperoxo analogue. A group of compounds containing an $MoO(O_2)_2$ core with non-deprotonated α-amino acid ligands and of general composition $[MoO(O_2)_2(L\text{-}L'H)]$, where L-L′H = glycine, alanine, proline, valine, leucine or serine, were found to be stable at ambient temperature and behaved as stoichiometric reagents for substrate oxidation, themselves being converted to their respective monoperoxo species.[14] However, the catalytic activity of those compounds have not yet been examined.[15]

Complexes of the type $[MoO(O_2)_2L]$[16] where L = $(Me_2N)_3PO$, R_3PO (R = alkyl or aryl), DMF, DMSO or pyridine, are known to be useful catalysts, mainly in the epoxidation of olefins.[17] Such epoxidation reactions were studied by Venturello *et al.*[18] and Ishii *et al.*,[19] using molybdenum complexes as catalysts during their work on alcohol oxidation. Notably, Modena and co-workers[20] reported a wide variety of stoichiometric[20a] as well as catalytic[20b] alcohol-to-aldehyde oxidation reactions by using Mo- and W-based oxoperoxo complexes. Interestingly, $[Mo^{VI}O_2(acac)_2]$ (acac = acetyl acetonate) was shown[11] to function as a catalyst in the homogeneous oxidation of alcohols to aldehydes or ketones by O_2, but the method is a bit cumbersome, requiring copper salts as co-catalyst and addition of toluene in the reaction mixture.[21] Trost and Masuyama[22] reported heptamolybdate-catalyzed alcohol oxidation by H_2O_2, but with very low turnover numbers (TON).

In a previous communication,[23] we have shown for the first time that an oxomonoperoxo molybdenum(VI) complex, $[MoO(O_2)(QO)_2]$ **1**, with QO^- = 8-quinolinolate, is able to catalyze (very efficiently) the oxidation of alkyl benzenes. **1** catalyzes the said oxidation using a moderate excess of H_2O_2 as oxidant, while large excesses lower the TON. Strangely enough, we found that its tungsten analogue $[WO(O_2)(QO)_2]$ **3**,

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which we reported very recently,[24] fails to catalytically oxidize alkyl benzenes, either with moderate or excessive amounts of H_2O_2. To rationalize the diminished catalytic ability of **1** in the presence of excess of H_2O_2, we have recently discovered that QOH is capable of coordinating to the $MO(O_2)_2$ core when the putative $[MO(O_2)_2 \cdot 2QOH]$ (M = Mo,[23] W[24]) adduct is dissolved in an excess of H_2O_2, to afford monoanionic diperoxo complexes $[MO(O_2)_2(QO)]^-$ [M = Mo (**2**) and W (**4**)], which could be isolated as PPh_4 salts.

In the present work, we report the detailed synthesis, structure and catalytic activity of **1-4**, where it will be apparent that the anionic complexes have lower catalytic capabilities than their neutral counterparts. Although **2** and **4** are inactive in the catalytic oxidation of alkyl benzenes, the key result of the present work is the selective conversion of benzyl and cinnamyl alcohol into benzaldehyde and cinnamaldehyde, that is, without further oxidation to their corresponding carboxylic acids. However, aliphatic alcohols did not show the above selectivity. The work is extended to other important substrates, such as phenol, various sulfides and amines.

Experimental

Materials

The chemicals $MoO_3 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, dinitrophenylhydrazine and 8-quinolinol were of extra pure quality and obtained from Loba Chemie (India). Hydrogen peroxide (30%), cyclohexanol, 1,4-diaminobenzene, acetonitrile, dichloromethane, light petroleum (40–60), diethyl ether and acetone were of analytical grade and were obtained from Merck (India). Tetraphenylphosphonium chloride (extra pure quality) and AnalaR grade dimethyl sulfide were obtained from Merck (Germany). Acetonitrile, dichloromethane and acetone were further purified before use following literature methods.[25] Sodium bicarbonate, triphenylphosphine, benzyl alcohol and phenol were from Sisco Research Laboratories (SRL, India) and were used as received. Acids and alkalis were of AR grade from Merck (India). Ethanol (90%) was obtained from Bengal Chemical and Pharmaceutical works (Calcutta) and was distilled over lime before use. Ultra high pure (UHP) grade dioxygen, dinitrogen, zero CO_2 air and dihydrogen gases were used whenever necessary, including in chromatographic analysis. HPLC or GR grade solvents (Merck, Germany) were used for quantitative gas chromatographic (GC) analysis, with di-*n*-butyl ether as internal standard.

Physical measurements

IR spectra were recorded as KBr pellets on a Perkin Elmer 597 IR spectrophotometer (4000–200 cm^{-1}) and electronic spectra on a Hitachi U-3410 UV-vis NIR spectrophotometer. A Systronics (India) model 335 digital conductivity bridge with a bottle-type cell was used to measure the solution conductance values of the isolated complexes at 25 °C using a thermostatic arrangement. A SUVNIC (UK) apparatus was used to measure melting points of organic substrates as well as their oxidation products. The magnetic susceptibilities were obtained by the Guoy method using $Hg[Co(NCS)_4]$ as calibre. Elemental analysis (C, H and N) was performed with a Perkin Elmer 240C elemental analyzer. W and Mo were estimated gravimetrically as WO_3 and $[MoO_2(QO)_2]$, respectively.[26] Triply distilled (all glass) water was used throughout. GC measurements were routinely done on a HP 5880A gas chromatograph using an OV-101 packed column. However, the data presented here were recorded with an Agilant model 6890 N gas chromatograph using HP-1 and INNOWAX capillary column in FID mode with dinitrogen as carrier gas.

Syntheses

$[MoO(O_2)(QO)_2]$ (1). $MoO_3 \cdot 2H_2O$ (1.25 g, 6.95 mmol) was dissolved in 30 wt % H_2O_2 (40 ml, 13.9 mmol) by stirring at room temperature, giving a pale yellow solution. Addition of 8-quinolinol (2.02 g, 13.9 mmol) as a dilute (4 M) acetic acid solution (10 ml) to the above mixture, under stirring, gave **5** $[MoO(O_2)_2 \cdot 2QOH]$ as a yellow solid.[21] The solid was filtered off, washed thoroughly with water, 95% ethanol and diethyl ether, then dried under vacuum. Yield of **5** was 2.76 g (86%). Slow crystallization from dichloromethane–hexane (5 : 1) gave pure **1** as shiny orange crystals (crystallization yield: 95%). **1** was soluble in dichloromethane, acetonitrile and acetone but insoluble in ethanol, benzene and diethyl ether. Anal. calcd for $C_{19}H_{14}Cl_2N_2O_5Mo$: C, 44.1; H, 2.7; N, 5.4; Mo, 18.6; found: C, 49.8; H, 2.7; N, 6.3; Mo, 23.1; IR (cm^{-1}): 1620 (w), 1525 (s), 1480 (s), 1400 (s), 1325 (s), 1250 (m), 1220 (m), 1200 (w), 1115 (s), 960 (s, $\nu_{Mo=O}$), 915 (m, $\nu_{O\text{–}O}$), 850 (s), 800 (w), 790 (m), 740 (s), 660 (s), 590 (s), 545 (m), 520 (w), 480 (w), 315 (m); UV-vis (λ_{max}/nm): 364 (ε = 4720 M^{-1} cm^{-1}).

$[MoO(O_2)_2QO][PPh_4]$ ($2 \cdot PPh_4$). **5** (1.17 g, 2.50 mmol) was dissolved in the minimum volume of acetonitrile (20 ml) in a conical flask fitted with an air condenser and was stirred for 1 h after the addition of an excess of H_2O_2 (30 wt %, 15 ml); a clear yellow solution was obtained. Dropwise addition of an aqueous solution (10 ml) of PPh_4Cl (0.86 g, 2.5 mmol), under constant stirring for another 30 min., gave crude $\mathbf{2} \cdot PPh_4$ as a shiny light yellow solid. The compound was found to be soluble in acetonitrile, acetone, dichloromethane and chloroform but insoluble in ethanol and diethyl ether. It was crystallized from dichloromethane–hexane (1 : 1) to provide pure **2** as rectangular light yellow crystals. Yield: 1.25 g (76%); anal. calcd for $C_{33}H_{26}O_6NPMo$: C, 60.0; H, 4.0; N, 2.1; Mo, 14.6; found, C, 60.2; H, 4.0; N, 2.2; Mo, 14.4; IR (cm^{-1}): 3040 (w), 1610 (w), 1600 (w), 1580 (m), 1560 (m), 1490 (s), 1460 (vs), 1455 (s), 1450 (sh), 1375 (s), 1320 (s), 1280(s), 1100 (vs), 1020 (sh), 1000 (m), 945 (s, $\nu_{Mo=O}$), 845, 810 (m, $\nu_{O\text{–}O}$), 800 (w), 780 (m), 760 (s), 740 (s), 720 (s), 645 (s), 580 (s), 530 (s), 460 (w), 380 (w), 310 (m); UV-vis (λ_{max}/nm): 357 (ε = 3725 M^{-1} cm^{-1}).

$[WO(O_2)(QO)_2)]$ (3). An aqueous solution (25 ml) of $Na_2WO_4 \cdot 2H_2O$ (1.98 g, 6.0 mmol) was acidified with a 6 M HCl solution until a white precipitate of $WO_3 \cdot nH_2O$ was obtained. It was filtered off and washed several times with water and ethanol. The precipitate was transferred quantitatively into a beaker and was dissolved in 30 wt % H_2O_2 (10 ml, 13.9 mmol) by stirring at room temperature (25 °C) until a clear and colourless solution was obtained. Addition of 8-quinolinol (1.74 g, 12.0 mmol) dissolved in acetic acid (6 M, 10 ml) to the clear solution while stirring (about 10 min) gave **6** $[WO(O_2)_2 \cdot 2QOH]$ as a yellow solid, which was filtered off, washed with water, 95% ethanol and diethyl ether. Yield of **6** was 2.73 g (*ca.* 82%). A fraction of **6** (1.39 g, 2.5 mmol) was dissolved in acetonitrile (20 ml) and refluxed for 20–25 min. The solution was then cooled and diethyl ether was added to the cold solution until the solvent mixture was 2 : 1 (*v*/*v*) in acetonitrile and diethyl ether, respectively. Upon standing for 15 h, this solution afforded pure **3** as orange crystals (crystallization yield: 1.2 g, 92%). Compound **3** was soluble in acetonitrile, dichloromethane, acetone and chloroform, but insoluble in diethyl ether, benzene and ethanol. Anal. calcd for $C_{18}H_{12}N_2O_5W$: C, 41.5; H, 2.3: N, 5.4; W, 35.4; found, C, 42.1; H, 2.4; N, 5.6; W, 35.2; IR (cm^{-1}): 1590 (w), 1510 (s), 1470 (s), 1460 (sh), 1380 (s), 1330 (s), 1270 (m), 1240 (w), 1110 (s), 960 (s, $\nu_{W=O}$), 890 (m, $\nu_{O\text{–}O}$), 825 (m), 790 (w), 780 (sh), 755 (s), 630 (m), 530 (m), 500 (m); UV-vis (λ_{max}/nm): 367 (ε = 2870 M^{-1} cm^{-1}).

$[WO(O_2)_2QO][PPh_4]$ ($4 \cdot PPh_4$). **6** (1.39 g, 2.5 mmol) was dissolved in the minimum volume (15 ml) of acetonitrile to which an excess (15 ml) of H_2O_2 (30 wt %) was added and the resulting solution was stirred for *ca.* 90 min, when the colour of the solution assumed a light yellow shade. Dropwise addition of PPh_4Cl (0.86 g, 2.50 mmol) dissolved in water (20 ml) to the above solution while stirring gave crude **4** · PPh_4 as a light yellow solid. Its solubility was the same as that of **1** and **2** · PPh_4 and the compound was crystallized as yellow rectangular plates from dichloromethane–*n*-hexane (1 : 1). Yield: 1.38 g (*ca.* 74%); anal. calcd for $C_{33}H_{26}O_6NPW$: C, 53.0; H, 3.2; N, 1.9; W, 24.6; found, C, 53.3; H, 3.7; N, 2.1; W, 24.4; IR (KBr disc, cm^{-1}): 1600 (w), 1580 (m), 1500 (s), 1480 (w), 1460 (s), 1440 (s), 1430 (sh), 1375 (s), 1325 (s), 1260 (m), 1190 (w), 1160 (w), 1105 (vs), 1025 (w), 1000 (m), 945 (s, $\nu_{W{=}O}$), *830* (sh), *825* (m), *820* (sh, italicized vibrations, $\nu_{O–O}$), 800 (w), 780 (m), 760 (m), 750 (sh), 720 (s), 690 (s), 625 (s), 575 (m), 525 (vs), 450 (w), 425 (w), 385 (w), 300 (m), 290 (sh); UV-vis (λ_{max}/nm): 395 (sh, 30), 336 (ε = 1510 M^{-1} cm^{-1}).

X-Ray crystallographic data collection and refinement

X-Ray intensity data for complexes $[MoO(O_2)(C_9H_6ON)_2] \cdot CH_2Cl_2$ ($1 \cdot CH_2Cl_2$), $[WO(O_2)(C_9H_6ON)_2]$ (**3**), $[MO(O_2)_2(C_9H_6ON)_2][PPh_4]$, M = Mo (**2** · PPh_4) or W (**4** · PPh_4), were collected at 20 °C (−123 °C for **3**) with an Enraf–Nonius CAD 4 diffractometer (ω scan) using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares refinements of setting angles for 25 reflections with $8 < \theta < 18°$. Data were corrected for Lorentz polarization effects. Empirical absorption correction using ψ scan[27] (DIFABS[28] for **3**) were applied. The crystal structures were solved by the heavy atom method using SHELXS-86[29] and refined on F^2 by SHELXS-97[30] with anisotropic thermal parameters for nonhydrogen atoms (disordered solvent CH_2Cl_2 atoms in the solvate of **1** were treated isotropically). The oxo group in **3** was disordered over two sites with occupancy factors of 0.5. The hydrogen atoms placed in the calculated positions were allowed to ride on the atoms to which they were attached with the thermal parameters tied to those of the parent atoms.†

Catalytic oxidation studies

All complexes exhibited general catalytic oxidizing activity towards alcoholic, sulfide and amine functions, converting organic substrates into their oxidized products with impressive yields as well as high turnover numbers (TON). The following equation is an example of the above mentioned catalytic reactions:

$$\text{Alcohols} \xrightarrow[\text{CH}_3\text{CN or CH}_2\text{Cl}_2,\ \text{H}_2\text{O}_2\ (4\ \text{equiv., } 400\,\text{mol}\ \%\ )]{[\text{MO(O}_2)_2\text{(QO)]}^-\ \text{M =Mo,W(0.1 mol}\ \%\ )} \text{Aldehydes/Ketones} \qquad \text{(i)}$$

Alcohols and other substrates (25.0 mmol) were weighed directly into 50 ml two-necked round-bottomed flasks and dissolved in 10 ml CH_3CN or 15 ml CH_2Cl_2; catalysts **2** or **4** were added to each of the above solutions as their PPh_4 salts (0.025 mmol, 0.1 mol %). The solutions were then treated with 30% H_2O_2, added in portions, for a total of 100 mmol (400 mol %, 4 equiv. with respect to the substrate and 4000 equiv. with respect to the catalysts); the resulting solutions were brought to reflux (78 °C for acetonitrile and 40 °C for CH_2Cl_2). Dioxygen was bubbled through the solutions at a rate of 4 bubbles per second when effect of dual additions was investigated. The reaction mixtures were then cooled to 25 °C and aliquots were taken out for GC analysis. For time *versus* yield studies, aliquots (1 µl) were injected into the GC equipment at 1 h intervals. For the isolation and quantitative estimation of the products, the solvent (CH_3CN) was distilled out and the residual liquid (H_2O from H_2O_2) was shaken with CH_2Cl_2 (5 ml) in a decanting flask in which aqueous and organic layer separated. The latter was isolated and the aqueous layer was repeatedly (3–4 times) washed with CH_2Cl_2. The organic extracts were combined and the solvent was distilled out. The residue was extracted with ether, from which the oxidation products were isolated and characterized, according to procedures I–III described below. The insoluble residue left after ether extraction looked like the catalyst, which was confirmed by IR spectroscopy. In all cases the identity and the concentration of the oxidation products were confirmed by gas chromatography. It should be mentioned that for all the procedures below the amount of products chemically separated corresponded closely to the GC results. Work-up procedure I was used to isolate aldehydes or ketones and procedures II and III were used to isolate carboxylic acids and other compounds.

Procedure I. Carbonyl compounds were isolated as yellow orange solids in the form of their 2,4-dinitrophenyl hydrazone derivatives, the corresponding carbonyls being generated by acid hydrolysis. The purity of the 2,4-dinitrophenyl hydrazone derivatives was checked by integration of the ^1H NMR spectra.

Procedure II. The reaction solutions presumed to contain carboxylic acids were treated with aqueous $NaHCO_3$; the aqueous layers were isolated and concentrated almost to dryness and allowed to stand for 30 min. The acids were isolated as their corresponding colourless sodium salts.

Procedure III. The sulfones were crystallized out as solids by concentrating the aqueous layer, while unreacted sulfides and sulfoxides, remaining in CH_2Cl_2, were separated by fractional distillation. 1,4-Benzoquinone (from phenol) was extracted from the reaction solution by diethyl ether; evaporation of ether deposited the off-white material. The mixture of products, 1,4-benzoquinone and 4-nitroaniline, obtained from 1,4-diaminobenzene was separated by steam distillation since the former is steam-volatile. Other amines and their oxidation products were separated by column chromatography and their identities were confirmed by NMR spectroscopy.

Results and discussion

Synthetic aspects and general characterization

1 and **3** were prepared by the same method, the former by using MoO_3 and the latter, freshly prepared WO_3 as starting materials. The putative compounds[23] $[MoO(O_2)_2 \cdot 2QOH]$ (**5**) and $[WO(O_2)_2 \cdot 2QOH]$ (**6**) were formed first, and crystallization from suitable solvents afforded **1** and **3**, respectively. The intermediates **5** and **6** were separately dissolved in excess H_2O_2 and stirred, thus forming the anionic species $[MO(O_2)_2QO]^-$ [M = Mo (**2**), W (**4**)]; the addition of PPh_4Cl allowed the precipitation of their respective PPh_4 salts.

While **1** and **3** are non-electrolytes, **2** · PPh_4 (125 ohm^{-1} cm^2 mol^{-1}) and **4** · PPh_4 (120 ohm^{-1} cm^2 mol^{-1}) behave, as expected, as 1 : 1 electrolytes in acetonitrile.[31] The $QO^- \rightarrow M(VI)$ LMCT in $[MoO(O_2)(QO)_2]$ (**1**) occurs at a lower wavelength (364 nm) than that in $[WO(O_2)(QO)_2]$ (**3**), where it occurs at 367 nm (see also the Experimental). The low-energy shift in the electronic transition on going from molybdenum to tungsten is more marked in the two anionic complexes: the $QO^- \rightarrow M(VI)$ LMCT transition in **2** · PPh_4 appears at 357 nm, while for **4** · PPh_4, the same occurs at 395 nm. This observed wavelength

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† CCDC reference numbers [CCDC NUMBER(S)]. See http://www.rsc.org/suppdata/nj/b4/b410984h/ for crystallographic data in .cif or other electronic format.

shift from Mo to W is due to the lower optical electronegativity of W(VI) compared to that of Mo(VI).

The ν(M=O) vibration appears as strong bands at 960, 945, 945 and 960 cm^{-1} in **1**, **2**·PPh$_4$, **3** and **4**·PPh$_4$, respectively. The corresponding ν(O–O) vibration appears as medium intensity bands at 915 (**1**), 845 and 810 (**2**·PPh$_4$), 890 (**3**), and 830, 825 and 820 (**4**·PPh$_4$) cm^{-1}, indicating that in **2**·PPh$_4$ and **4**·PPh$_4$ the oxodiperoxo core does not assume a strictly median plane with respect to the entire molecule. This is also evident from their molecular structures (Fig. 1 and Fig. 2). The ν(M–N) and ν(M–O) from the quinolinol ligand complexation may be assigned to the weak bands around 450 and 425 cm^{-1}, respectively, in all cases. A medium-to-strong intensity band in the 590 cm^{-1} region and another at 530 cm^{-1} are assignable to the asymmetric and symmetric vibrations of the MO$_2$ triangle, respectively.[32] In the case of **2**·PPh$_4$ and **4**·PPh$_4$, the symmetric vibration is hidden by the very strong Ph$_4$P$^+$ vibration in that region. Other major vibrations originate from the 8-quinolinol ligands, modified as typical in metal-coordinated bidentate species.[33]

Molecular structures

Crystal data and refinement results for the studied compounds are given in Table 1. The crystal structure determinations of [MO(O$_2$)(QO)$_2$] [M = Mo (**1**), W (**3**)] have been reported in earlier communications.[23,24] The coordination geometry around the metal center in **1** and **3** can be described as distorted pentagonal bipyramids with the two essentially planar QO$^-$ ligands being approximately orthogonal to each other; the dihedral angles between the least-square planes through the ligand atoms in **1** and **3** are 84.6(1)° and 83.1(1)°, respectively.

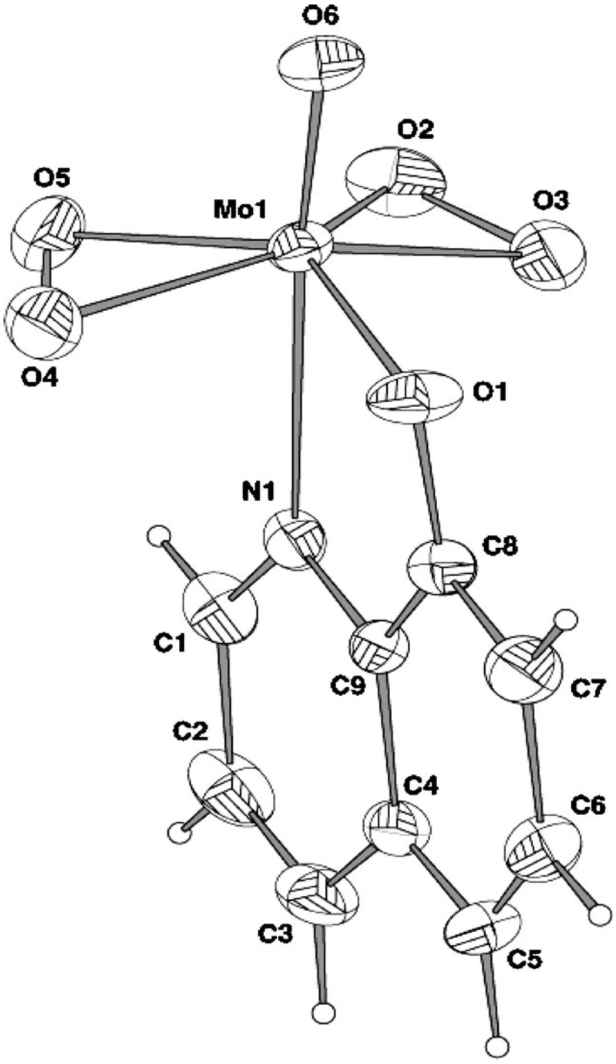


Fig. 1 Molecular structure of the anion [MoO(O$_2$)$_2$(QO)]$^-$, **2**, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

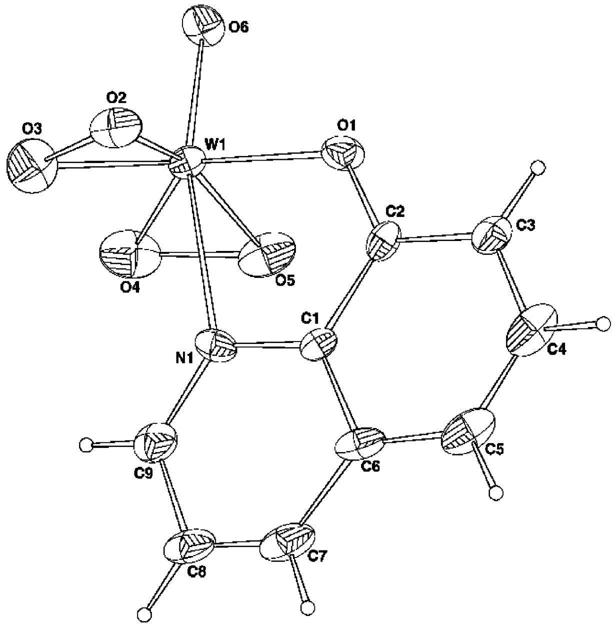


Fig. 2 Molecular structure of the anion [WO(O$_2$)$_2$(QO)]$^-$, **4**, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

The structures of **2**·PPh$_4$ and **4**·PPh$_4$ consist in discrete monomeric anions, [MO(O$_2$)$_2$(QO)]$^-$ [M = Mo (**2**) , W (**4**)], and PPh$_4$$^+$ cations held together in the lattice. Both PPh$_4$ salts are characterized by an MO^{4+} center with the oxo groups occupying the apical positions. The geometry about the metal center in **2**·PPh$_4$ and **4**·PPh$_4$ can be best described as pentagonal bipyramids (Fig. 1 and Fig. 2) with the axial sites occupied by the oxo (O6) and the quinoline (N1) ligands. Two η^2-peroxo moieties (O2, O3 and O4, O5) and the phenol oxygen O1 from the quinoline ligand define the equatorial planes in **2** and **4** with the metal atoms being displaced towards the oxo oxygen by 0.340(1) Å in **2** and 0.345(1) Å in **4**, from the corresponding equatorial plane. This is in agreement with the observation from various structurally characterized oxodiperoxo complexes of molybdenum(VI) and tungsten(VI),[34] in which a high stability of the oxodiperoxo molybdate and tungstate complexes is attained when the two peroxide groups coordinate in the equatorial plane. The essentially planar 8-quinolinolate ligand (N1, C1–C9) is almost orthogonal to the equatorial plane (O1–O5) in both complexes, the dihedral angles between the two least-squares planes in **2** and **4** being 92.2(2)° and 91.6(2)°, respectively. Selected bond distances and angles for **2** and **4** (Table 2) correspond well to those of other seven-coordinate Mo and W oxoperoxo complexes.[23,35] The lengthening of the Mo–N [2.395(2) Å] and W–N [2.364(10) Å] distances in **2** and **4** compared to the Mo–N [2.194(3)–2.269(3) Å] and W–N [2.264(6)–2.273(6) Å] bond lengths in **1** and **3** reflects the strong trans influence of the oxo ligand.[36]

Catalytic properties of the isolated complexes

All complexes possess general catalytic and selective oxidizing properties towards alcoholic functions from organic substrates (Table 3), such as benzyl and cinnamyl alcohol selectivity to benzaldehyde and cinnamaldehyde or isopropanol and cyclohexanol to acetone and cyclohexanone, respectively, with impressive yields. However, this selectivity is not observed when the substrates are aliphatic alcohols, since a mixture of the

Table 1 Crystal and refinement data for the studied compounds

	1 · CH_2Cl_2	**2** · PPh_4	**3**	**4** · PPh_4
Formula	$C_{19}H_{14}Cl_2N_2O_5Mo$	$C_{33}H_{26}NO_6PMo$	$C_{18}H_{12}N_2O_5W$	$C_{33}H_{26}NO_6PW$
Formula weight	517.16	659.46	520.15	747.37
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.791(1)	9.928(1)	7.930(2)	9.883(3)
b/Å	10.643(1)	11.221(1)	8.221(2)	11.205(5)
c/Å	10.964(2)	13.236(1)	12.625(2)	13.138(2)
α/°	117.70(2)	86.48(1)	89.71(1)	86.25(7)
β/°	90.14(1)	78.97(1)	78.99(1)	79.40(5)
γ/°	105.08(1)	78.57(1)	82.00(1)	78.52(3)
U/Å^3	966.5(3)	1418.2(3)	799.9(3)	1400.9(19)
Z	2	2	2	2
D_{calcd} (D_o)/mg m^{-3}	1.770 (1.720)	1.544 (1.560)	2.160 (2.130)	1.772 (1.760)
F(000)	516	672	496	736
μ/mm^{-1}	0.990	0.567	7.255	4.229
Reflections collected	3359	5411	3193	3654
Observed reflections [$I > 2\sigma(I)$]	3006	4175	2565	2820
R_1	0.041	0.030	0.034	0.047
$wR2$	0.1190	0.077	0.087	0.119

respective aldehydes and carboxylic acids are obtained. Lack of selectivity in the case of aliphatic alcohols is due to the fact that resonance stabilization of the C=O bond in aromatics makes it reasonably immune against a nucleophilic attack[37,38] (here by O_2^{2-}). Actually, as long as there is a noticeable concentration of H_2O_2, the aromatic aldehydes are not oxidized to their corresponding acids. It is observed that, when increasing length in aliphatic alcohols, the rate of catalytic oxidation decreases and, for instance, the corresponding aldehyde can be obtained exclusively from *n*-dodecanol (entry 12). We have singled out the CH_3OH-to-HCHO oxidation scheme for its industrial and pharmacological significance and work is ongoing in this area to make it a selective reaction using additives and to improve yields.

Notably, oxidation of 1,4-diaminobenzene (entry 17) to quinone is an important industrial process, though the simultaneous production of quinone along with *p*-nitroaniline is interesting from the reactivity viewpoint. A reduction in refluxing time increases the proportion of *p*-nitroaniline produced; the same occurs with aniline (entry 19), with an increase of nitrosobenzene production. In the case of diaminocyclohexane (entry 18), the amount of corresponding oxidized product, dioxime, increases when increasing reflux time. The oxidation of dimethylsulfide (entry 14) to dimethylsulfone goes *via* a dimethylsulfoxide intermediate. If the time of reflux and the amount of peroxide are reduced, it is possible to get a selective and quantitative yield of DMSO and the same observations were made for the other two sulfides (entries 15 and 16).

Table 2 Selected bond length (Å) and angles (°) for anions **2** and **4**

	2 (M = Mo)	**4** (M = W)
M–O1	2.017(2)	1.996(8)
M–O3	1.948(2)	1.879(11)
M–O5	1.910(2)	1.947(9)
M–N1	2.395(2)	2.364(10)
M–O2	1.909(2)	1.937(9)
M–O4	1.953(2)	1.857(11)
M–O6	1.684(2)	1.688(8)
O2–M–O3	44.1(1)	45.6(4)
O1–M–N1	72.6(1)	73.0(3)
O4–M–N1	78.0(1)	84.3(4)
O4–M–O5	44.3(1)	47.8(5)
O3–M–O6	101.7(1)	105.2(4)
O6–M–N1	166.0(1)	165.3(4)

As shown in Table 3, the tungsten anion **4** is a more efficient catalyst than the analogous molybdenum anion **2**. Tungsten complex **3** is also superior[24] to the corresponding molybdenum complex **1**. Plots of yield percentage *versus* time for the oxidation of some representative substrates, that is, cyclic aliphatic (entry 1), aromatic (entry 2), olefinic aromatic (entry 3), and primary aliphatic (entry 5) alcohols are presented in Fig. 3 and those of a secondary alcohol (entry 11), a phenol (entry 13) and an aromatic amine (entry 19) are shown in Fig. 4, with **4** as a representative catalyst and H_2O_2 as the oxidant.

The complexes $[MO(O_2)(QO)_2]$ (M = Mo, W) stoichiometrically oxidize benzyl alcohol almost quantitatively to benzaldehyde; both charge and mass balances are shown in eqns. (1)–(3).

$$[MO(O_2)(QO)_2] + 2e^- \rightarrow [M(O)_2(QO)_2] + O^{2-} \qquad (1)$$

$$C_6H_5CH_2OH \rightarrow C_6H_5CHO + 2H^+ + 2e^- \qquad (2)$$

Adding eqns. (1) and (2) gives eqn. (3):

$$[MO(O_2)(QO)_2] + C_6H_5CH_2OH \rightarrow [M(O)_2(QO)_2] + C_6H_5CHO + H_2O \qquad (3)$$

It has been experimentally verified by us that $[M(O)_2(QO)_2]$ is the end product of this stoichiometric reaction [eqn. (3)] and the said dioxo species, upon H_2O_2 treatment produce $[MO(O_2)(QO)_2]$, which again oxidize benzyl alcohol to benzaldehyde. So, one may presume that $[M(O)_2(QO)_2]$ is a catalyst precursor and $[MO(O_2)(QO)_2]$ the active catalyst. Still, we have shown[23] that, when H_2O_2 is the oxidant, it reacts with $[MO(O_2)(QO)_2]$ to produce either $[MO(O_2)_2 \cdot 2QOH]$ in the presence of a moderate excess of H_2O_2 or the anionic complex $[MO(O_2)_2(QO)]^-$ in the presence of a large excess of H_2O_2, as shown in the present work where this anionic complex has been isolated as its PPh_4 salt and structurally characterized. Hence, it is quite safe to assume that the QOH adducts[22] (**5** and **6**, see Experimental) are the active catalysts in a reaction media with a moderate excess of H_2O_2 and the anionic complexes are the active catalysts when large excesses of H_2O_2 are used. With these assumptions, we suggest the probable reaction routes for catalytic oxidation reactions with $[MO(O_2)(QO)_2]$ as catalyst precursor and H_2O_2 as oxidant, both in the presence of a moderate excess of the oxidant [eqns. (4)–(10)] and with a large excess of H_2O_2 [eqns. (11)–(16)]. A possible mechanism is presented in Scheme 1.

Table 3 Catalytic oxidation of various alcohols, sulfides and amines in refluxing acetonitrile (78 °C) using **2** or **4** as catalysts and H_2O_2 or $H_2O_2 + O_2$ (values in parentheses) as oxidants.[a]

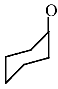
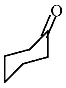
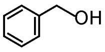
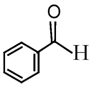
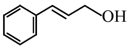
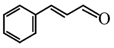
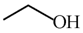
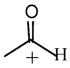
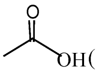
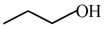
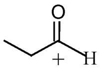
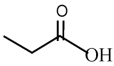
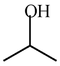
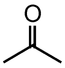
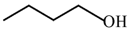
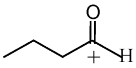
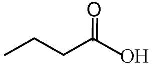
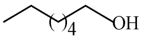
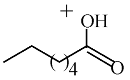
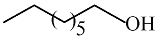
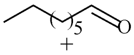
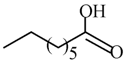
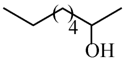
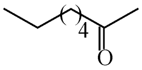
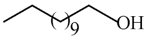
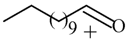
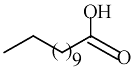
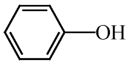
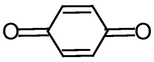
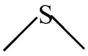
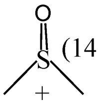
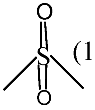
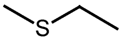
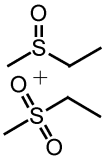
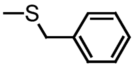
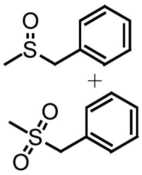
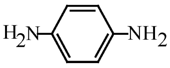
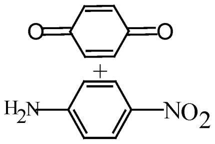
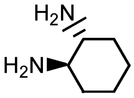
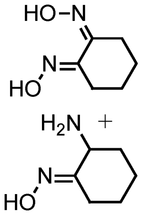
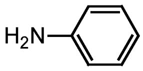
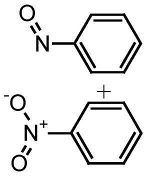
				% Yield[b]		TON[c]	
Entry	Substrate	Time/h	Product	**2**	**4**	**2**	**4**
1		24 (19)		81 (84)	85 (86)	810 (840)	850 (860)
2		15 (12)		84 (81)	89 (84)	840 (810)	890 (840)
3		14 (11)		83 (82)	86 (85)	830 (820)	860 (850)
4	CH_3OH	13 (10)	HCHO (4a) + HCOOH (4b)	46 (52) + 34 (43)	48 (53) + 33 (45)	460 (520) + 340 (430)	480 (530) + 330 (450)
5		13 (10)	 (5a) +  (5b)	48 (51) + 28 (33)	51 (51) + 29 (37)	480 (510) + 280 (330)	510 (510) + 290 (370)
6		12 (9)	 (6a) +  (6b)	56 (58) + 22 (24)	59 (59) + 23 (27)	560 (580) + 220 (240)	590 (590) + 230 (270)
7		11 (9)		84 (91)	87 (94)	840 (910)	870 (940)
8		14 (11)	 (8a) +  (8b)	60 (62) + 22 (24)	62 (61) + 23 (25)	600 (620) + 220 (240)	620 (610) + 230 (250)
9		17 (13)	 (9a) +  (9b)	65 (64) + 18 (20)	68 (65) + 17 (24)	650 (640) + 180 (200)	680 (650) + 170 (240)
10		18 (15)	 (10a) +  (10b)	70 (76) + 9 (11)	72 (78) + 9 (12)	700 (760) + 90 (110)	720 (780) + 90 (120)
11		20 (16)		81 (83)	85 (86)	810 (830)	850 (860)
12		22 (22)	 (12a) +  (12b)	76 (79) + 1 (1)	79 (82) + 1 (1)	760 (790) + 10 (10)	790 (820) + 10 (10)

Table 3 (*continued*)

				% Yield[b]		TON[c]	
Entry	Substrate	Time/h	Product	2	4	2	4
13		12 (9)		82 (80)	84 (84)	820 (800)	840 (840)
14[d]		1 (1)	 (14a) +  (14b)	18 (6) + 82 (94)	10 (2) + 90 (98)	180 (60) + 820 (940)	100 (20) + 900 (980)
15[d]		1 (1)		50 (40) + 48 (60)	46 (32) + 54 (68)	500 (400) + 480 (600)	460 (320) + 540 (680)
16[d]		1 (1)		54 (55) + 31 (43)	55 (52) + 33 (48)	540 (550) + 310 (430)	550 (520) + 330 (480)
17		6 (5)		57 (66) + 27 (28)	59 (70) + 28 (27)	570 (660) + 270 (280)	590 (700) + 280 (270)
18		10 (7)		62 (66) + 30 (29)	65 (70) + 32 (28)	620 (660) + 300 (290)	650 (700) + 320 (280)
19		7 (5)		82 (70) + 14 (30)	84 (86) + 15 (34)	820 (700) + 140 (300)	840 (660) + 150 (340)

[a] Blank experiments were also performed, that is, eliminating the catalyst only while other parameters remaining the same. Oxidation for entries 1–3 and 8–12 was found to be negligible but for entries 4&5, 6&7, 13& 17, 14–16 and 18&19 were *ca.* 8%, 4%, 5%, 10% and 3%, respectively (*cf.* 100% = oxidation obtained using the catalyst). [b] Based on substrate. [c] Turnover number is defined as the ratio of the moles of product obtained to the moles of catalyst used. [d] In dichloromethane (reflux temp. 40 °C).

A possible reaction pathway with moderate excess H_2O_2 is the following:

$$[MO(O_2)(QO)_2] + O_2^{2-} + 2H^+ \rightarrow [MO(O_2)_2 \cdot 2QOH]^{23} \quad (4)$$

$$C_6H_5CH_2OH \rightarrow C_6H_5CHO + 2H^+ + 2e^- \quad (5)$$

$$[MO(O_2)_2 \cdot 2QOH] + 2e^- \rightarrow [MO(O_2)(QO)_2] + H_2O + O^{2-} \quad (6)$$

$$[MO(O_2)(QO)_2] + e^- \rightarrow [M(O)_2(QO)_2] + 1/2O_2^{2-} \quad (7)$$

$$[M(O)_2(QO)_2] + 1/2O_2^{2-} \rightarrow [MO(O_2)(QO)_2] + e^- \quad (8)$$

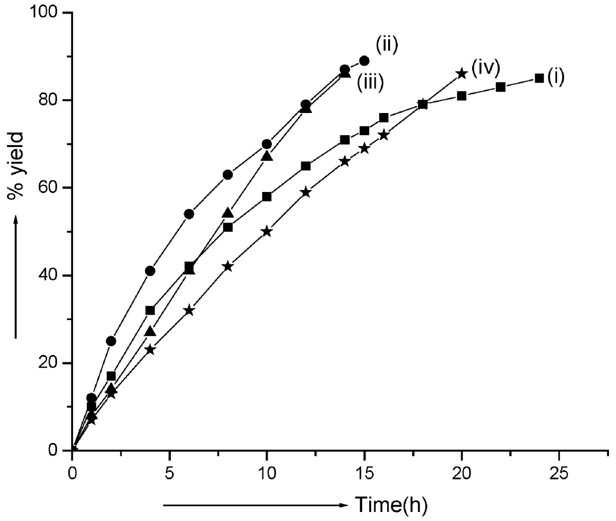


Fig. 3 Plot of yield (based on amount of substrate) *versus* time for the conversation of: (i) cyclohexane to cyclohexanone, (ii) benzyl alcohol to benzaldehyde, (iii) cinnamyl alcohol to cinnamaldehyde and (iv) 2-octanol to 2-octanone using **4** as catalyst.

Adding eqns. (4)–(8) gives eqn. (9):

$$C_6H_5CH_2OH + O_2^{2-} \rightarrow C_6H_5CHO + H_2O + O^{2-} \quad (9)$$

So, the overall reaction is:

$$C_6H_5CH_2OH + H_2O_2 \rightarrow C_6H_5CHO + 2H_2O \quad (10)$$

A possible reaction pathway with large excess H_2O_2 is the following:

$$[MO(O_2)(QO)_2] + O_2^{2-} + 2H^+ \rightarrow [MO(O_2)_2 \cdot 2QOH] \quad (11)$$ [22]

$$[MO(O_2)_2 \cdot 2QOH] \rightarrow [MO(O_2)_2(QO)]^- + QOH + H^+ \quad (12)$$ [39]

$$C_6H_5CH_2OH \rightarrow C_6H_5CHO + 2H^+ + 2e^- \quad (13)$$

$$[MO(O_2)_2(QO)]^- + QOH + 3H^+ + 2e^- \rightarrow [MO(O_2)(QO)_2] + 2H_2O \quad (14)$$

Adding eqns. (11)–(14) gives eqn. (15):

$$C_6H_5CH_2OH + O_2^{2-} + 2H^+ \rightarrow C_6H_5CHO + 2H_2O \quad (15)$$

So, the reaction equation is:

$$C_6H_5CH_2OH + H_2O_2 \rightarrow C_6H_5CHO + 2H_2O \quad (16)$$

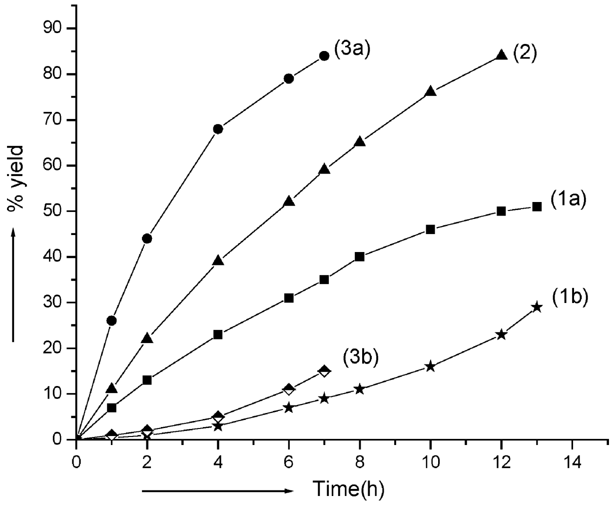
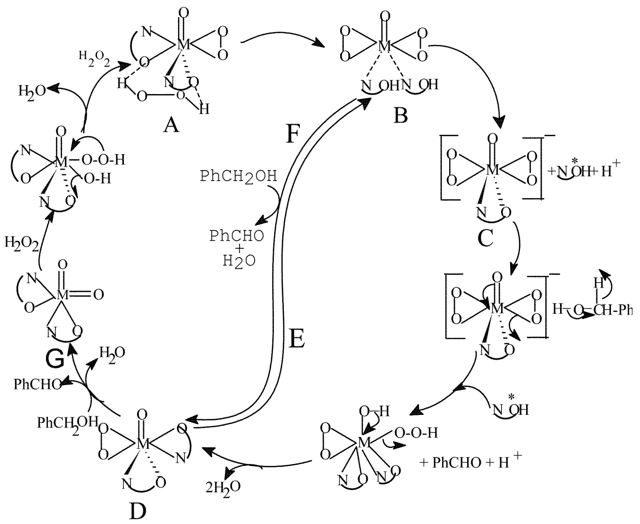


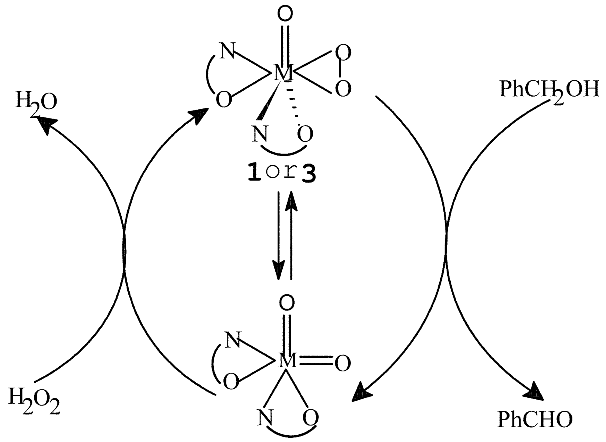
Fig. 4 Plot of yield (based on amount of substrate) *versus* time for the conversation of: (1a) ethanol to acetaldehyde, (1b) ethanol to acetic acid, (2) phenol to quinone, (3a) aniline to nitrosobenzene and (3b) aniline to nitrobenzene using **4** as catalyst.



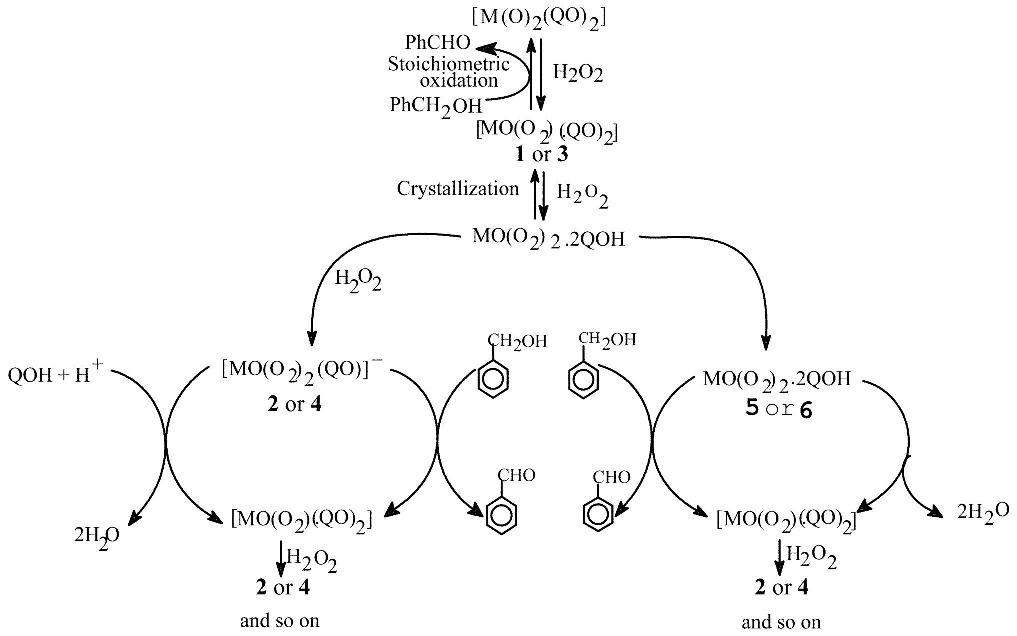
Scheme 1 Plausible mechanism of **1–4** catalytic oxidation of benzyl alcohol to benzaldehyde showing the use of moderate and large excesses of H_2O_2. Here **A** = a probable H_2O_2 associated intermediate of $[MO(O_2)(QO)_2]$ (**D**; **1** and **3**), isolated and structurally characterized; **B** is isolable (**5** and **6**) with the structure being drawn by inference[23]; **C** = $[MO(O_2)_2(QO)]^-$ (**2** and **4**), also isolated and structurally characterized; E = shunt pathway for large excess of H_2O_2 in the reaction mixture; F = shunt pathway for moderate excess of H_2O_2. G = $[M(O)_2(QO)_2]$.

Also, it may be suggested that, when the H_2O_2 concentration becomes minimal, catalytic oxidation still persists as shown in Scheme 2, though for a very few turnovers only, and the oxidant should then be replenished to sustain the catalytic cycle. Intermittent addition of H_2O_2 is a very common procedure. It minimizes side reactions, such as decomposition of H_2O_2 into H_2O and O_2. This would not only decrease the amount of $[O_2^{2-}]$ species in the reaction medium, but the water formed would also have a deactivating effect on the catalysts.

All the above-mentioned experimental observations, including catalytic and stoichiometric oxidations, are summarized in Scheme 3. We reported[23] that in the case of oxidation of methyl benzenes with **1** as catalyst the reaction proceeded *via* a radical mechanism, but in the present alcohol-to-aldehyde conversion, the reaction proceeds *via* a nonradical pathway since the reaction rate is immune to AIBN and benzoquinone. The double additive H_2O_2 + O_2 makes the catalyst more potent. The exact reason is at present obscure. The oxidation products listed in Table 3 were identified and quantified by gas chromatography using di-*n*-butyl ether as internal standard. Notably, in each case, we were able to separate and characterize the reaction products as well as the catalyst from the reaction mixture.



Scheme 2 Catalytic oxidation of benzyl alcohol to benzaldehyde at low H_2O_2 concentrations: **1** and **3** act as active catalysts.



Scheme 3 Schematic representation of experimental observations including stoichiometric and catalytic oxidation of benzyl alcohol to benzaldehyde using catalysts **1–4** (here **2** and **4** are representative cases) in the presence of H_2O_2.

Concluding remarks

A solution obtained by dissolving MO_3 (M = Mo, W) in H_2O_2 when treated with 8-quinolinol, gives $[MO(O_2)_2 \cdot 2QOH]$ (**B**) is formed and this on crystallization affords $[MO(O_2)(QO)_2]$ (**D**), the catalyst precursor for oxidizing aromatic and aliphatic alcohols including sulfides and amines (for details, see text). Interestingly, the monoperoxo species can be obtained first by treating $[M(O)_2(QO)_2]$ (**G**), with a moderate excess of H_2O_2. **D** on treatment with H_2O_2 affords **A**, a yellow solid, which on further H_2O_2 treatment yields $[MO(O_2)_2(QO)]^-$ (**C**). $[M(O)_2(QO)_2]$ (**G**) is incapable of stoichiometric oxidation of the above mentioned organic substrates, but $[MO(O_2)(QO)_2]$ is capable in doing so, itself being converted to $[M(O)_2(QO)_2]$ (**G**). Again, the highly reactive **B** performs the above type of substrate oxidation, itself being transformed into **D**. These are the basic experimental observations made by us before we worked out a protocol for catalytic substrate oxidation using H_2O_2 or H_2O_2 and O_2 as oxidants. The observation that **C** is a less effective catalyst than **B** or **D** may be due to the fact that in **C**, the respective metal ions (Mo, W) have a higher electron density than in **B** and **D**. Selectivity in the catalytic oxidation of aromatic alcohols to corresponding aldehydes may be attributed to the higher electron density on the aldehydic carbon of the aliphatic series, compared to that when the said carbon is linked with a phenyl group. The elicited philosophy of using a twin catalyst, $H_2O_2 + O_2$, is that it is experimentally observed that this system makes the oxidation faster and more efficient than when H_2O_2 is used alone. It may be stressed that the oxidation of sulfides to sulfones *via* sulfoxides with a high yield percent and catalyst turnover is one of the most important aspects of the present work on which we have already started detailed investigations.

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39 This product is formed only when a large excess of H_2O_2 is present in the reaction medium. This indicates the existence of another pair of equations, between eqn. (11) and eqn. (12), involving the formation of an activated complex, but at present the exact interpretation remains obscure..