COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Highly efficient epoxidation method of olefins with hydrogen peroxide as terminal oxidant, bicarbonate as a co-catalyst and oxodiperoxo molybdenum(VI) complex as catalyst†

Narottam Gharah,[a] Santu Chakraborty,[b] Alok K. Mukherjee[b] and Ramgopal Bhattacharyya*[a]
[a] Department of Chemistry, Jadavpur University, Kolkata – 700 032, India.
E-mail: argibhatta@yahoo.co.in; Fax: (+91)(+33) 2414-6584; Tel: (+91) (+33) 2414-6193
[b] Department of Physics, Jadavpur University, Kolkata – 700 032, India

Received (in Corvallis, OR, USA) 11th June 2004, Accepted 6th August 2004
First published as an Advance Article on the web 28th September 2004

A combination of the newly synthesized and structurally characterized compound, [MoO(O_2)$_2$(saloxH)] (saloxH$_2$ = salicylaldoxime) as catalyst, H_2O_2 as terminal oxidant and $NaHCO_3$ as co-catalyst when stirred in CH_3CN (10 cm^3) at room temperature (rt) shows a very pronounced efficiency epoxidation of olefinic compounds, the method being green and economical.

Epoxidation of olefins and arenes[1,2] is a very outstanding transformation in organic synthesis,[1] since the epoxy compounds are widely used as such,[2] or in the preparation of a wide variety of commodity chemicals.[3] In this respect aqueous hydrogen peroxide is possibly the best terminal oxidant after dioxygen from environmental and economic considerations.[3,4] Much work has been done in homogenous catalytic epoxidation with hydrogen peroxide as oxidant and a wide variety of transition metal complexes as catalysts.[3,5a,b] Considering all this work[5a,b] it has recently been realized that methyltrioxorhenium (MTO)[5a,b] with some additives introduced by Sharpless and his co-workers[6] might be regarded as the best epoxidation method to date for fairly unreactive substrates, with H_2O_2 as terminal oxidant. Strikingly, despite the success (albeit moderate) of oxoperoxo-tungsten[4] and other tungsten-based catalysts[5c,d,e] the corresponding Mo-analogs are reportedly much less successful as peroxidic (H_2O_2) epoxidation catalysts even under special[5k,l] and sometimes harsh reaction conditions.[4] Recent studies of Thiel *et al.*[7] also support this and reveal that peroxo complexes of molybdenum with chelating pyrazolyl pyridine ligand systems fail to activate H_2O_2, though the latter may be tuned in their catalytic activity to activate alkyl hydroperoxides by introducing electron withdrawing substituents in the said ligand system. In our continued interest in using oxoperoxo-molybdenum and -tungsten complexes as substrate oxidation catalysts[8] we wondered at the failure of the Mo-complexes to activate H_2O_2 and herein is reported a new molybdenum complex, *viz.* PPh$_4$[MoO(O_2)$_2$(saloxH)] (**1**)[9] (saloxH$_2$ = salicylaldoxime; for the structure[10] of **1** see Fig. 1) as catalyst which can be used along with $NaHCO_3$ as co-catalyst[11] to function as one of the (two) most efficient peroxidic epoxidation catalysts known so far.[12–14] Conversion percentage, selectivity, catalyst turnover number (TON) achieved, along with the cost input, extremely small amount of catalyst loading and environment friendliness implied in our present work lead us to claim that this method along with another method using a Mn^{III}-porphyrin system as catalyst[13] displays a matchless efficiency[14] in catalytic epoxidation of olefinic compounds.

The structure of the catalyst (**1**) consists of discrete monomeric anions, [MoO(O_2)$_2$(saloxH)]$^-$, (saloxH$_2$ = salicylaldoxime, a N,O donor), and [PPh$_4$]$^+$ cations held in the crystal lattice. The geometry around the Mo atom can best be described as distorted pentagonal bipyramidal (Fig. 1) with the axial sites being occupied by the nitrogen (N1) and the oxo (O5) ligands. The phenolate oxygen (O7) and the peroxo moieties (O1, O2, and O3, O4) define the equatorial plane with the Mo atom displaced by 0.384(1) Å from the equatorial plane towards the oxo oxygen (O5). This is consistent with the observation that greater stability of the diperoxo molybdate complexes is attained when the two peroxo groups coordinate in the equatorial plane.[15] The chelated salicylaldoximate ligand fragment (C1–C7, N1, O6, O7) is essentially planar (rms deviation 0.045 Å) and is approximately orthogonal to the equatorial plane (O1–O4, O7); the dihedral angle between the two planes is 79.0(1)°. In addition to the strong intramolecular O–H···O hydrogen bond [O6···O3, 2.784(2) Å] weak intermolecular C–H···O hydrogen bonds between the anions, and the cations and anions, stabilize the structure.

The present experimental procedure for the epoxidation reaction involving a wide variety of olefin substrates is described as follows: an acetonitrile (10 cm^3) solution containing a given substrate (*ca.* 9.5 mmol), $NaHCO_3$ (2.38 mmol), molybdenum catalyst (0.005 mmol) and 30% H_2O_2 (47.5 mmol; 4.8 cm^3) taken in a flat bottom two neck reaction flask with one neck fitted with a reflux condenser (to check evaporation), the other neck being closed with a septum, was stirred at room temperature (25 °C) for a definite period as quoted in the Table 1. As and when required an aliquot of the reaction solution was withdrawn from, and H_2O_2 added to, the contents of the flask with the help of a syringe through the septum. The withdrawn 0.5 cm^3 solution was subjected to multiple ether extractions and the extract concentrated also up to 0.5 cm^3 from which 1 μl of solution was withdrawn with the help of a gas syringe and injected to the GC port. The retention times of the peaks were compared with those of commercial standards and for GC yield calculation nitrobenzene was used as an internal standard. The above experiment was repeated with Na_2MoO_4 (**2**) and [MoO$_2$(acac)$_2$] (**3**) as catalyst for the sake of comparison. The yields% obtained with **2** and **3** as catalysts under identical

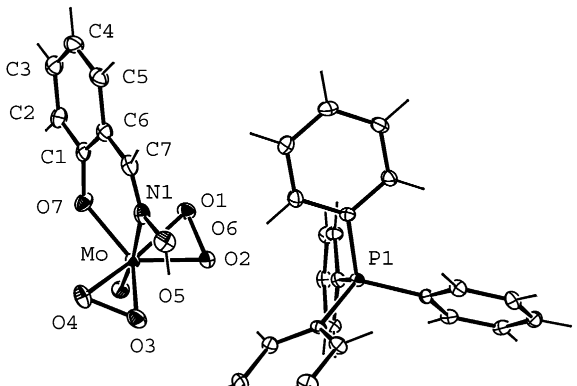


Fig. 1 The ORTEP view of complex **1**, the catalyst with selected bond distances (Å) and angles (°): Mo–O5, 1.693(2); Mo–O1, 1.952(2); Mo–O2, 1.929(2); Mo–O3, 1.946(2); Mo–O4, 1.964(2); Mo–O7, 1.983(2); Mo–N1, 2.374(2); O5–Mo–O2, 102.80(7); O5–Mo–O3, 103.33(7); O2–Mo–O3, 86.16(7); O5–Mo–O1, 103.80(7); O2–Mo–O7, 129.10(6); O5–Mo–N1, 174.49(7); O5–Mo–O7, 97.16(7).

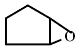
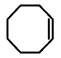
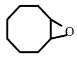
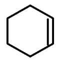
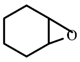
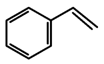
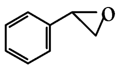
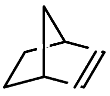
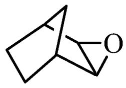
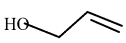
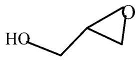
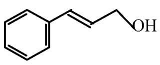
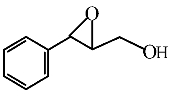
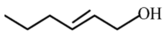
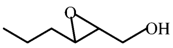
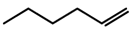
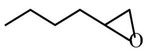
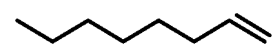
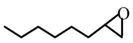
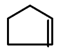
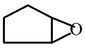
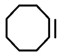
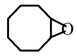
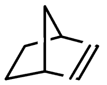
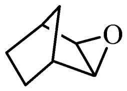
---

† Electronic supplementary information (ESI) available: determination of GC yield. See http://www.rsc.org/suppdata/cc/b4/b408946d/

DOI: 10.1039/b408946d

Table 1 Details of the catalytic epoxidation of olefinic compounds

$$\text{Olefin} \xrightarrow[\text{5-6equiv.} H_2O_2, \text{25 mol\% } NaHCO_3, \text{rt} (25\,^{\circ}C)]{\text{0.05 mol\% } PPh_4[MoO(O_2)_2(\text{saloxH})], \text{Acetonitrile}} \text{Epoxide}$$

					Yield (%)				
Entry	Substrate	Product	Time	Conversion[a] (%)	GC[b]	Isolated	Yield[c] (%)	Selectivity[d] (%)	TON[e] (TOF)[f]
(moles of catalyst : moles of substrate) = 1 : 2000									
1			10 min	92	92	—	30	100	1840 (11 040)[g]
2			10 min	99	99	93	11	100	1980 (11 880)[g]
3			45 min	98	98	—	20	100	1960 (2610)[g]
4			3 h	84	84	—	24	100	1680 (560)
5			20 min	99	99	94	34	100	1980 (5940)[g]
6			1.5 h	99	99	—	65	100	1980 (1320)
7			45 min	70	70	64	20	100	1400 (1867)[g]
8			1 h	98	98	91	60	100	1960 (1960)
9			2.5 h	82	82	—	55	100	1640 (656)
10			15 h	97	97	—	8	100	1940 (129)
(moles of catalyst : moles of substrate) = 1 : 10 000, that is mol% of catalyst = 0.01									
1			30 min	99	99	—	68	100	9900 (19 800)[g]
2			30 min	72	72	62	35	100	7200 (14 400)[g]
5			10 min	96	96	93	20	100	9600 (57 600)[g]

[a] A control experiment (omission of **1** as well as HCO_3^-) does not show any conversion to epoxide or other probable product; [b] The detailed calculation of GC yield is given as ESI. [c] This is the yield of the control experiment, excluding the catalyst **1** only, but not $NaHCO_3$ which remains in the reaction solution at the same 25 mol% concentration. When this control experiment uses $NaHCO_3$ at a catalytic concentration the conversion and yield% become negligible. [d] Selectivity is really spectacular in the given time frame. If the stirring is continued for still longer periods, entries 4, 6, 7, and 8 start showing a peak due perhaps to the formation of diols. This, however, is another interesting area of work and investigation into this is continuing. [e] TON = ratio of moles of product (here epoxide) obtained to the moles of catalyst used. [f] The corresponding TOFs (TON h^{-1}). [g] Values extrapolated.

conditions are 44, 30, 26% and 53, 36, 30% respectively, for the representative entries, 1, 4 and 7. The isolated yield in a few cases (Table 1) is obtained by multiple ether extractions of the reaction solution after the reaction is over and then evaporating the ether and acetonitrile by distilling at a mildly reduced pressure (using a water aspirator) and kept over P_2O_5 in a desiccator and weighed (when the GC yield was 98–99%) in a micro-balance and then the identity of the products was confirmed by IR and NMR probing. For lower yields% the liquid (for solid epoxides obtained from liquid olefins, the former are simply dried and weighed) products were subjected to preparative TLC and the highly intense spot was cut out and plunged in CH_2Cl_2 which serves as an eluant and then the resulting solution was dried over $MgSO_4$, filtered through a short silica gel pad and finally evaporated to yield only the epoxide as residue by the distillation method as described above. The residue was then kept over P_2O_5 for 15 min and then weighed. The efficiency of this catalyst–co-catalyst combination extends to wide varieties of substrates, *viz.*, benzylic, carbocyclic, aromatic and aliphatic systems which include functionalised as well as non-functionalised olefins. Speed of reaction, yield, and turnover frequency (TOF) follow the substrate order carbocyclic > aromatic > aliphatic. Moreover, in the cases of aliphatic open chain olefins, the functionalised olefins are easier to epoxidise than the non-functionalised analogs. 1-Octene is most difficult to epoxidise and next difficult substrate is styrene. The reactivity trend obtained by us is similar to what other authors obtained, but in our case the reactions occur at much faster rates, excepting 1-octene.

The enormous efficiency of our molybdenum catalyst in epoxidation reactions on the background of the failure of Thiel's catalyst, which is structurally not much different from that of ours, in H_2O_2 medium, possibly stems from our use of the $NaHCO_3$ co-catalyst. The generated monoperoxycarbonate HCO_4^- (by reaction with H_2O_2), which is capable of forcing highly facile reaction with oxodiperoxomolybdate(VI) on the one hand and the olefins on the other, helps not only the speedy and efficient production of the epoxides, but also to stabilize the same (100% selectivity). This hypothesis can be tested by using Thiel's catalyst with $NaHCO_3$ as an additive. Other minor differences that exist between the two catalyst structures should not induce such a difference in their properties. Notwithstanding this, some features in the structure of the present catalyst, especially, the presence of H-bonding centers in both the anion and cation (see the structure description) make the catalyst quite conducive to affording activated species incorporating both H_2O_2 and HCO_4^-. However, in such a complex system, it is very difficult to propose a plausible mechanism of the epoxidation reaction involved. That the reaction proceeds *via* a non-radical pathway has been concluded from the insensitivity of the reaction towards azoisobutyronitrile (AIBN) and benzoquinone. Also, when the contents of the reaction flask are irradiated with the help of a projected tungsten lamp the speed of the catalytic reaction remains the same.

We acknowledge CSIR, New Delhi for financial assistance under the project [01 (1818)/ 02/ EMR-II] and DST, Govt. of India, for financing the purchase of the Agilent 6890N gas chromatograph. We thank Prof. P. Bharadwaj of IIT Kanpur for single crystal XRD data. S. C. thanks UGC for a fellowship.

Notes and references

1 A. S. Rao, in *Comprehensive organic synthesis*, ed. B. M. Trost, I. Fleming, S. V. Ley, Pergamon, Oxford, 1991, **vol. 7**, p. 357.

2 (*a*) H. B. Bode, B. Wegner and A. Zeek, *J. Antibiot.*, 2000, **53**, 153–157; (*b*) S. P. de Visser and S. Shaik, *J. Am. Chem. Soc.*, 2003, **125**, 7413–7424; (*c*) S. L. H. Rebelo, M. M. Q. Simões, M. Graca, P. M. S. Neves, A. M. S. Silva and J. A. S. Cavaleiro, *Chem. Commun.*, 2004, **5**, 608–609.

3 W. Adam, *Peroxide chemistry – Mechanistic and preparative aspects of oxygen transfer*, Wiley–VCH, Weinheim, FRG, 2000.

4 B. S. Lane and K. Burgess, *Chem. Rev.*, 2003, **103**, 2457–2473 and references cited therein.

5 For examples of catalytic systems for olefin epoxidation using aqueous H_2O_2 see: Methyltrioxorhenium: (*a*) J. Rudolph, K. L. Reddy, J. P. Chiang and K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189–6190; (*b*) W. A. Herrmann, R. W. Fischer and D. W. Marz, *Angew. Chem., Int. Ed.*, 1991, **30**, 1638–1641; Tungsten complexes including heteropolyoxo tungstates; (*c*) X. Zuwei, Z. Ning, S. Yu and L. Kunlan, *Science*, 2001, **292**, 1139–1141; (*d*) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J. Org. Chem.*, 1996, **61**, 8310–8311; (*e*) C. Venturello, E. Alneri and M. Ricci, *J. Org. Chem.*, 1983, **48**, 3831–3833; (*f*) C. Venturello, R. D. Aloisio, J. C. Bart and M. Ricci, *J. Mol. Catal.*, 1985, **32**, 107–110; Mn complexes; (*g*) A. Berkessel and C. A. Sklorz, *Tetrahedron Lett.*, 1999, **40**, 7965–7968; (*h*) D. De Vos and T. Bein, *Chem. Commun.*, 1996, **8**, 917–918; (*i*) See ref. 4; (*j*) J. Brinksma, L. Schmieder, G. Van Vliet, R. Boaron, R. Hage, D. E. De Vos, P. L. Alsters and B. L. Feringa, *Tetrahedron Lett.*, 2002, **43**, 2619–2622; Fe complexes; (*k*) M. C. White, A. G. Doyle and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 7194–7195; (*l*) Mo complex $[MoO(O_2)_2L]$ (L = $OAsnDodec_3$), see p. 354 of ref. 3; (*m*) $[MoO(O_2)_2L]$ (L = HMPA (hexamethyl phosphoric amide), DMF, py, Ph_3PO, *etc.*) are stoichiometric epoxidation agents while 7-coordinate complexes $[Mo(O_2)_2(L)_2]$, function as epoxidation catalysts in the presence of H_2O_2 and *tert*-BuOOH, see, for instance: H. Mimoun, I. Seree de Roch and L. Sajus, *Tetrahedron*, 1970, **26**, 37–50.

6 H. Adolfsson, A. Converso and K. B. Sharpless, *Tetrahedron Lett.*, 1999, **40**, 3991–3994.

7 (*a*) W. R. Thiel and J. Eppinger, *Chem. Eur. J.*, 1997, **3**, 696–705; (*b*) A. Hroch, G. Gemmecker and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2000, **5**, 1107–1114.

8 (*a*) R. Bandyopadhyay, S. Biswas, S. Guha, A. K. Mukherjee and R. Bhattacharyya, *Chem. Commun.*, 1999, **17**, 1627–1628; (*b*) S. K. Maiti, K. M. A. Malik and R. Bhattacharyya, *Inorg. Chem. Commun.*, 2004, **7**, 823–828; (*c*) T. K. Si, K. Chowdhury, M. Mukherjee, D. C. Bera and R. Bhattacharyya, *J. Mol. Catal. A: Chem.*, 2004, **219**, 241–247.

9 **1** was synthesized by adding methanol solution of salicylaldoxime ($SaloxH_2$) to a solution of MoO_3 in 30% H_2O_2 in a 1 : 1 molar ratio to get an orange red solution, which on treatment with PPh_4Cl afforded $PPh_4[MoO(O_2)_2(SaloxH)]$, yield 90%. X-ray quality, diffractable orange yellow crystals were obtained by slow crystallization from a dichloromethane hexane (2 : 1) solvent mixture. IR: (KBr) ν (cm^{-1}) 955 (Mo=O), 915 and 855(O–O), 1610 (C=N), 3450 {broad} (OH). Electronic spectrum, λ (nm): SaloxH → Mo4dπ, LMCT 321 (ε = 3590), 268 (8927), 261 (8770); for the ligand: 303 (4710), 258 (14160). ^1H NMR: δ (ppm), 9.908 (0.43 H, H6 indicating that this H is attached to O6 and intramolecularly strongly H-bonded with O3, O6···O3 = 2.7849(0.002) Å), 8.840 (1H, H7 attached to C7). The aromatic proton signal of the phenyl group of the sal moiety and those for the PPh_4 groups are intermixed and 22 signals appear in the aromatic region.

10 Crystyal data: $C_{31}H_{26}O_7NPMo$, $M = 651.44$, triclinic, space group $P\bar{1}$ orange yellow plate crystal (0.30 mm × 0.25 mm × 0.15 mm), $a = 9.637(1)$, $b = 10.675(1)$, $c = 13.335(1)$ Å, $\alpha = 97.33(1)$, $\beta = 90.02(1)$, $\gamma = 91.08(1)^\circ$, $V = 1362.4(2)$ Å^3, $Z = 2$, $D_c = 1.588$ g cm^3, $\mu = 0.592$ mm^{-1}, 293 K. 9137 reflections measured, 6470 independent. Bruker SMART CCD area-detector diffractometer, Mo Kα ($\lambda = 0.71073$ Å), ω–2θ scans, $2\theta_{max} = 56.6^\circ$. An empirical absorption correction based on ψ scan and a Lorentz–polarization correction were applied to the data. The crystal structure was solved with SHELXS 97, a full-matrix least-squares refinement using SHELXL 97 converged to $R(F) = 0.0312$ for 6136 reflections with $I > 2\sigma(I)$. Hydrogen atoms were placed geometrically and were treated as riding, with C–H (0.93 Å), O–H (0.82 Å) distances and $U_{iso}(H) = 1.2\ U_{eq}$ of the atoms to which they were attached. CCDC 241874. See http://www.rsc.org/suppdata/cc/b4/b408946d/ for crystallographic data in .cif or other electronic format. See also: G. M. Sheldrick, SHELXT 97, *Program for Crystal Structure Solution and Refinement*, University of Göttingen, Germany, 1997.

11 The bicarbonate co-catalyst when used alone can also cause epoxidation. It has been shown that bicarbonate and hydrogen peroxide react to produce peroxy monocarbonate, HCO_4^-. Our experience is that the monocarbonate causes epoxidation mainly stoichiometrically. For details, see the footnotes of Table 1. See also: (*a*) D. E. Richardson, H. Yao, K. M. Frank and D. A. Bannett, *J. Am. Chem. Soc.*, 2000, **122**, 1729–1739; (*b*) B. S. Lane, M. Vogt, V. J. DeRose and K. Burgess, *J. Am. Chem. Soc.*, 2002, **124**, 11946–11954.

12 Molybdenum catalyst systems of Thiel *et al.*[7] have their structural arrangement grossly similar to that of ours. One of the Thiel catalysts, [2-(4-nitro-1-octyl-3-pyrazolyl) pyridineoxodiperoxomolybdenum(VI)] activates alkyl hydroperoxide (but not H_2O_2) and under this condition it shows a TOF = 6470 h^{-1} in the case of epoxidation of cyclooctene (only this substrate has been studied by those authors). Hydroperoxides are much costlier than H_2O_2 and appropriate alcohols, as against H_2O when H_2O_2 is used, are given off in the process. Again, the TOF calculated for the conversion of cyclooctene to its epoxide using H_2O_2 with the most efficient (so far known) Mo-based catalyst, *viz.* $[Mo(O_2)_2L(H_2O)]$ (L = tri-n-dodecyl arsane oxide) under phase transfer conditions is 100 h^{-1} as against 11 880 h^{-1} obtained by us with our catalyst. The vast difference in catalyst efficiency is obvious, considering both alkyl hydroperoxide used by Thiel and H_2O_2 used by other authors, as oxidant.

13 S. Banfi, F. Legramandi, P. Montanari, G. Possi and S. Quici, *Chem. Commun.*, 1991, **18**, 1285–1287.

14 Besides the Mn^{III}-porphyrin work which shows a TOF of 20 000 h^{-1} with cyclooctene as substrate, all other work, to the best of our knowledge, shows much lower TOF than what we have obtained with **1**. The next best TOFs are: (i) Mo: see notes and ref. 12; (ii) W: purely homogenous, TOF = 100 h^{-1}, see ref. 3 p. 355; in polymethacrylate grafted phosphotriamide supported peroxotungstate (VI) complexes the TOF = 1000 h^{-1}, see for instance: G. Grigoropoulou, J. H. Clark and J. A. Elings, *Green Chem.*, 2003, **5**, 1–7; (iii) Re (MTO): TOF = 38 h^{-1} (for styrene); highest TOF for any substrate (here 1-phenyl cyclohexene) = 190 h^{-1}.

15 C. Djordjevic, N. Vuletic, B. A. Jacobs, M. Lee–Renslo and E. Sinn, *Inorg. Chem.*, 1997, **36**, 1798–1805.