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Novel oxo-peroxo molybdenum(VI) complexes incorporating 8-quinolinol: synthesis, structure and catalytic uses in the environmentally benign and cost-effective oxidation method of methyl benzenes: $Ar(CH_3)_n$ ($n = 1, 2$)

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A hitherto unknown distorted pentagonal bipyramidal complex, $[MoO(O_2)(QO)_2]$, very efficiently catalyses homogeneous liquid phase oxidation of methylbenzenes, *viz.* toluene and *o*- and *p*-xylenes to benzoic acid, phthalic acid and *p*-toluic acid respectively, using H_2O_2 and O_2 as oxidants.

Oxo-peroxo molybdenum complexes[1] catalytically oxidise a variety of organic substrates,[2] *viz.* alkenes, alcohols, amides and nitro compounds *etc.*, *via* homogeneous as well as heterogeneous routes.[3] However, homogeneous liquid-phase hydrocarbon oxidation is rare.[4] In this communication, besides reporting two new oxo-peroxo molybdenum(VI) compounds, *viz.* $MoO(O_2)_2{\cdot}2QOH$ (**1**) and $[MoO(O_2)(QO)_2]$ (**2**) (QOH = 8-quinolinol),† and elucidating the structure of **2** by X-ray crystallography,‡ we also report and substantiate that **2** is the catalyst precursor and **1** the active catalyst in the homogeneous and selective oxidation of toluene, *o*-xylene and *p*-xylene to benzoic acid, phthalic acid and *p*-toluic acid respectively, under very mild conditions, with an impressive yield and turnover number and smooth catalyst recovery technique. This can be regarded as one of the most inexpensive, environmentally benign and industrially feasible methods of oxidising methylbenzenes (which are very important by-products in coal-tar distillation and petroleum cracking) to the corresponding carboxylic acids, which have many uses in the chemical and pharmaceutical industries.

The structure of **2** consists of discrete monomeric units of $[MoO(O_2)(QO)_2]$ (QO = 8-quinolinolate anion), and disordered CH_2Cl_2 molecules held in the lattice. The geometry around the Mo atom can be best described as distorted pentagonal bipyramidal (Fig. 1) with the axial sites being occupied by the oxo (O5) and a phenolate oxygen (O1) ligands. The other phenolate oxygen (O2), two N atoms (N1,N2) of the bidentate QO^- ligands and the η^2-peroxo moiety (O3,O4) define the equatorial plane with the Mo atom being displaced by 0.175(1) Å from the equatorial plane towards the oxo oxygen. The two essentially planar five-membered chelate rings (Mo, O1, C8, C9, N1 and Mo, O2, C17, C18, N2) are approximately orthogonal to each other,‡ the dihedral angle between the least square planes through the ring atoms is 81.0(1)°. The bond distance and angles (Fig. 1) correspond well to those of other seven coordinate molybdenum oxo-peroxo complexes.[5]

Empirically **1** contains two atoms of oxygen and two atoms of hydrogen more than **2**. During crystallization or oxidation the yellow solution of **1** changes to orange and displays a UV-Vis spectrum which is identical to that of **2**; **2** is actually deposited from this orange solution. When in isolation **2** reacts with an excess ($Mo:H_2O \approx 1:4$) of H_2O_2 to yield **1** (this is also observed under a UV-Vis probe). Analytical and infrared data (see Notes and references) indicate that **1** may be formulated as $MoO(O_2)_2{\cdot}2QOH$ (**1**) or $MoO(O_2)(QO)_2{\cdot}H_2O_2$ (**1a**). However, preliminary rate data show that the conversion of **1** to **2** at room temperature is rather slow which is not compatible with its formulation as **1a**. Moreover, when **1** (but not **2**) is treated with $FeCl_3$ solution, a deep green colour appears instantaneously due to the formation of $[Fe(QO)_3]$. Also, the $\{MoO(O_2)_2\}$ moiety is formed readily.[6] Hence, it appears that, albeit putatively, **1** is correctly formulated. Interestingly, **1** reacts§ with toluene to give benzoic acid (72%), with *o*-xylene to give phthalic acid (55%) and with *p*-xylene to give *p*-toluic acid (61%) (all were confirmed using the undepressed mixed melting point, and the superimposability of the IR and NMR spectra with those of the respective authentic acids as well as their methyl esters), with **2** produced also. The reaction with toluene is shown by eqn. (1) as

$$MoO(O_2)_2{\cdot}2QOH + C_6H_5\text{–}CH_3 + O_2 \rightarrow C_6H_5COOH + [MoO(O_2)(QO)_2] + 2H_2O \qquad (1)$$

a representative case. These observations led to the prediction that **2** may be the catalyst precursor and **1** the active catalyst in the oxidation of methylbenzenes. This has been excellently verified by observing that **2** in a catalytic concentration furnishes the same oxidations (Table 1) in refluxing acetonitrile in the presence of H_2O_2 and a brisk bubble of dioxygen/air. The yield is reduced when only H_2O_2 is used as the oxidant, and trace when exclusively O_2 is used. The data in Table 1, suggest that the catalytic process may be shown as Scheme 1. Table 1 shows that the use of an excess of H_2O_2 imparts a negative effect on the catalytic oxidation, even in the double additive case. The reason for this is at present obscure. When H_2O_2 is used as the sole oxidant, it may undergo disproportionation ($H_2O + O_2$) under the catalytic influence of **2**, and the O_2 produced is utilized to drive the reaction in a similar fashion as in the twin reagent case. This hypothesis is supported by the fact that the process needs a much greater amount of H_2O_2 than is necessary in the double additive method.

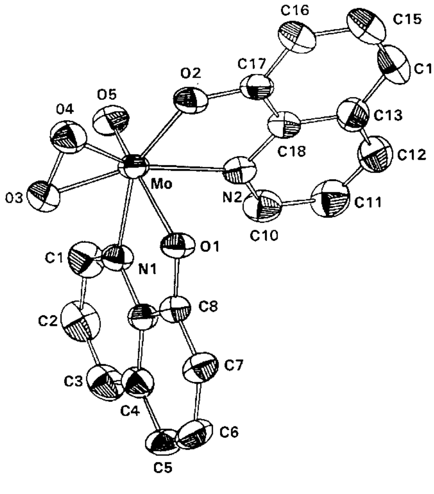
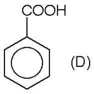
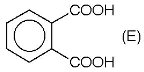
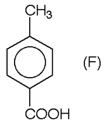
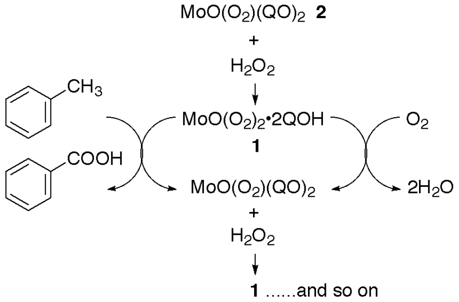


Fig. 1 An ORTEP view of $[MoO(O_2)(QO)_2]$ **2** with selected bond distances (Å) and angles (°): Mo–O1, 2.037(3); Mo–O3, 1.933(3); Mo–O5, 1.685(3); Mo–N2, 2.269(3); Mo–O2, 1.993(3); Mo–O4, 1.925(3); Mo–N1, 1.441(4); O3–Mo–O4, 43.86(13); O2–Mo–N2, 75.36(12); O1–Mo–N1, 74.87(11); O1–Mo–O5, 156.25(14); O3–Mo–N2, 159.72(13).

Table 1 Oxidation of methylbenzenes by H_2O_2 and O_2 catalysed by $[MoO(O_2)(QO)_2]$[a]

Substrate[b]	Time/h	Oxidant[c]	Product[d]	Yield[e] (%)	Turnover no.[f]
$C_6H_5CH_3$ (A)	6	H_2O_2 (0.038) + O_2		95	1310
A	10	H_2O_2 (0.076)	D	72	1019
A	10	H_2O_2 (0.190) + O_2	D	15	21
o-$C_6H_4(CH_3)_2$ (B)	6	H_2O_2 (0.038) + O_2		76	1047
B	10	H_2O_2 (0.076)	E	55	757
p-$C_6H_4(CH_3)_2$ (C)	6	H_2O_2 (0.038) + O_2		88	1221
C	10	H_2O_2 (0.076)	F	60	832

[a] **2** is the catalyst precursor (1.15×10^{-5} moles used in each case), while **1** is the active species. No oxidation occurs without using **2** (or **1**, though much less efficiently). [b] 0.016 mol used in each case. [c] Figures in parentheses indicate mol of H_2O_2. Rate of flow of O_2 = one bubble per second. [d] See footnote ¶. [e] Based on mol of substrates used. Temp = reflux, solvent = acetonitrile. [f] Is defined here as the ratio of the number of mol of product obtained to the number of mol of catalyst used, in 1 batch.



Scheme 1

It is extremely satisfying to note that the recovered catalyst in the double additive process can be used again to oxidize a new batch of the corresponding methylbenzenes showing similar catalytic efficiency, but from the third batch onwards the efficiency falls to a marked extent. Interestingly no oxidation occurs if benzoquinone is added to the reaction medium, and a 98% yield (*vs.* 30% without AIBN) is obtained after only 3 h reflux when using AIBN [azobis(isobutyronitrile)], indicating that the oxidation proceeds *via* a radical mechanism. All these aspects will be detailed in due course.

Data collection for X-ray crystallography was done from RSIC, Bose Institute, Calcutta. We thank the Alexander von Humboldt-Foundation, Germany for the donation of the IR spectrophotometer used and UGC and CSIR, New Delhi, for financial support.

Notes and references

† **1** was synthesised by dissolving MoO_3 in 30% H_2O_2 and adding an acetic acid solution of QOH at 1:2 molar ratio. Yield 80%. IR (KBr) ν/cm^{-1}: (Mo=O) 960; (O–O) 860, 910(sh);[7] (O–H) 3080 (b, H-bonded); Electronic spectrum of **1**, λ/nm: {QOH $\rightarrow$ $MoO(O_2)_2$ CT} 355, {$O_2^{2-} \rightarrow$ Mo(VI) LMCT} 375 (sh). **2** was obtained by slow crystallization of **1** from CH_2Cl_2–hexane or CH_3CN–Et_2O, yield 60%. IR (KBr) ν/cm^{-1}: (Mo=O) 945; (O–O) 920; vibrations of QO^- comparable to those of $[MoO_2(QO)_2]$[8] where QO^- is bidentate;[9] electronic spectrum, λ/nm: {$QO^- \rightarrow$ Mo(VI) LMCT} 400;[10] {$O_2^{2-} \rightarrow$ Mo(VI) LMCT} 375 (sh). Satisfactory elemental analyses (C,H,N,Mo) were obtained for all the isolated complexes.

‡ *Crystal data* for **2**: $[MoO(O_2)(QO)_2]$, $C_{19}H_{14}Cl_2N_2O_5Mo$, M = 517.16, orange, triclinic, space group $P\bar{1}$, a = 9.791(1) Å, b = 10.643(1) Å, c = 10.964(2) Å, α = 117.70(2)°, β = 90.14(1)°, γ = 105.08(1)°, V = 966.5 (3) Å^3, T = 293(2) K, Z = 2, λ = 0.71093 Å, D_c = 1.777 g cm^{-3} D_m = 1.73 g cm^{-3}, μ(Mo-Kα) = 0.990 mm^{-1}. 3359 observed [$I > 2\sigma(I)$] reflections. Enraf Nonius CAD4 diffractometer. Mo-Kα, R_1 = 0.0414, wR_2 = 0.1190 and GOF on F^2 = 1.099. Structure solved and refined by Patterson (SHELXS86) and successive Fourier and full matrix least squares (SHELXL93) methods. CCDC 182/1330. See http://www.rsc.org/suppdata/cc/1999/1627/ for crystallographic files in .cif format.

§ In three different experiments **1** (0.05 g; 0.15 mmol) and (a) toluene (0.01 g; 0.11 mmol), (b) *o*-xylene (0.012 g; 0.11 mmol) and (c) *p*-xylene (0.012 g; 0.11 mmol) were separately dissolved in acetonitrile (15 ml), refluxed for 4 h and then cooled. In the case of toluene the resulting mixture was evaporated to dryness, the mass extracted with diethyl ether and the extract shaken with aqueous bicarbonate. On acidifying the aqueous layer, benzoic acid was obtained. In the cases of *o*- and *p*-xylenes the respective products separated out on standing the solutions after CH_3CN reflux.

¶ **2** and (a) toluene, (b) *o*-xylene, (c) *p*-xylene were separately dissolved in acetonitrile (15 ml) and 30% H_2O_2 (4 ml; 38 mmol) was added. The resulting solution was refluxed for 6 h under bubbling dioxygen, cooled, acetonitrile expelled, aqueous remains treated with diethyl ether and the separated catalyst filtered from the aqueous solution. The ether extract was treated with aqueous bicarbonate and the aqueous layer was acidified to obtain benzoic acid. For phthalic acid (b) and *p*-toluic acid (c), after evaporating off the CH_3CN the aqueous layer was subjected to CH_2Cl_2 extraction to separate the catalyst. The aqueous portion was then concentrated using a rotary evaporator to get the respective acids. All the acids obtained were chromatographically and analytically pure.

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