Highly facile homogeneous epoxidation of olefins using oxo-diperoxo tungstate(VI) complex as catalyst, bicarbonate as co-catalyst and hydrogen peroxide as a terminal oxidant†

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Addition of a dilute acetic acid solution of 8-quinolinol to an H_2O_2 solution of freshly precipitated $H_2WO_4 \cdot 2H_2O$ furnishes a yellow adduct $[WO(O_2)_2 \cdot 2QOH]$ **1** which, on crystallization from a suitable solvent, affords orange-yellow complex $[WO(O_2)(QO)_2]$ **2**. When **2** reacts stoichiometrically with olefinic compounds in a 1 : 1 molar ratio, the respective olefins are epoxidized and **2** is converted to the orange-red $[WO_2(QO)_2]$ **3**. When **1** is treated with an excess of H_2O_2 (greater than 6 equiv.) and PPh_4Cl, an anionic light yellow complex $PPh_4[WO(O_2)_2(QO)]$ **4** is obtained. **4** reacts with cyclopentene (a representative olefin) in a 1 : 1 molar ratio producing cyclopentene oxide and itself is converted to $PPh_4[WO_2(O_2)(QO)]$ **5**. If the above reaction is conducted at a 1 : 2 molar ratio (instead of 1 : 1) then 2 moles of the corresponding epoxide is formed and **4** is converted to $PPh_4[WO_3(QO)]$ **6**. All these peroxo complexes have remarkable catalytic efficiencies in the epoxidation of olefinic compounds when used *in tandem with* $NaHCO_3$ *as co-catalyst and* H_2O_2 *as oxidant in a* CH_3CN *medium at room temperature*, the method being green and economical. The catalyst **4** *under the above experimental conditions* shows so far unmatched efficiency in epoxidizing a wide variety of olefinic substrates.

Introduction

Epoxidation of terminal as well as electron deficient olefinic compounds still remains a challenging problem in organic synthesis. Suitable transition metal compounds as catalysts are shown to dramatically enhance the speed and selectivity of epoxidation.[1] In this context H_2O_2 is probably the best ecologically sustainable "green" terminal oxidant[2] after dioxygen. Indeed, in certain circumstances it is better than dioxygen insofar as O_2–organic mixtures sometimes spontaneously ignite.[3] The inaugural report of Na_2WO_4 catalyzed epoxidation of olefins with H_2O_2 as oxidant was made by Payne and Williams.[4] Venturello and co-workers[5] used their catalysts, *viz*., $(R_4N)_3[PO_4\{W(O)(O_2)_2\}_4]$ for olefin epoxidation with H_2O_2 economy in biphasic systems often involving chlorinated solvents. The efficiency of the system was not very high but higher than the corresponding Mo-catalyst, which gave lower turnovers and selectivities.[6] BASF patents[7] using Noyori-type[8] diperoxo–tungsten and –molybdenum complexes further encouraged the studies on the Mo and W catalysts in the area of olefin epoxidation. Mimoun and co-workers[9] reported that a ternary system consisting of Na_2WO_4, amino methyl phosphoric acid and *n*-octylammonium hydrogen sulfate in the presence of H_2O_2 in a solvent-free medium behaved as a very efficient catalyst for alkene epoxidation including that of 1-dodecene. Kamata *et al.*[10] recently reported a silicotungstate compound $(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)]$ as catalyst with H_2O_2 as oxidant in a CH_3CN medium and claimed that their catalyst showed the highest efficiency among the known epoxidation catalysts.[10] Homogeneous molybdenum catalyzed epoxidations all generally used alkyl hydroperoxide since many catalysts reportedly failed to activate H_2O_2.[11] In spite of the high cost component of the ARCO-Halcon process in using TBHP (*tert*-butyl hydroperoxide) oxidant,[12] the process is still in use in industries. Besides the cost factor, since alkyl hydroperoxides are traditionally obtained by the reaction of H_2O_2 and aliphatic acids or acid derivatives, the epoxidation reaction in hydroperoxide cases generates a significant amount of waste and co-products.[13]

With this background we recently reported an olefin epoxidation method using an Mo-based catalyst, namely $PPh_4[MoO(O_2)_2(SaloxH)]$ (**A**)[14] with H_2O_2 as oxidant and $NaHCO_3$ as additive and claimed an uncommon efficiency in this area of activity. However, despite the immense success, our method was not very effective in the case of 1-octene and marginally effective for higher alkenes like decene and dodecene. Subsequently we prepared a catalyst where W replaced Mo in **A** and the superior catalytic potentiality of the W-analogue of A prompted us to take up the present W-complex for this epoxidation work. Now we are very much delighted to report the most efficient epoxidation method so far with a W-based catalyst *viz*. $Ph_4P[WO(O_2)_2(QO)]$ (**4**, QOH = 8 quinolinol),[15] which, in tandem with $NaHCO_3$ and aqueous H_2O_2 in a CH_3CN medium, displays a most pronounced efficiency (% yield, TON, low catalyst loading, a better H_2O_2 economy, very fast conversion rate and high selectivity) in olefin epoxidation (see Table 1).

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Table 1 Details of the catalytic epoxidation of olefinic compounds Olefin $\xrightarrow[\text{3–4 equiv·H}_2\text{O}_2\text{, 25 mol\% NaHCO}_3\text{, rt (25 °C), CH}_3\text{CN}]{\text{0.1–0.0067 mol\%, PPh}_4[\text{WO(O}_2)_2(\text{QO})]\ \mathbf{4}}$ Epoxide

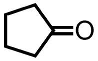
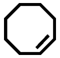
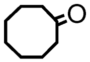
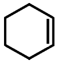
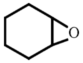
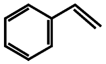
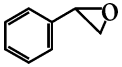
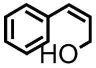
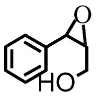
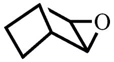
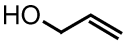
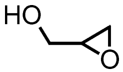
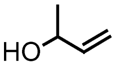
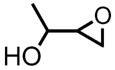
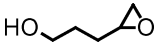
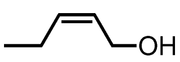
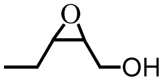
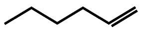
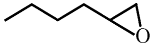
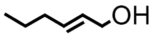
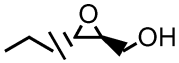
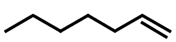
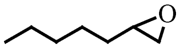
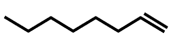
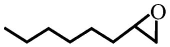
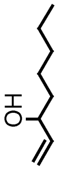
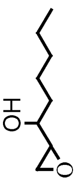
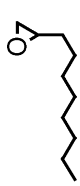
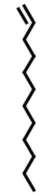
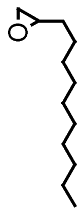
Entry	Substrate	Product	Time	% Conversion[a]	% Yield GC	% Yield Isolated	[c]Yield (%)	% Selectivity[d]	TON[e] (TOF)[f]
1			15 min	99	99	—	30	100	14 850 (59 400)[g]
2			30 min	80	80	74	38	100	8000 (16 000)[g]
3			50 min	91	91	—	22	100	4550 (5460)[g]
4			2 h	75	75	—	21	100	3750 (1875)
5			45 min	72	72	67	25	100	1440 (1920)[g]
6			10 min	93	93	88	21	100	9300 (55 800)[g]
7			2 h	81	81	—	61	100	4050 (2025)
8			2 h	90	90	—	45	100	4500 (2250)
9			1.25 h	99	99	—	35	100	4950 (4950)[g]
10			1 h	99	99	—	37	100	4950 (4950)
11			1.5 h	99	99	—	38	100	4950 (3000)
12			30 min	88	88	90	55	100	4900 (9800)[g]
13			1 h	99	99	—	53	100	4950 (4950)[g]
14			1.25 h	99	99	—	26	100	4950 (3960)

Table 1 (*continued*)

Entry	Substrate	Product	Time	% Conversion[a]	% Yield GC	% Yield Isolated	[c]Yield (%)	% Selectivity[d]	TON[e] (TOF[f])
15			1.5 h	92	92	—	40	100	4600 (3066)
16			1.5 h	98	98	—	24	100	1960 (1306)
17			1.25 h	92	92	83	25	100	1840 (1472)
18			1.75 h	97	97	88	17	100	970 (352)

[a] Control experiments (omission of **4** as well as HCO_3^-) do not show any conversion to epoxide or other probable products. [b] The detailed calculation of GC yield is given as supplementary material.† [c] This is the yield of the control experiment, excluding the catalyst **4** 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] Selectivity is really spectacular in the given time frame. If the stirring is continued for still longer periods, entries 5, 7, 8 and 9 start showing a peak due perhaps to the formation of diols. [e] TON = ratio of moles of product (here epoxide) obtained to the moles of catalyst used. [f] The corresponding TOFs (TON h^{-1}) are shown in the parenthesis. [g] Values extrapolated. The mole ratio of catalyst–substrate = 1 : 15 000 (for entry 1), 10 000 (for entries 2 and 6), 5000 (for entries 3–4 and 7–15), 2000 (for entries 5, 16, 17) and 1000 (for entry 18). For entries 16, 17 and 18, acetonitrile and acetone solvent mixtures were used in a 2 : 1 volume ratio.

Experimental

Materials

The compound $Na_2WO_4 \cdot 2H_2O$ was of an extra pure variety and obtained from Loba Chemie (India). Hydrogen peroxide (30%), hydrochloric acid, sodium bicarbonate, acetonitrile, dichloromethane, light petroleum (40–60), diethyl ether and acetone were of analytical grade and were obtained from E. Merck (India). Acetonitrile, dichloromethane, diethyl ether and acetone were further purified[16] before use. Cyclopentene, cyclohexene, cyclooctene, norbornene, 1-buten-3-ol, 4-penten-1-ol, *cis*-2-penten-1-ol, 1-hexene, 2-hexen-1-ol, 1-heptene, 1-octene, 1-octene-2-ol, 1-decene, *trans*-5-decene and 1-dodecene were the products of Sigma-Aldrich Chemie GmbH, Germany and were used directly. Styrene, cinnamyl alcohol and allyl alcohol were obtained from E. Merck (Germany). The epoxides of the corresponding olefins were the products of Aldrich, Germany. Ethanol (95%) was obtained from Bengal Chemical and Pharmaceutical works (Calcutta), and was lime-distilled before use. IOLAR II grade dioxygen, dihydrogen, zero air and dinitrogen gas used for chromatographic analysis were obtained from Indian Refrigeration Stores, Calcutta. Triply distilled (all glass) water was used whenever necessary. All the solvents used for chromatographic analysis were either of HPLC-, spectroscopic-, or GR-grade.

Physical measurements

The IR spectra were recorded using KBr pallets on a Perkin-Elmer 597 IR spectrophotometer (4000–200 cm^{-1}) and electronic spectra on a Hitachi U-3410 UV/Vis-NIR spectrophotometer. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker AM 360 (300 MHz) FT NMR spectrometer using TMS as an internal standard. A systronics (India) model 335 digital conductivity bridge with a bottle type cell was used to determine the molar conductance values of the isolated complexes at 25 °C using a thermostatic arrangement. A SUNVIC (UK) apparatus was used to measure the melting points of the organic substrates as well as their oxidized products. The magnetic susceptibilities were obtained by the Guoy method using $Hg[Co(NCS)_4]$ as a standard. Elemental analyses were performed with the help of a Perkin-Elmer 240C elemental analyzer and tungsten was estimated gravimetrically as WO_3.[17] HPTLC tests were performed in a CAMAG HPTLC system (Switzerland). GLC measurements were done in an Agilent model 6890 gas chromatograph using an HP-1 capillary column in FID mode with dinitrogen as the carrier gas.

Syntheses

$[WO(O_2)_2 \cdot 2QOH]$ 1. An aqueous solution (25 cm^3) of $Na_2WO_4 \cdot 2H_2O$ (1.98 g; 6.0 mmol) was acidified with 6 M HCl solution and a white precipitate of $H_2WO_4 \cdot 2H_2O$ 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% (w/v) H_2O_2 (10 cm^3) by stirring at room temperature (25 °C) to obtain a clear and colourless solution. Addition of 8-quinolinol (1.74 g; 12.0 mmol) dissolved in acetic acid (6 M; 10 cm^3) to the above solution with stirring (about 10 min) gave a yellow solid. It was filtered off, washed with water, 95% ethanol and finally with diethyl ether. The yield of **1** was 2.73 g (*ca.* 82%). The compound is moderately soluble in dichloromethane, acetonitrile and acetone but insoluble in ethanol, benzene and diethyl ether. Found, C, 38.62; H, 2.65; N, 5.12; W, 32.84. Calc. for $C_{18}H_{14}N_2O_7W$: C, 38.98; H, 2.52; N, 5.05 and W, 33.21%. IR (KBr disc; cm^{-1}): 1590 (w), 1570 (w), 1550 (w), 1490 [s; ν (C–N)], 1470 (m), 1360 (s), 1310 (m), 1260 (w), 1100 [s; ν (C–O)], 960 [s; ν (W =O)], 880, 820 [s; ν (O–O)], 760 (s), 635 (m), 580 (w), 520 (w), 510 (w). λ_{max}(nm): 400 (ε = 2760 M^{-1} cm^{-1}), 341 (4230).

[WO(O_2)(QO)] 2. **1** (1.39 g; 2.5 mmol) was dissolved in acetonitrile (20 cm^3) and was refluxed for 20–25 min. The solution was then cooled and diethyl ether was added to the cold solution until the mixed solvent became 2 : 1 (v/v) with respect to acetonitrile and diethyl ether, respectively. The solution, on standing for 15 h, afforded orange crystals. Yield 1.2 g (92%). The solubility of the compound parallels that of **1**. Found, C, 42.1; H, 2.4; N, 5.6; W, 35.2. Calc. for $C_{18}H_{12}N_2O_5W$: C, 41.5; H, 2.3: N, 5.4 and W, 35.4%. IR (KBr disc, cm^{-1}): 1590 (w), 1510 (s), 1470 (s), 1460 (sh), 1380 (s), 1330 (s), 1270 (m), 1240 (w), 1110 (s), 960 [s; ν (W=O)], 890 [m; ν (O–O)], 825 (m), 790 (w), 780 (sh), 755 (s), 630 (m), 530 (m), 500 (m). λ_{max}(nm): 367 (ε = 2870 M^{-1} cm^{-1}), 312 (4090).

[$WO_2(QO)_2$] 3. 0.52 g (1.0 mmol) of **2** and 0.068 g (1.0 mmol) of cyclopentene were dissolved in 10 ml acetonitrile in a 50 ml stoppered conical flask and the mixture was stirred for about 2 h to complete the stoichiometric reaction (checked by GC and the GC yield was found to be >99%). After the reaction was over, the acetonitrile was expelled from the reaction mixture by rotavapor. Diethyl ether was added to the remaining solid to dissolve the corresponding epoxide. The undissolved orange-red compound **3** was filtered off, washed with diethyl ether and then vacuum dried. The yield of **3** was 0.48 g (95%). Its solubility was the same as that of **2**. Found C, 43.05; H, 2.46; N, 5.60; W, 36.20. Calc. for $C_{18}H_{12}N_2O_4W$: C, 42.85; H, 2.38; N, 5.55; W, 36.48%. IR (KBr disc, cm^{-1}): 1580 (w), 1500 (m), 1480 (m), 1370 (s), 1310 (vs), 1250 (s), 1100 (vs), 940 [s; ν (W=O)], 900 [s; ν (W=O)], 825 (m), 790 (w), 740 (s), 640 (m), 530 (w). λ_{max}(nm): 385 (ε = 1460 M^{-1} cm^{-1}), 242 (3020).

[PPh_4][WO(O_2)$_2$QO] 4. The synthesis, characterization and crystal structure have previously been reported.[15]

[PPh_4][WO_2(O_2)(QO)] 5. 0.747 g (1.0 mmol) of **4** and 0.068 g (1.0 mmol) of cyclopentene, dissolved in 10 ml acetonitrile, were stirred for about 2 h following the same procedure as used for the preparation of **3**. The yield of [PPh_4][WO_2(O_2)(QO)] **5** was 0.70 g (96%). The solubility of the compound parallels that of **4**. Found, C, 54.24; H, 3.53; N, 1.92; W, 24.94. Calc. for $C_{33}H_{26}NO_5W$: C, 54.10; H, 3.50; N, 1.9; W, 25.13%. IR (KBr disc, cm^{-1}): 1636 (m), 1582 (m), 1499 (s), 1484 (m), 1470 (s), 1400 (s), 1320 (m), 1260 (m), 1160 (vs), 975 [s; ν (W=O)], 943 [m; ν (O–O)], 917 (w), 900 [s; ν (W=O)], 814 (vs), 751 (s), 722 (s), 690 (s), 645 (w), 586 (m), 526 (s), 445 (s). λ_{max}(nm): 365 (ε = 1000 M^{-1} cm^{-1}), 275 (3000), 251 (5700).

[PPh_4][WO_3(QO)] 6. **6** was prepared by taking 1.0 mmol of **4** and 2 mmol of cyclopentene and adopting the same procedure as for **3**. The yield of **6** was 0.68 g (95%). The solubility of the compound parallels that of **4**. Found, C, 55.52; H, 3.62; N, 1.96; W, 25.52. Calc. for $C_{33}H_{26}NO_4W$: C, 55.40; H, 3.60; N, 2.04; W, 25.69%. IR (KBr disc, cm^{-1}): 1575 (w), 1492 (s), 1462 (m), 1430 (m), 1365 (s), 1312 (s), 1250 (m), 1225 (w), 1160 (w), 1095 (vs), 968 (vs), 938 (m), 912 (m), 895 (s) [underlined vibrations, ν (W=O)], 805 (vs), 745 (s), 715 (s), 685 m), 640 (w). λ_{max}(nm): 365 (ε = 600 M^{-1} cm^{-1}), 276 (4860), 269 (5010).

Notably, the elemental analyses results of **5** and **6** are quite close. This is due to their very close and at the same time high molecular weight. However, their structural composition can be differentiated by qualitative as well as quantitative chemical analysis. **5** responds the starch iodide test in aqueous acetonitrile medium in the presence of H_3BO_3, where a blue-violet colour develops, but **6** does not respond to this test. Moreover, an acetonitrile solution of **5**, when acidified with 1.5 N H_2SO_4 and treated with 0.1 N $KMnO_4$, starts evolving O_2 gas. When gas evolution ceases, an excess of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ is added to the above solution and the unreacted Fe^{2+} determined by titration with 0.1 N $KMnO_4$ which gives[18] the % O_2^{2-} in **5**. Anal. calc. for $C_{33}H_{26}NO_5W$: 4.38%; found, 3.80%. Another convincing proof that **5** contains O_2^{2-} whereas **6** does not is found in the fact that the former can stoichiometrically epoxidize one mole of the olefinic compound (GC probe) whereas **6** cannot. These indicate that **5** contains one peroxo group but **6** does not.

Procedure of the epoxidation reaction

An acetonitrile (10 cm^3) solution containing a given substrate (*ca.* 10–15 mmol), $NaHCO_3$ (2.5–3.75 mmol), tungsten catalyst (0.01–0.001 mmol) and 30% H_2O_2 (30–40 mmol) 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 time period as quoted in the Table 1. As and when required an aliquot of the reaction solution was withdrawn from, or 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 extraction and the extract concentrated also up to 0.5 cm^3 from which 1 μl solution was withdrawn with the help of a syringe of 10 μl capacity 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. For a few cases, especially for olefinic alcohols, the identity of the product was confirmed by GC-MS analysis. The isolated yield in a few cases (Table 1) was obtained by multiple ether extraction 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), keeping over P_2O_5 in a desiccator and weighing (when the GC yield was 98–99%) in a micro-balance and the identity of the products was then confirmed by IR and NMR probing. For lower % yields the liquid (for solid epoxides obtained from liquid olefins, the former are simply

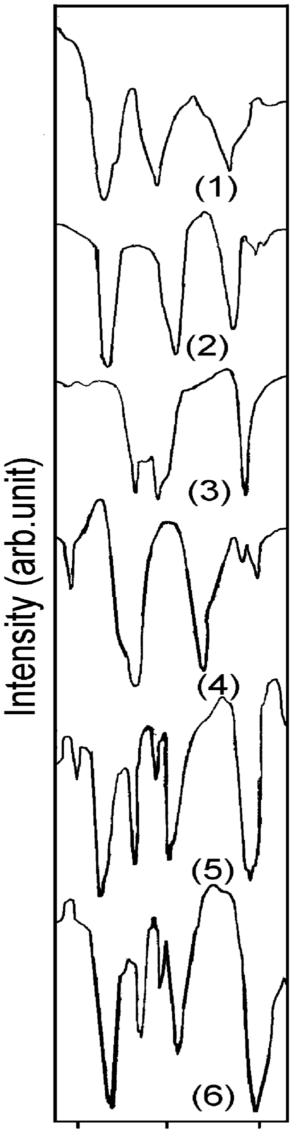


Fig. 1 Profile and positions of the IR spectra for the ν (W=O) and ν (O–O) bands for the complexes **1–6**.

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 minutes and then weighed.

Recovery of catalyst. The residue left after distilling ether and acetonitrile at mildly reduced pressure, was thoroughly shaken with diethyl ether repeatedly in which each of the substrates and the products were almost quantitatively extracted. The yellow solid residue left was the catalyst as verified by IR spectroscopy.

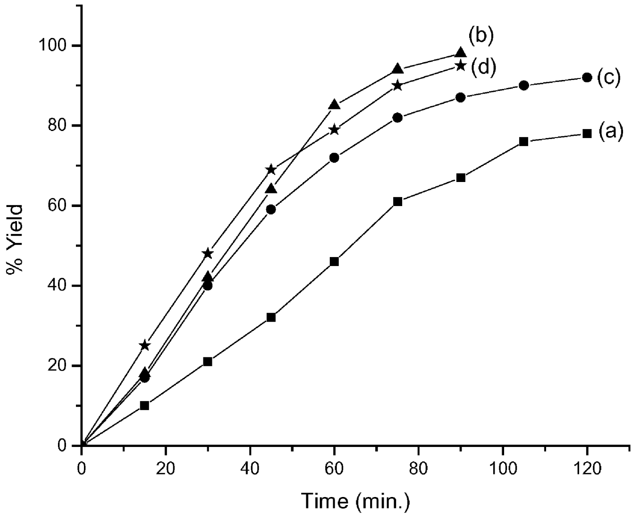


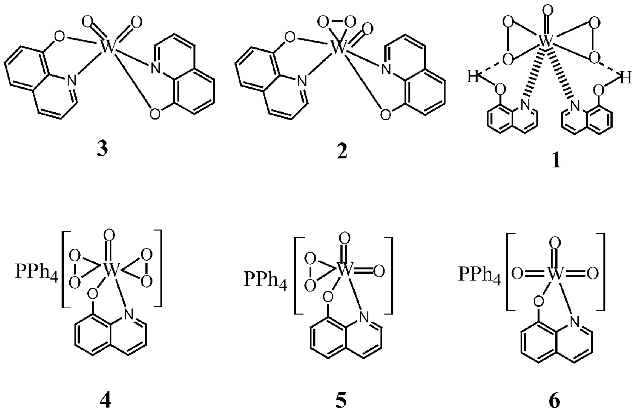
Fig. 2 Plot of % yield *versus* time using **4** as catalyst keeping all other parameters the same as in Table 1 for the oxidation of (a) styrene, (b) 1-hexene, (c) 3-butenol and (d) 1-decene.

Kinetic studies. In order to find out the initial rate of the epoxidation reaction, we carried out a few sets of catalytic experiments involving four substrates, *viz*. styrene, 1-hexene, 3-buten-1-ol and 1-decene. We injected a 1 μl ether extract of the reaction mixture through the GC port after every 15-min time interval, until the optimum GC yield was achieved. The % yield *vs*. time plot is shown in Fig. 2.

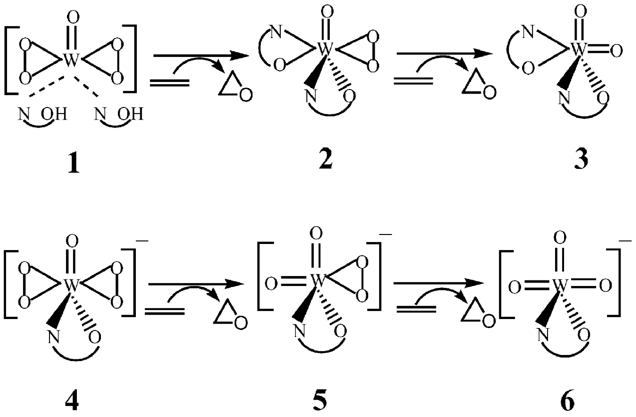
Results and discussion

Synthetic aspects

A solution obtained by dissolving freshly precipitated $H_2WO_4 \cdot 2H_2O$ in a moderate excess of H_2O_2 (4 equiv. wrt tungstic acid) reacts with 8-quinolinol in dilute acetic acid solution (4 M) furnishing a yellow adduct $[WO(O_2)_2 \cdot 2QOH]$ **1** (an analogue of the respective Mo-compound)[19] which on crystallization from acetonitrile affords an orange-yellow complex $[WO(O_2)(QO)_2]$ **2**. When **2** is allowed to react stoichiometrically with an olefin in a 1 : 1 ratio, an orange-red complex $[WO_2(QO)_2]$ **3** is formed. When **3** is treated with an excess of H_2O_2 (greater than 6 equiv.), an anionic light yellow complex $[WO(O_2)_2(QO)]^-$ is isolated as the PPh_4^+ salt **4**. **4** shows stoichiometric reaction with 1 : 1 and 1 : 2 molar ratios with respect to cyclopentene (a representative olefin) producing, besides the appropriate amount of epoxide, the complexes $PPh_4[WO_2(O_2)(QO)]$ **5** and $PPh_4[WO_3(QO)]$ **6**, respectively. Interconversion of **3** to **1** *via* **2** and that of **6** to **4** *via* **5** are reversible but such conversion of **1** to **4**, occurring only when excess H_2O_2 is added to the system, is irreversible. The facile conversion of **3** to **1** *via* **2** and **4** to **6** *via* **5** and the same from **3** to **6**, all depending on the concentration of H_2O_2 added, makes the oxo and oxoperoxo chemistry of tungsten highly interesting. This interesting chemistry is one of the main reasons why these complexes are such highly effective catalysts in epoxidation. The graphical representations of the formulae of the complexes are shown in Scheme 1.



Scheme 1 Chemical formulae of all the isolated and characterized complexes acting as catalysts.



Scheme 2 The pathway of stoichiometric reactions. N–O = 8-quinolinolate.

General characterization

While **1**, **2** and **3** are non-electrolytes in acetonitrile, **4** (Λ = 120 ohm^{-1} cm^2 mol^{-1}), **5** (Λ = 125 ohm^{-1} cm^2 mol^{-1}) and **6** (Λ = 128 ohm^{-1} cm^2 mol^{-1}) behave as 1 : 1 electrolytes[20] as expected from their molecular formulae.

In the electronic spectra of the complexes the highest wavelength bands (see experimental) for each of **1–6** can be assigned as the QO^- → W(VI) LMCT transition. The $\pi \rightarrow \pi^*$ transition of the uncoordinated QOH occurs at 308 nm but in the QO^- complexes the said band shifts to a larger wavelength region in the following cases: 341 for **1**, 342 for **2** and 336 for **4**. This energy decrease of the $\pi \rightarrow \pi^*$ transition in going from uncoordinated (QOH) to coordinated QO^- ligand is due to the drainage of electron density from the N and O donors resulting in the reduction of the aromatic character of the quinolinol moiety. This increases the ground state energy (energy of the bonding π MO) of the ligand causing the decrease in the energy of the $\pi \rightarrow \pi^*$ transition.

The ν (W=O) and ν (O–O) bands for the complexes are already assigned (see for instance the experimental section). The appearance of three ν (O–O) bands in **4** indicates that the two oxo-diperoxo core does not assume strictly a median plane with respect to the entire molecule. For the sake of comparison the ν (W=O) and ν (O–O) regions of the spectra of **1–6** are shown in Fig. 1. This figure clearly illustrates that the core structure assigned for each case has a sound basis. The ν (W–N) and ν (W–O) vibrations may be assigned as weak bands around 450 and 425 cm^{-1}, respectively in all the cases. A medium to strong intensity band in the 590 cm^{-1} region and another at 530 cm^{-1} in **1**, **2**, **4** and **5** are assignable to the asymmetric and symmetric vibrations of the WO_2 triangle, respectively.[21] In the case of complexes **4–6**, the symmetric vibration is engulfed within the very strong Ph_4P^+ vibration in that region. Other major vibrations originating from the coordinated QO^- ligands are positionally modified with respect to uncoordinated QOH, as is expected for an uncoordinated bidentate quinolinolate ligand.[22]

Reactivity

Stoichiometric reactivity. As described under the heading *Synthetic aspects*, the stoichiometric reactivity of the oxoperoxo tungsten(VI) complexes can be shown by eqn (1)–(4). The mechanistic pathway for overall stoichiometric reactions is shown in Scheme 2.

$$\{WO(O_2)_2 \cdot 2QOH\}\ \mathbf{1} + RCH{=}CHR' \rightarrow [WO(O_2)(QO)_2]\ \mathbf{2} + H_2O + RCH(O)CHR' \quad (1)$$

$$[WO(O_2)(QO)_2]\ \mathbf{2} + RCH{=}CHR' \rightarrow [WO_2(QO)_2]\ \mathbf{3} + RCH(O)CHR' \quad (2)$$

$$PPh_4[WO(O_2)_2(QO)]\ \mathbf{4} + RCH{=}CHR' \rightarrow PPh_4[WO_2(O_2)(QO)]\ \mathbf{5} + RCH(O)CHR' \quad (3)$$

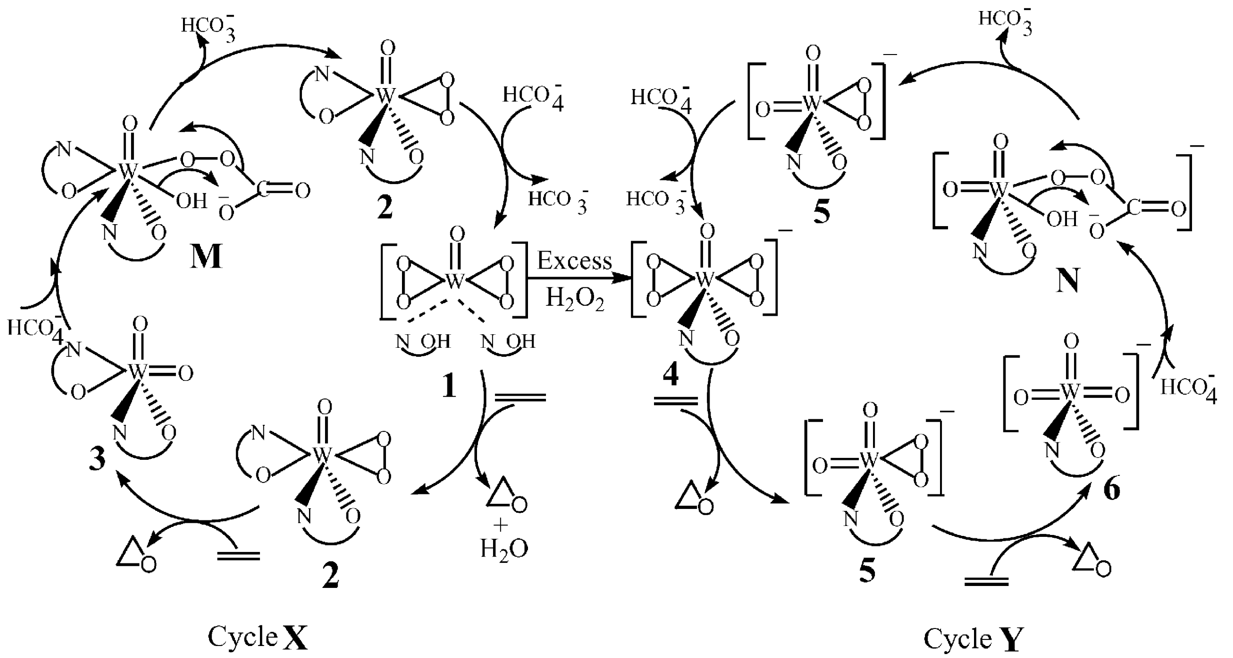
$$PPh_4[WO_2(O_2)(QO)] + RCH{=}CHR' \rightarrow PPh_4[WO_3(QO)]\ \mathbf{6} + RCH(O)CHR' \quad (4)$$

Catalytic reactivity. Catalytic efficiency when H_2O_2 is used as the sole oxidant is rather poor, but when $NaHCO_3$ is added as an additive (a co-catalyst) the efficiency of the system becomes enormous. The key aspect[23,24] of such a reaction is that H_2O_2 and bicarbonate react in an equilibrium process to produce peroxymonocarbonate >eqn (5)] which is a more reactive nucleophile than H_2O_2 and speeds up the reactions leading to epoxidation.

$$HCO_3^- + H_2O_2 \leftrightharpoons HCO_4^- + H_2O \quad (5)$$

The deprotonation of bicarbonate (pK_a = 10.3) to carbonate becomes significant at pH values ≈ 8–9. This deprotonation should decrease the concentration of bicarbonate in the above equilibrium and reduces the amount of peroxymonocarbonate present, which in turn reduces the rate of reaction. Richardson[23] showed that the epoxide yield in the Mn-catalyzed styrene derivative (*p*-vinyl benzoic acid) reduces from ≈95% at pH values less than 8.2 to less than 50% at pH = 9.

The basic principle of the catalytic reaction is the generation of monoperoxo or diperoxo complexes by the terminal oxidant /HCO_4^- from the appropriate precursor oxo complexes. Such peroxo complexes then epoxidize an olefin and themselves revert back to the oxo complexes which again react with H_2O_2/HCO_4^- to regain the catalytic properties and so on. This principle is explained by eqn (6)–(16) and is illustrated in Scheme 3. The scheme consists of two cycles **X** and **Y**. While **X** illustrates eqn (5)–(10), **Y** pictorially represents eqn (11)–



Scheme 3 The plausible catalytic reaction pathway comprising of two cycles, **X** and **Y**, where N–O = 8-quinolinolate, **M** and **N** = intermediate complexes.

(16). The eqn (11) is the connecting pathway for both the cycles.

$$[WO(O_2)(QO)_2] + RCH{=}CHR' \rightarrow [W(O)_2(QO)_2] + RCH(O)CHR' \quad (6)$$

$$[W(O)_2(QO)_2] + HCO_4^- \rightarrow [WO(O_2)(QO)_2] + HCO_3^- \quad (7)$$

$$[WO(O_2)(QO)_2] + H_2O_2 \rightarrow \{WO(O_2)_2 \cdot 2QOH\} \quad (8)$$

$$\{WO(O_2)_2 \cdot 2QOH\} + RCH{=}CHR' \rightarrow [WO(O_2)(QO)_2] + RCH(O)CHR' + H_2O \quad (9)$$

[Adding (6)–(9) we have eqn (10)]

$$[WO(O_2)(QO)_2] + 2RCH{=}CHR' + HCO_4^- + H_2O_2 \rightarrow [WO(O_2)(QO)_2] + HCO_3^- + H_2O + RCH(O)CHR' \quad (10)$$

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

$$[WO(O_2)_2(QO)]^- + RCH{=}CHR' \rightarrow [WO_2(O_2)(QO)]^- + RCH(O)CHR' \quad (12)$$

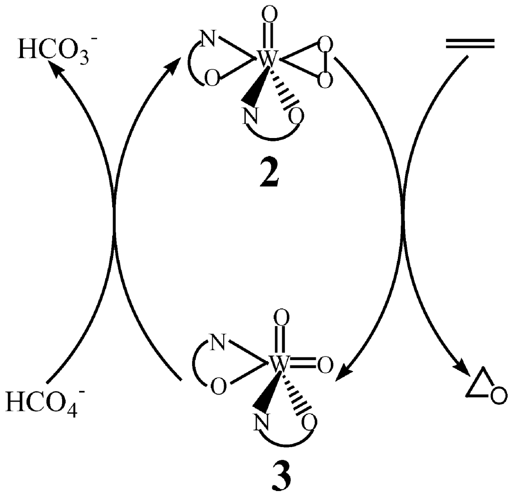
$$[WO_2(O_2)(QO)]^- + RCH{=}CHR' \rightarrow [WO_3(QO)]^- + RCH(O)CHR' \quad (13)$$

$$[WO_3(QO)]^- + HCO_4^- \rightarrow [WO_2(O_2)(QO)]^- + HCO_3^- \quad (14)$$

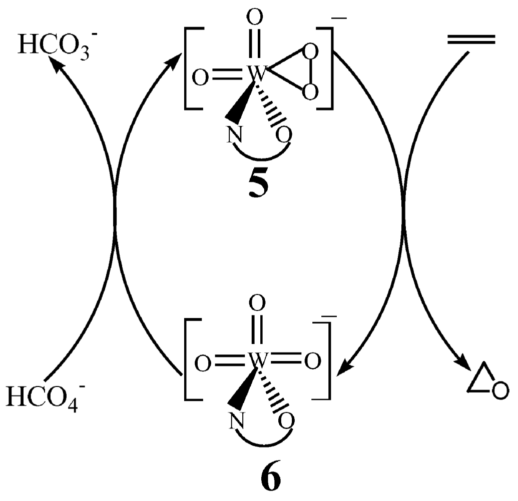
$$[WO_2(O_2)(QO)]^- + HCO_4^- \rightarrow [WO(O_2)_2(QO)]^- + HCO_3^- \quad (15)$$

[Adding (11)–(15) we have eqn (16)]

$$\{[WO(O_2)_2(QO)]^-\} + 2RCH{=}CHR' + 2HCO_4^- \rightarrow \{[WO(O_2)_2(QO)]^-\} + 2RCH(O)CHR' + 2HCO_3^- \quad (16)$$

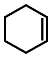
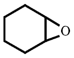
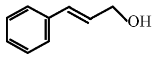
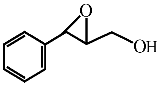
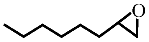


Scheme 4 The fate of the catalytic pathway **X** (in Scheme 3) when $[H_2O_2]$ is minimum in the reaction media.



Scheme 5 The fate of the catalytic pathway **Y** (in Scheme 3) when $[H_2O_2]$ is minimum in the reaction media.

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

				% Yield (GC)				TON			
Entry	Substrate	Product	Time	**1**	**2**	**4**	**5**	**1**	**2**	**4**	**5**
1			50 min	93	72	90	68	4650	3600	4500	3400
2			45 min	82	58	74	53	1640	1160	1480	1060
3			75 min	99	83	95	76	4950	4150	4750	3800

It may be suggested that, when the H_2O_2 concentration becomes minimal, catalytic oxidation still persists as shown in Scheme 4 (for cycle **X**) and Scheme 5 (for cycle **Y**), though for a few turnovers only, and the oxidant should then be replenished to sustain the catalytic cycle. Intermittent addition of H_2O_2 is advantageous as 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 $[O_2^{2-}]$ as well as $[HCO_4^{-}]$ species in the reaction medium, but the water formed may increase the possibility of converting epoxides to respective diols and would have deactivating effects on the catalysts.

Catalytic studies

Efficiency. All the isolated complexes (**1–6**) behave as good epoxidation catalysts or catalyst precursors but the peroxo rich complexes are found to be excellent catalysts. To find the best among the peroxo rich catalysts, we studied the comparative epoxidation efficiencies, the results of which are given in Table 2. The result shows that catalyst **1** is most effective followed by catalyst **4** and then by **2** and **5**. But the detailed catalytic activity of **4** is reported in the present paper since the structural characterization of **1** is not possible because during crystallization it is converted to **2**. Increased efficiency of the neutral complexes may be due to the fact that the same attack the olefins in an electrophilic manner, the partial charges at the peroxo oxygen atoms of the free catalyst should be considered to be a measure of epoxidation activity.[25]

The results were obtained using a wide variety of substrates, starting from the highly reactive (to show that the TOF may be as high as 59 400 h^{-1}) to much less reactive olefins, including functionalized olefins shown in Table 1 clearly indicate the superiority of the present synthetic method based on the unparalleled efficiency of the catalyst. The simplicity, greenness and high cost-effectiveness of the method (compared to hypochlorite and iodosyl benzene) make it a probable real life process.

Table 3 Efficiency of the catalyst **4** using different amount of H_2O_2 as oxidant keeping all other parameters the same as in Table 1

Equivalents of H_2O_2 used (wrt substrate)	Oxidation of cyclohexene (t = 50 min)		Oxidation of styrene (t = 2 h)	
	% Yield (GC)	TON	% Yield (GC)	TON
1	65	3250	50	2500
2	79	3950	66	3300
3	91	4550	75	3750
4	95	4750	80	4000
5	96	4800	82	4100

The results obtained in Table 1 indicate that 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 (alcoholic) olefins are *generally* harder to epoxidize than the non-functionalized analogues. On the other hand, non-terminal olefins are more easily epoxidized than their terminal analogues. At this moment it is very difficult to propose a plausible mechanism for the epoxidation but exhibition of very high selectivity precludes any radical mechanism. This was further corroborated by an AIBN (azoisobutyronitrile) and *p*-benzoquinone test.

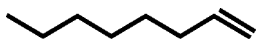
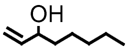
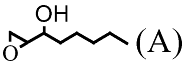
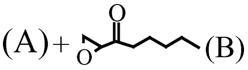
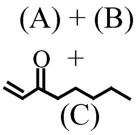
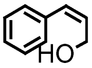
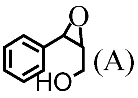
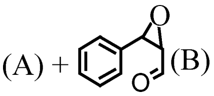
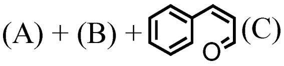
Role of bicarbonate in the reaction system. Control experiments without using catalyst and $NaHCO_3$ fail to produce the desired product in each case. Interestingly it has been observed that epoxidation also occurs in the presence of bicarbonate alone. From Table 1, we see that good yields of epoxides were achieved using 0.25 equiv. of $NaHCO_3$ as co-catalyst. Interestingly, $NaHCO_3$ alone can produce epoxides with low to moderate yields. This signifies that the epoxidation is *catalytic in bicarbonate* although TON varies from >1 to <2. The use of a catalytic amount of bicarbonate in the absence of W-complex fails to produce any epoxides. Bicarbonate activated H_2O_2 shows a higher efficiency of epoxidation than H_2O_2 alone.

Use of greater than 0.25 equivalents of bicarbonate increases the pH of the reaction medium to greater than 8,

Table 4 Comparative catalytic epoxidation efficiencies of the peroxo complexes in different amounts of H_2O_2, taking styrene as a representative substrate and keeping all other parameters the same as in Table 1

Entry	Catalyst	Equivalents of H_2O_2	% Yield	TON
1	**1**	3	81	4050
		5	90	4500
		7	87	4350
2	**2**	3	60	3000
		5	86	4300
		7	84	4200
3	**4**	3	75	3750
		5	82	4100
		7	85	4250
4	**5**	3	56	2800
		5	76	3800
		7	82	4100

Table 5 Effect of temperature on some representative olefins and olefinic alcohols using **4** as catalyst and keeping all other parameters the same as in Table 1

Entry	Temperature (°C)	Time (h)	Substrate	Product	% Yield[a]	TON[a]
1	25	1.25			99	4950
	50	1			98	4900
	78	1.5			62	3100
2	25	1.5			92	4600
	50	1.25			91, 2	4550, 100
	78	2			32, 4, 2	1600, 200, 100
		6 (cat : sub = 1 : 1000)		(A) + (B) + (C)	50, 21, 11	500, 210, 110
		6 (cat : sub = 1 : 1000) (without $NaHCO_3$)		(A) + (B) + (C)	55, 23, 10	550, 230, 100
3	25	0.75			72	1440
	50	0.75			80, 4	1600, 80
	78	1			34, 6, 2	680, 120, 40
		6 (cat : sub = 1 : 1000)		(A) + (B) + (C)	40, 24, 16	400, 240, 160

[a] Where more than one product is formed, % yields and the respective TONs are represented separated horizontally by commas.

which can reduce the efficiency of the epoxidation reaction. Hence, use of 0.25 equivalents of $NaHCO_3$ is found to be optimum.

Ligand effect. The enhancement of catalytic potentiality using 8-quinolinol as ligand lies in the fact that the ligand, seemingly a spectator ligand, has donor atoms (N and O) whose ligating properties are complementary to each other. While both are good donors for a d^0 metal, the ring nitrogen is capable of interacting with the π-cloud of the aromatic moiety. Hence, it can control the push–pull behaviour experienced by the aromatic system by exhibiting both +I and −I effect.

Role of peroxide concentration on the efficiency of the catalysts. In order to make the method cost effective, H_2O_2 economy is important. Hence, we performed a comparative study on two representative substrates using catalyst **4** and different molar equivalents of H_2O_2 as shown in Table 3. The results show that the use of 3–4 equivalents of H_2O_2 is the optimal condition for cost effectiveness as well as catalyst efficiency.

The results in Table 4 indicate that, at moderate concentrations of H_2O_2 (3–4 equiv.), all the catalysts, *viz*., **1**, **2**, **4** and **5**

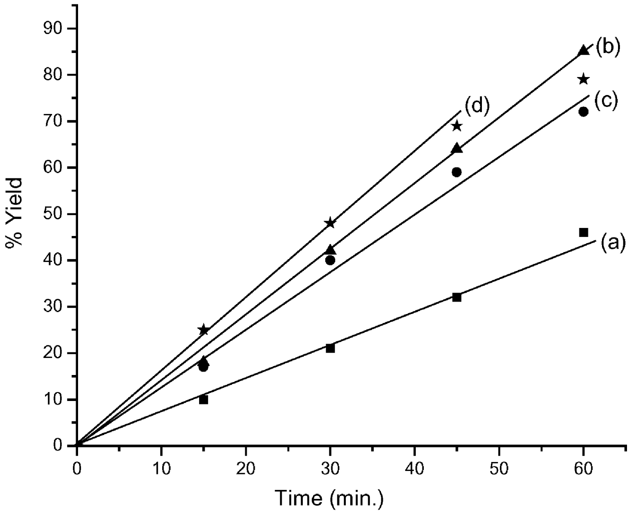
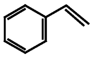
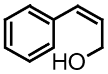
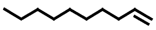


Fig. 3 Plot of % yield *versus* time, selecting the linear portions of each of the corresponding curves shown in Fig. 2.

Table 6 Catalytic activity of the recovered catalyst (**4**) with all other parameters the same as in Table 1

Entry	Substrate[a]	Batch 1, % yield (TON)	Recovery[b] of catalyst[c] (%)	Batch 2,[d] % yield (TON)	Recovery[b] of catalyst [e](%)	Batch 3, % yield (TON)
1	 (1:5000)	75 (3750)	55	58 (2900)	15	32 (1600)
2	 (1:2000)	72 (1440)	68	50 (1000)	40	27 (540)
3	 (1:2000)	98 (1960)	70	71 (1420)	38	35 (700)

[a] The figures in parentheses indicate the molar ratios of catalyst to substrate. [b] The IR spectra of the recovered catalyst after batch 1 is quite similar to the original catalyst in profile and position, but that after batch 2 shows broadened bands with band heights decreased and weaker bands disappearing, indicating that catalyst deactivation has started. [c] Catalyst recovered in % with respect to the amount of catalyst in batch 1. [d] Results express the % yield when the recovered catalyst is used in the same molar ratio as in batch 1. [e] Recovery of catalyst after batch 2 with respect to the amount of catalyst in batch 1.

show[26] their epoxidation activities commensurate with their structure (peroxo rich or peroxo poor). But at excess H_2O_2 concentrations (5 equiv.), efficiencies of the catalysts **1** and **4** increase a little bit whereas for **2** and **5**, they are drastically increased. This obviously occurs due to the interconversion of peroxo poor complexes to the peroxo rich ones, for instance **5** being changed to **4** and **2** to **1**. When a large excess of H_2O_2 (7 equiv.) is used, an interesting observation is noted. In that case the catalysts **4** and **5** show slightly increased but comparable efficiencies with each other. **1** and **2** show decreased efficiencies. The fact that the catalyst **5** shows comparable efficiency to that of **4** can be explained by saying that, at large excess of peroxide, **5** is readily converted to **4**. The reduced efficiencies of **1** and **2** occur due to the rapid conversion of both to **4**, which shows lesser efficiency, compared to **1**.

Temperature effect. All the olefins including olefinic alcohols as shown in Table 1 are catalytically oxidized to epoxides at room temperature. For olefinic alcohols, only the olefinic group is chemoselectively oxidized to the epoxide, alcoholic groups remained unreacted. In order to check the effect of temperature on both the functional groups (C=C and –OH), we employed the oxidation reaction on some representative olefins at various temperatures as shown in Table 5. The results in this table indicate that at higher temperature (50 °C), the epoxide formation for non-functionalized olefins, *viz*., 1-octene becomes more efficient, but in the cases of olefinic alcohols *viz*., cinnamyl alcohol and 1-octene-3-ol, chemoselectivity is lost as, here, besides epoxide, epoxy aldehyde is also formed to some extent. At still higher temperatures, *i.e.*, under refluxing conditions (78–80 °C), besides epoxy alcohol, corresponding olefinic and epoxy aldehydes are formed. It is the alcoholic group in the olefinic alcohol, which is activated at higher temperature. Oxidation of the alcoholic group is much more energy intensive compared to that of the olefinic group. So, much time is required to oxidize the alcoholic group under refluxing conditions. Not only that, the effectivity of $NaHCO_3$ as co-catalyst is lost at higher temperatures as it is converted to Na_2CO_3 according to the reaction [eqn (17)].

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \qquad (17)$$

To ensure the deactivation of $NaHCO_3$ at higher temperatures we employed a blank test, taking cinnamyl alcohol as a representative substrate in the absence of bicarbonate, and observed a slight but consistently higher yield as shown in Table 5. Formation of Na_2CO_3 increases the pH of the reaction media, which not only facilitates the decomposition of H_2O_2 but also reduces the reaction rate. The excess water formation due to decomposition of $NaHCO_3$ also has a deactivating effect on the reaction.

Kinetic study. Using **4** as a representative catalyst, $NaHCO_3$ (0.25 equiv.) as co-catalyst and H_2O_2 as terminal oxidant, a plot of % yield *versus* time for the oxidation of some representative substrates, *viz*., styrene (entry 4), 1-hexene (entry 11), 3-butenol (entry 8) and 1-decene (entry 16) is presented in Fig. 2 where each curve maintains a gross linearity up to 1 h time span but thereafter deviates from linearity showing a slowed reaction rate. The plot, % yield *vs*. time, selecting the linear portion of the corresponding curve shown in Fig. 2, is presented in Fig. 3. Fig. 3 shows that the initial rate of the reaction (up to 1 h) follows first order kinetics and hence the TOF rightly has the unit, h^{-1}.

Reuse of catalyst. Since a low catalyst loading was used, some loss of catalyst occurs during recovery in the laboratory system (for a pilot plant system this difficulty may be avoided). Notably, in the second batch there occurs a considerable decrease in the % yield of the products. But a marked decrease in efficiency was noted for the third batch when it becomes practically non-productive. These observations are based on the fact that we have chosen three different types of substrates as representatives and conducted catalytic epoxidation on them (for details see Table 6).

Concluding remarks

The most interesting feature of the present work is the revealing of the chemistry involved in the interconversion of one catalytic form to another depending on the concentration of H_2O_2 used.

We can conclude that it is a really interesting observation that in the presence of H_2O_2 the catalyst **4** alone functions as a mediocre one, the co-catalyst alone, even more mediocre, but when both the catalyst and co-catalyst are used together, the highest efficiency so far is achieved.

The simplicity, greenness, high cost effectiveness and high selectivity of the method make it a probable real life process.

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26 Actually, in the presence of a sufficient amount of H_2O_2 all the complexes **1–6** are catalysts. We label **1**, **2**, **4** and **5** as catalysts as they can epoxidize olefins stoichiometrically (without the H_2O_2 oxidant). Complexes **3** and **6** are labelled as catalyst precursors since they fail to oxidize olefins without the help of H_2O_2.