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Unmatched efficiency and selectivity in the epoxidation of olefins with oxo-diperoxomolybdenum(VI) complexes as catalysts and hydrogen peroxide as terminal oxidant

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ABSTRACT

A great variety of olefinic substrates having aromatic, carbocyclic and aliphatic olefins are effectively and selectively oxidized with oxygen-rich molybdenum(VI) complexes, namely $[MoO(O_2)_2 \cdot 2QOH]$ **1**, $[MoO(O_2)(QO)_2]$ **2**, $[Mo(O)_2(QO)_2]$ **3**, $[PPh_4][MoO(O_2)_2(QO)]$ **4**, $[PPh_4][Mo(O)_2(O_2)(QO)]$ **5** and $[PPh_4][Mo(O)_3(QO)]$ **6** (QOH = 8-quinolinol) as catalyst, $NaHCO_3$ as co-catalyst and H_2O_2 as the terminal oxidant, at room temperature. Catalysts **1** and **4** show unmatched yield, turnover number (TON) and turnover frequency (TOF), and hence shortest reaction time.

Epoxidation of olefins and arenes is an important transformation in organic synthesis since the epoxy compounds are widely used as such or for manufacturing a wide variety of high demand commodity chemicals like polyurethanes, unsaturated resins, glycols, surfactants, paints and many other important products.[1] Transition metal complexes have a dominant role as catalysts, which dramatically enhance the reaction yield, selectivity and rate of epoxidation.[2–5] Diverse types of transition metal complexes containing Mo,[6,7] W,[8,9] Mn,[10,11] Fe[12,13] and Re[14–16] have been used as olefin epoxidation catalysts, which only exhibit a moderate efficiency. However, we have recently reported[17–20] a highly efficient epoxidation method of olefinic compounds with excellent yields and turnover frequencies (TOF = TON h^{-1}, and TON = ratio of moles of product obtained to the moles of catalyst used) using oxo-peroxo molybdenum and tungsten catalysts with H_2O_2 as a terminal oxidant. The latter is the best oxidant (after O_2) with respect to environmental (including global heating) and economic considerations. Indeed in certain circumstances H_2O_2 is better than dioxygen since organic compounds when refluxed under dioxygen sometimes spontaneously ignite.[21] Diperoxo complexes of d^0 transition metals are generally believed to be more reactive than the corresponding monoperoxo complexes, though examples exist where the reverse is also true.[22,23] The effect of the chelating ligand in the transition metal complexes is also important.[24] We recently noted that the efficiency of epoxidation furnished by oxo-peroxo molybdenum complexes with secondary hydroxamic acids as chelating ligands was by far the best.[19] Since QOH (8-quinolinol) has also been noted by us[18] as an efficient chelator for the oxygen-rich molybdenum(VI) moieties and moreover as a ligand of more compact character than the hydroxamic acids, we thought that these might give better dividends as catalysts for epoxide synthesis. Thus, in the present Letter we report the catalytic efficiency of 8-quinolinolato oxo-peroxo molybdenum(VI) complexes **1**–**6** (the synthesis and spectroscopic characterization of all the complexes are given as Supplementary data) for olefin epoxidation. Besides the gas chromatographic identification of the products, we also include further characterization of the isolated epoxides by ^1H and ^{13}C NMR as well as by electrospray mass spectrometry in some cases. It is apparent from the text and tables that the present method using the abovementioned catalysts in tandem with $NaHCO_3$ as co-catalyst and H_2O_2 as terminal oxidant displays matchless efficiency (yield %, TON and TOF) in the olefin epoxidation. It should be mentioned that a recent report[25] using Mimoun-type oxodiperoxo molybdenum complexes as catalyst, afforded olefin epoxidation with an extremely slow rate and very low turnovers (calculated by us from the published experimental data) using H_2O_2 or TBHP as oxidant.

An acetonitrile (10 cm^3) solution containing a given substrate (ca. 10–15 mmol), $NaHCO_3$ (2.5 mmol), molybdenum catalyst (0.01–0.001 mmol) and 30% H_2O_2 (50–60 mmol) in a flat-bottomed two-neck reaction flask, with one neck fitted with a reflux condenser (to check evaporation) and the other neck closed with a septum, was stirred at room temperature (25 °C) for the period

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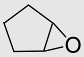
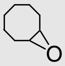
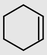
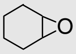
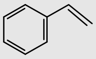
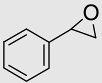
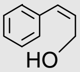
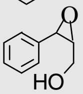
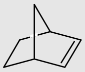
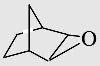
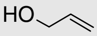
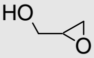
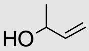
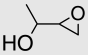
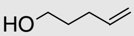
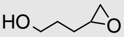
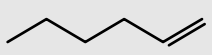
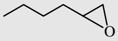
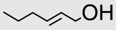
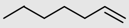
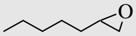
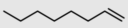
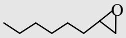
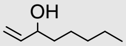
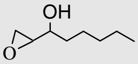
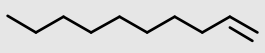
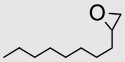
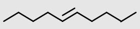
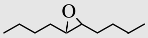
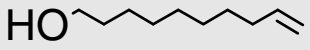
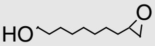
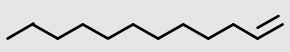
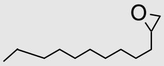
Table 1

Details of olefin epoxidation using catalyst **4**, $NaHCO_3$ (25 mol %), H_2O_2 (3–5 equiv) and CH_3CN as solvent at rt

Entry	Substrate	Product	Time (h)	% Conversion	% Yield[a]		% Yield[c]	TON[d]	TOF[e]
					GC[b]	Iso			
1			0.17	99	99	–	25	14,825	89,100[f]
2			0.33	80	80	73	35	8000	24,000[f]
3			0.75	93	93	81	22	4650	6200[f]
4			1.00	99	99	–	20	3960	3960
5			0.75	80	80	–	25	1600	2133[f]
6			0.17	98	98	–	21	9800	58,800[f]
7			1.50	84	84	–	58	4200	2800
8			1.25	85	85	–	35	4250	3400
9			2.00	92	92	78	40	4600	2300
10			1.25	94	94	–	35	4700	3700
11			0.33	92	92	78	52	4600	13,800[f]
12			0.83	98	98	–	30	4900	5904[f]
13			1.25	94	94	83	24	4700	3760
14			0.75	86	86	73	20	4300	5733[f]
15			1.50	93	93	79	18	1860	1240
16			1.50	98	98	–	20	1960	1306
17			1.42	95	95	81	23	1900	1338
18			2.50	94	94	85	15	940	376

[a] A control experiment (omission of **1** as well as HCO_3^-) did not show any conversion to epoxide or other probable products.

[b] The detailed calculation of GC yield is given in the supplementary data.

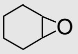
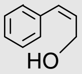
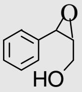
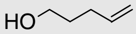
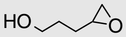
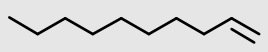
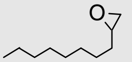
[c] This is the yield of control experiment, excluding the catalyst **1** only, but not $NaHCO_3$ which remains in the reaction solution at the same 25 mol % concentration. When the control experiment uses $NaHCO_3$ at a catalytic concentration the conversion and yield % become negligible.

[d] TON = ratio of moles of product (here epoxide) obtained to the moles of catalyst used.

[e] The corresponding TOFs (TON h^{-1}) are shown in the parentheses.

[f] Values extrapolated. The mole ratio of catalyst:substrate = 1:15,000 (for entry 1), 10,000 (for entries 2 and 6), 5000 (for entries 3 and 7–14), 4000 (for entry 4), 2000 (for entries 5, 15, 16 and 17), 1000 (for entry 17). For entries 15, 16, 17 and 18, acetonitrile and acetone solvent mixtures were used in 2:1 volume ratio. Values for ^1H and ^{13}C NMR of the isolated epoxides are given below. (a) 1,2-Epoxycyclooctane: ^1H NMR ($CDCl_3$): δ 1.25–1.29 (m, 2H), 1.43–1.68 (m, 8H), 2.12–2.17 (m, 2H), 2.87–2.93 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 25.6, 26.3, 26.6, 55.7. (b) 1,2-Epoxycyclohexane: ^1H NMR ($CDCl_3$) δ 0.89–1.05 (m, 4H), 1.45–1.58 (m, 4H), 3.1 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.4, 24.4, 52.1. (c) 4,5-Epoxypentan-1-ol: ^1H NMR ($CDCl_3$): δ 1.25–1.41 (m, 4H), 2.35 (dd, $J_1 = 2.77$, $J_2 = 2.78$ Hz, 2H), 2.62 (dd, $J_1 = 4.12$, $J_2 = 4.85$ Hz, 1H), 3.51 (br s, 1H), 4.01 (t, $J = 5.67$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 27.8, 31.8, 46.8, 52.3, 57.7. (d) 2,3-Epoxyhexan-1-ol: ^1H NMR ($CDCl_3$): δ 0.73 (t, $J = 7.3$ Hz, 3H), 1.19–1.26 (m, 4H), 2.62–2.66 (m, 2H), 3.83 (d, $J = 4.71$ Hz, 2H), 4.07 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 13.2, 25.2, 32.2, 57.4, 59.1, 62.6. (e) 1,2-Epoxyoctane: ^1H NMR ($CDCl_3$): δ 0.81 (t, $J = 6.5$ Hz, 3H), 1.17–1.55 (m, 10H), 2.45 (dd, $J_1 = 1.43$, $J_2 = 1.59$ Hz, 1H), 2.73 (dd, $J_1 = 2.96$, $J_2 = 3.49$ Hz, 1H), 2.91 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 13.9, 22.5, 25.8, 29.0, 31.7, 32.4, 47.1, 52.1. (f) 1,2-Epoxyoctan-3-ol: ^1H NMR ($CDCl_3$): δ 0.77 (t, $J = 6.8$ Hz, 3H), 1.15–1.41 (m, 8H), 1.85 (m, 1H), 2.57 (dd, $J_1 = 1.87$, $J_2 = 2.15$ Hz, 1H), 2.61 (dd, $J_1 = 2.29$, $J_2 = 2.66$ Hz, 1H), 2.89 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 13.6, 22.3, 24.8, 27.8, 31.8, 46.7, 52.1, 72.6. (g) 1,2-Epoxydecane: ^1H NMR ($CDCl_3$): δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.28–1.53 (m, 14H), 2.15 (dd, $J_1 = 1.5$ Hz, 1H), 2.73 (dd, $J_1 = 4.9$, $J_2 = 5.7$ Hz, 1H), 2.88–2.89 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 31.9, 32.6, 47.0, 52.4. (h) 9,10-Epoxydecan-1-ol: ^1H NMR ($CDCl_3$): δ 1.14–1.37 (m, 14H), 1.91 (m, 1H), 2.55 (dd, $J_1 = 4.04$, $J_2 = 4.84$ Hz, 1H), 2.73 (dd, $J_1 = 2.73$, $J_2 = 3.89$ Hz, 1H), 3.36 (t, $J = 6.74$ Hz, 2H), 3.80 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 22.3, 25.6, 28.7, 29.1, 31.5, 32.3, 33.4, 46.5, 51.9, 61.9. (i) 1,2-Epoxydodecane: ^1H NMR ($CDCl_3$): δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.26–1.56 (m, 18H), 2.44 (dd, $J_1 = 2.70$, $J_2 = 2.73$ Hz, 2H), 2.73 (dd, $J_1 = 4.23$, $J_2 = 4.83$ Hz, 1H), 2.86–2.92 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1. 22.7, 26.1, 29.4, 29.5, 29.6 (double intensity), 29.7, 31.9, 32.6, 47.1, 52.4, 58.2. NMR spectra of the products corresponding to entries 4, 5 and 12 are superimposable with the literature data. Electrospray mass spectra: (a) 1,2-Epoxydecane: ES MS *m/z* (rel. int.%): 197.21 $[M+CH_3CN]^+$ (47), 156.15 $[M]^+$ (9), 128.12 $[C_8H_{16}O]^+$ (100). (b) 9,10-Epoxydecan-1-ol: ES MS *m/z* (rel. int.%): 213.21 $[M+CH_3CN]^+$ (64), 195.07 $[M+Na]^+$ (100), 172.15 $[M]^+$ (13).

Table 2
Comparative catalytic activities of the peroxo complexes **1**, **2**, **4** and **5**, maintaining the parameters same as in Table 1

Entry	Substrate	Product	Time (h)	% Yield				TON			
				1	**2**	**4**	**5**	**1**	**2**	**4**	**5**
1			0.75	95	76	93	71	4750	3800	4650	3550
2			0.75	83	64	80	59	1660	1280	1600	1180
3			2.00	96	79	92	72	4800	3950	4600	3600
4			1.50	97	75	93	69	1940	1500	1860	1380

quoted in Table 1. Aliquots of the reaction solution were withdrawn, and H_2O_2 was added with the help of a syringe through the septum. In a typical operation, 0.5 cm^3 solution was pipetted out with the help of a micro-pipette and the solution was subjected to multiple ether extractions and the extract was concentrated, from which a 1 μl 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 isolated yield of the epoxide was obtained by shaking the reaction mixture with CH_2Cl_2 (at least 4–5 times) and the extracted organic layers were combined and dried by standing the CH_2Cl_2 extract for 24 h in a $MgSO_4$ desiccator. Insoluble residues (if any) were filtered off, and the filtrate was concentrated carefully by rotary evaporation using a room temperature bath. Then the separated crude product was purified by column chromatography through a short silica gel pad, and finally evaporated to yield the product. The residue was then kept over P_2O_5 for 15 min and then weighed.

GC yields of the product for all the epoxidation reactions conducted are given in Table 1. The method of calculation of GC yield is given as supplementary information.

The compactness of the bidentate organic ligand QOH has a definite role in the efficiency of epoxidation, since other bidentate N, O donor ligands like $SaloxH_2$ (salicylaldoxime)[17] and N,N donors like pyrazolyl pyridine derivatives[26,27] forming similar Mo(VI) complexes exhibit much less catalytic efficiency than that of the presently employed QOH ligand. Besides compactness, the enhancement of catalytic potentiality of QOH ligand lies on the fact that the ring nitrogen in the coordinated QO^- can act as electron source or sink depending on the requirement of the catalytic reactions.[6] The results obtained using a wide variety of substrates, from the highly reactive (to show that TOF may be as high as 89,100 h^{-1}) to much less reactive olefins including functionalized olefins (see Table 1), clearly indicate the superiority of the present method. A comparative catalytic efficiency in olefin epoxidation of all the peroxo complexes synthesized in this work (**1**, **2**, **4** and **5**) is shown in Table 2. We conducted a stoichiometric epoxidation work with the molybdenum complexes **1** and **4** as reagents and found that in all probability (C, H, N analysis and IR evidence) the reagents are themselves converted into $[Mo(O)_2(QO)_2]$ **3** and $[Mo(O)_3(QO)]^-$ **6** (comparable with $[Re(O)_3(CH_3)]$[28]), respectively. In the catalysis cases, addition of H_2O_2 speedily converts HCO_3^- to a more reactive nucleophile, HCO_4^- (permonocarbonate),[29,30] than H_2O_2. The catalyst **4** can be used for at least 3 batches (Fig. 1) of olefin epoxidation with steadily decreasing efficiency. It may be mentioned here that the non-peroxo complexes **3** and **6** require excess of H_2O_2 to exhibit only a moderate efficiency in epoxidation.

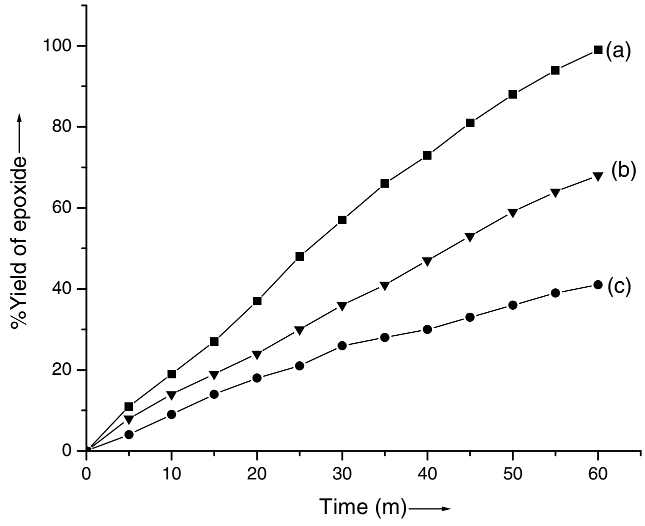


Figure 1. Reaction profile (yield of epoxide vs time) for the homogeneous epoxidation of styrene using catalyst **4**; (a) batch 1, (b) batch 2 and (c) batch 3.

The efficiency of the catalyst–co-catalyst combination extends to wide varieties of substrates, viz., benzylic, carbocyclic, aromatic and aliphatic systems, which include functionalized as well as non-functionalized olefins. Speed of reaction, yield % and TOF follow the substrate order carbocyclic > benzylic > lower alkenes > higher alkenes. Moreover, in the cases of aliphatic open-chain olefins, the functionalized olefins are easier to epoxidize than the non-functionalized analogues. When the contents of the reaction flask were irradiated with tungsten lamp, the speed of the catalytic reaction remained the same. This observation favours a non-radical pathway for the epoxidation reaction. This was also confirmed by using AIBN (azoisobutyronitrile) and benzoquinone in the reaction mixture.

We believe that the homogeneous epoxidation described here is the best method known so far: very simple reaction accessories, operation at room temperature, high yield, very fast conversion, high TON, high TOF, very low catalyst loading, environmental benignity including the absence of global warming effect and cost-effectiveness.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.08.028.

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