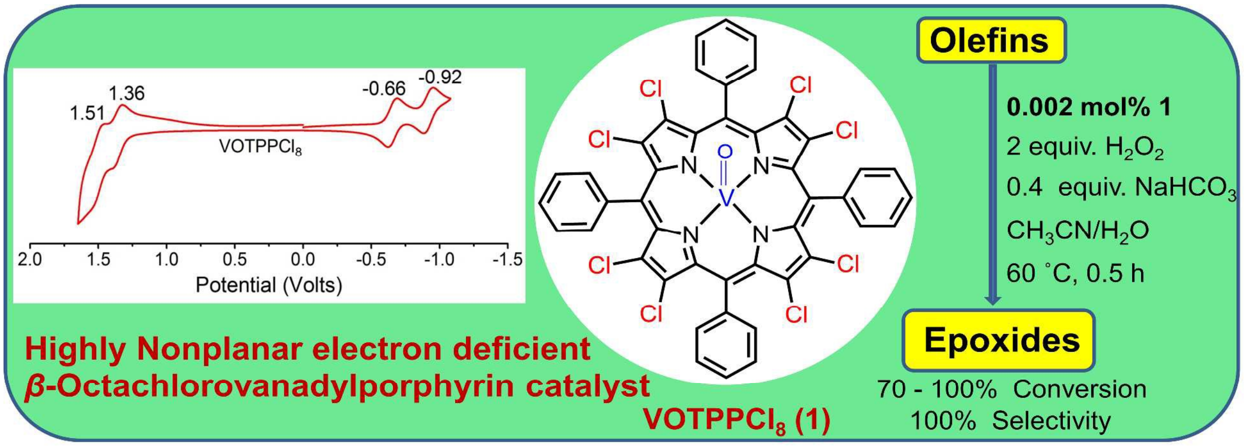
Dalton Transactions

Graphical Abstract



We have synthesized *β*-octachloro-*meso*-tetraphenylporphyrinatooxidovanadium(IV) (VOTPPCl$_8$) and characterized. It exhibited highly nonplnar electron deficient porphyrin core having very high thermal stability. Further, it was utilized for selective epoxidation of olefins in good yields with very high TOF numbers (6566-9650 h^{-1}).

Journal Name

ARTICLE

Electron Deficient Nonplanar β-Octachlorovanadylporphyrin as Highly Efficient and Selective Epoxidation Catalyst for Olefins†

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We have synthesized 2,3,7,8,12,13,17,18-octachloro-*meso*-tetraphenylporphyrinatooxidovanadium(IV) (VOTPPCl$_8$) and characterized by various spectroscopic (UV-Vis, IR and EPR) techniques, MALDI-TOF mass spectrometry and elemental analysis. DFT optimized structure of VOTPPCl$_8$ in CH_3CN exhibited severe nonplanar saddle shape conformation of porphyrin macrocycle. Cyclic voltammogram of VOTPPCl$_8$ showed 500 mV anodic shift in first ring reduction and 220 mV in first ring oxidation potentials as compared to VOTPP indicating the electron deficient nature of porphyrin π-system and further proves the existence of nonplanar conformation of the macrocycle in solution. Further, VOTPPCl$_8$ exhibited very high thermal stability till 390 °C as indicated in its thermogram. The oxidation state of metal ion (V^{IV}) was confirmed by EPR spectroscopy and VOTPPCl$_8$ exhibited axial spectrum which corresponds to axially compressed d_{xy}^1 configuration. VOTPPCl$_8$ was utilised for the selective epoxidation of various olefins in good yields with very high TOF numbers (6566-9650 h^{-1}) in presence of H_2O_2 as an oxidant and $NaHCO_3$ as promoter in CH_3CN/H_2O mixture. The oxidoperoxidovanadium(V) species is expected to be the intermediate during the catalytic reaction which is probed by ^{51}V NMR spectroscopy and MALDI-TOF mass analysis. Notably, VOTPPCl$_8$ is stable after catalytic reaction and doesn't form μ-oxo dimer due to highly electron deficient nonplanar porphyrin core and can be reused for several cycles.

Selective oxidation of olefins to epoxy compounds has always been an interesting area of research for the chemists owing to their great importance in the production of highly valued commodity chemicals such as polyurethanes, unsaturated resins, glycols, surfactants, and other products.[1] Transition metal complexes play a vital catalytic role in various organic transformations e.g. epoxidation, hydroxylation, C-H activation, hydrogenation, polymerisation, carbon-carbon coupling reactions, halogenation, dehalogenation and so on in homogeneous and heterogeneous media.[2,3] Among them, metalloporphyrins have been found to be efficient catalysts for alkene epoxidation using various oxygen atom donors[4,5] due to their high chemical and thermal stability, interesting physicochemical properties, strong absorption in the visible region and flexible architectural modification to tailor redox properties and conformational features. Apart from catalysis, they were widely utilized in dye-sensitised solar cells (DSSCs),[6] photodynamic therapy (PDT),[7] anion sensing[8] and nonlinear optical studies.[9] The β-functionalization of *meso*-tetraphenylporphyrin (TPP) is of great interest since the electronic properties of the porphyrin π-system can be altered by tuning the size, shape and electronic nature of the β-substituents[10] as compared to the substituents at the *meso*-aryl positions.

Iron and manganese porphyrin complexes were widely utilized as effective homogenous catalysts for such oxygenation reactions in last few decades.[2-3,11] The major drawbacks of homogenous MTPP-based catalysts are (i) the macrocyclic ring is liable for oxidative self-destruction; (ii) aggregation of metalloporphyrins through π-π interactions; (iii) lower turnover frequency (TOF) and; (iv) poor product selectivity. Recently, highly efficient and stable Mn^{III}porphyrinic framework (MOF) was demonstrated for selective epoxidation of olefins in heterogeneous media.[12] Among various metalloporphyrins, vanadyl ($V^{IV}O$) porphyrins merit special attention owing to their use as anti-HIV agents[13] as compared to other vanadium complexes as potential therapeutics,[14] 3D supramolecular assemblies[15] and catalysts for oxidation reactions.[15-16] Notably, VOTPP was utilised for oxidation of cyclohexene under homogeneous[16] and heterogeneous conditions,[17] respectively, leading to mixture products (viz. epoxide, alcohol and ketone) with very low TOF. So, there is a quest for highly efficient vanadylporphyrin catalyst for selective oxidation of olefins. Besides dioxygen, aqueous H_2O_2 is the most widely used oxidant since it is inexpensive, environmentally benign and biologically important nature.[18-20] The use of $NaHCO_3$ as promoter and H_2O_2 as a terminal oxidant has been evolved as a highly efficient method for epoxidation of olefins catalyzed by W, Mo and Mn complexes.[18-19,21-22] H_2O_2 and HCO_3^- are used together to increase the activity of H_2O_2 by *in situ* generation of peroxymonocarbonate ion which is more nuleophilic than H_2O_2 and thus attributes to the enhanced

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†Electronic Supplementary Information (ESI) available: IR and mass spectra of VOTPPCl$_8$ and table containing bond lengths and bond angles of DFT optimized structure of VOTPPCl$_8$ and CV and DPV traces. See DOI: 10.1039/x0xx00000x

oxidizing activity of the metal complexes.[18-22] To the best of our knowledge, there is no report on selective epoxidation of olefins in almost quantitative yields catalyzed by oxidovanadium porphyrin complexes in homogenous media. Herein, we present the selective epoxidation of olefins using biologically important oxidant (i.e., H_2O_2) catalyzed by robust $VOTPPCl_8$ using $NaHCO_3$ as promoter with very high turnover frequency (TOF).

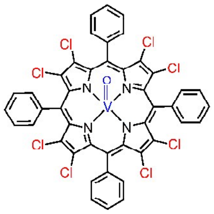


Figure 1. Molecular structure of β-octachlorovanadylporphyrin ($VOTPPCl_8$) employed in this study.

Results and Discussion

Synthesis and Characterisation

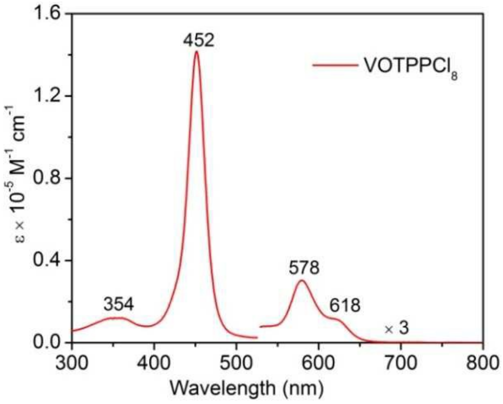


Figure 2. Electronic absorption spectrum of $VOTPPCl_8$ in CH_2Cl_2 at 298 K.

We have synthesised free base β-octachloro-*meso*-tetraphenylporphyrin (H_2TPPCl_8) using reported procedure.[23] $VOTPPCl_8$ was prepared by reacting H_2TPPCl_8 with 10 equivalents $VOSO_4$ in refluxing DMF for 16 hours under argon atmosphere. Then the porphyrin was precipitated by adding excess water, filtered and air dried. The crude porphyrin was purified on silica column using $CHCl_3$ as eluent. The yield was found to be 79%. In general, our vanadium metallation procedure is much simpler as compared to reported literature methods so far.[24,15] $VOTPPCl_8$ was characterised by optical absorption, IR and EPR spectroscopic techniques, mass spectrometry and elemental analysis. Figure 2 represents the UV-Vis spectrum of $VOTPPCl_8$ in CH_2Cl_2. $VOTPPCl_8$ exhibited a characteristic UV-Vis spectrum for a metalloporphyrin[25] which is blue shifted as compared to that of H_2TPPCl_8. The IR spectrum of H_2TPPCl_8 exhibited a characteristic peak at ν ~3328 cm^{-1} for NH stretching frequency which disappeared upon metallation and appearance of a new peak at ~1003 cm^{-1} for V=O stretching confirmed the insertion of VO into the porphyrin core (Figure S1 in the electronic supporting information (ESI)).[15] Further, the MALDI-TOF mass analysis showed a molecular ion peak at 954.95 (m/z) which is in agreement with the corresponding calculated mass number (m/z = 954.96) as shown in the Figure S2 in the ESI. Our attempts to obtain X-ray quality single crystals were failed. So, we have carried out DFT studies using B3LYP functional with LANLD2Z basis set. Figure 3 represent the top and side views of optimised geometries of $VOTPPCl_8$ in CH_3CN. V^{IV} ion is present in square pyramidal geometry with axial oxido ligand. From the side view (Figure 3b), it is clear that $VOTPPCl_8$ adopts nonplanar saddle shape conformation due to steric hindrance between peripheral β-chloro and *meso*-phenyl groups.[23] The selected average bond angles and bond lengths of $VOTPPCl_8$ are listed in table S1 in the ESI. Herein, V^{IV} ion resides 0.515 Å above the porphyrin mean plane formed by 24 atoms core. V=O distance is slightly shorter (1.60 Å) than β-octaethyl-vanadylporphyrin (1.62 Å).[26] Further, $VOTPPCl_8$ exhibited a large deviation of 24 atoms core (Δ24 = 0.535 Å) and β-pyrrole carbons, ($\Delta C_\beta = \pm$ 1.128 Å) from the porphyrin mean plane (Table S1, ESI). This is further supported by longer C_β-C_β bond length (1.375 Å) and the increment in C_β-C_α-C_m angle (~128°) with the concomitant decrement in the N-C_α-C_m angle (~123.8°) as compared to reported quasi planar vanadyl porphyrin.[26] Furthermore, DFT analysis of free base H_2TPPCl_8 in CH_3CN slightly increases nonplanarity (Figure S3, ESI) as reflected by increment in ΔC_β (± 1.185 Å) and Δ24 (± 0.674 Å) as compared to $VOTPPCl_8$ (Table S2, ESI). The insertion of vanadyl (VO^{2+}) into H_2TPPCl_8 core slightly alters the nonplanarity of the macrocycle.

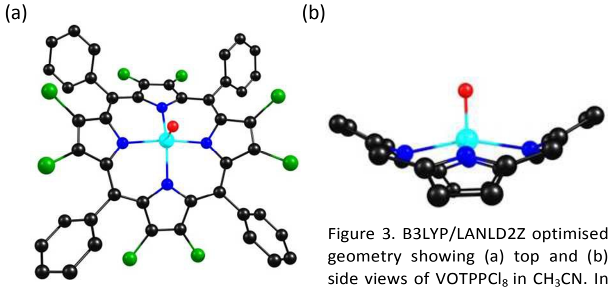


Figure 3. B3LYP/LANLD2Z optimised geometry showing (a) top and (b) side views of $VOTPPCl_8$ in CH_3CN. In side view, β-chloro and *meso*-phenyl substituents are omitted for clarity.

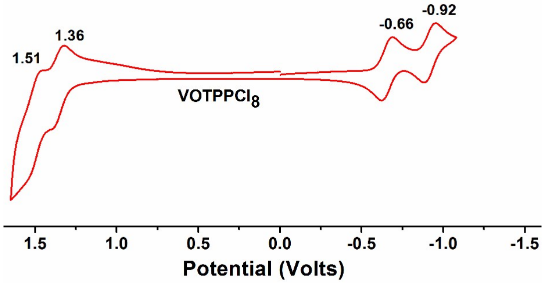


Figure 4. CV of $VOTPPCl_8$ (1 mmol) in dichloromethane containing 0.1 M $TBAPF_6$ at 298 K. Potentials are measured with respect to Ag/AgCl electrode.

Electrochemical studies of VOTPP have been examined in non-aqueous media.[27] Figure 4 represents the cyclic voltammogram

(CV) of VOTPPCl$_8$ which is measured in dichloromethane containing TBAPF$_6$ as supporting electrolyte at 298 K. It exhibited ring-centred two one electron oxidations and reductions which are further supported by the differential pulse voltammogram (DPV) of VOTPPCl$_8$ by showing four redox peaks with almost same amplitude (Figure S4, ESI). Notably, VOTPPCl$_8$ exhibited a remarkable anodic shift (ΔE_{red} = 500 mV) in the first ring reduction as compared to VOTPP whereas in oxidation only 220 mV anodic shift was observed due to nonplanar conformation of macrocycle which destabilizes the HOMOs and makes oxidation easier relative to reduction (Figure S5, ESI).[9] The anodic shift in redox potentials is due to the strong electron withdrawing effect of eight β-chloro groups. The thermogram of VOTPPCl$_8$ exhibited almost a flat line till 390 °C indicating the high thermal stability of this porphyrin (Figure S6, ESI). The high stability of VOTPPCl$_8$ is possibly due to sterically hindered porphyrin periphery (nonplanar saddle shape conformation) and electron withdrawing β-chloro groups which prevent the oxidative decomposition.[4a] To the best our knowledge, this is the first example of metalloporphyrin showing very high thermal stability (till 390 °C) which prompted us to do catalytic oxidation studies using this vanadylporphyrin complex.

We have recorded the X-band EPR spectrum of VOTPPCl$_8$ in toluene (Figure 5). VOTPPCl$_8$ has exhibited axial EPR spectrum with well resolved ^{51}V hyperfine lines at 120 K. The spin Hamiltonian parameters were obtained from simulated EPR spectrum which is in close agreement with experimentally observed one. The obtained $g_{||}$ and $g_{\perp}$ values are 1.965 and 1.985, respectively and $A_{||}$ and $A_{\perp}$ values are 172×10^4 cm^{-1} and 61×10^4 cm^{-1}, respectively. The $g_{||} < g_{\perp}$ and $A_{||} >> A_{\perp}$ relationships are normal for the axially compressed d^1_{xy} configuration.[24c,28] These results clearly indicate that vanadium is in IV oxidation state. Further, we couldn't observe well resolved superhyperfine splitting from porphyrin N atoms since the unpaired electron resides on a σ-non-bonding orbital pointing away from these N atoms which is present in the equatorial (xy) plane.[28]

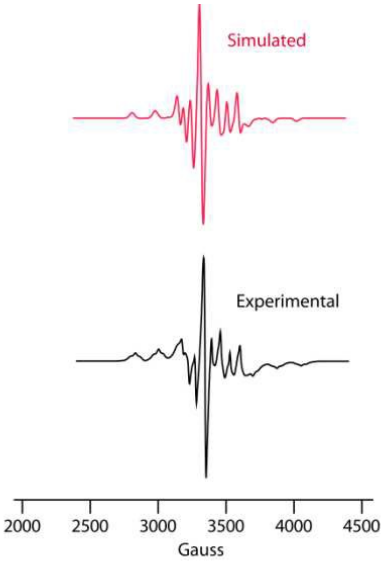
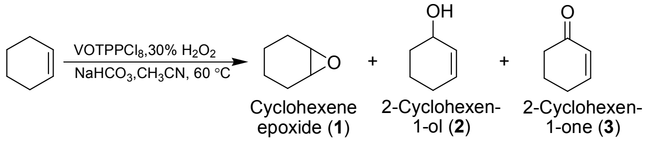


Figure 5. X-Band EPR spectrum of VOTPPCl$_8$ was recorded in toluene at 120 K (bottom). EPR parameters: microwave frequency, 9.453 GHz; incident microwave power, 0.189 mW; modulation frequency, 100.0 kHz; modulation amplitude, 5.0 G; receiver gain, 1×10^4. Simulated EPR spectrum of VOTPPCl$_8$ is shown at the top.

Catalytic Studies

To explore the catalytic potential of synthesized vanadium porphyrin complex (VOTPPCl$_8$), we conducted a series of experiments. Catalytic oxidation of cyclohexene by VOTPPCl$_8$ using H_2O_2 as oxidant and $NaHCO_3$ as co-catalyst gave three products: cyclohexene epoxide (**1**), 2-cyclohexen-1-ol (**2**) and 2-cyclohexen-1-one (**3**).



Scheme 1 Oxidation of cyclohexene catalyzed by VOTPPCl$_8$.

The catalytic activity of VOTPPCl$_8$ was initially investigated for cyclohexene as a representative oxidation substrate and different reaction parameters were optimized for 5 mmol (0.410 g) of cyclohexene in 6 hours of reaction time. All the catalytic experiments were carried out in a 50 mL round bottom flask containing cyclohexene (0.410 g, 5 mmol), appropriate amount of aqueous 30% H_2O_2, $NaHCO_3$ in 5mL of desired solvent and fitted with a condenser. At first, the effect of different types of solvents *viz.* acetonitrile, methanol, dichloromethane and toluene (5 mL each), on the oxidation of 5 mmol (0.410 g) of cyclohexene was studied using 10 mmol (1.13 g) of 30% H_2O_2 and 1 mmol (0.084 g) of $NaHCO_3$ as promoter at 60 ^{o}C. CH_3CN was found to be the most suitable solvent with the maximum of 61% conversion followed by 57% conversion of cyclohexene using methanol as a solvent (data not shown). The possible reason for the increased conversion is due to the enhanced formation of oxidohydroperoxido- or oxidoperoxidovanadium(V) species. Therefore, CH_3CN was used as a solvent for the optimization of remaining reaction conditions.

The catalyst amount was optimized by taking three different amounts of catalyst (0.0005 g, 0.0010 g and 0.0015 g) while keeping other reaction parameters constant such as 30% H_2O_2 (1.13 g, 10 mmol), $NaHCO_3$ (0.084 g, 1 mmol), acetonitrile (5 mL) and reaction temperature (60 ^{o}C). The conversion increased from 61% to 73% by increasing the catalyst amount from 0.0005 g to 0.0010 g as presented in Table 1 (entry 2). Thereafter, no considerable improvement in conversion was obtained (77%) upon increasing the catalyst amount up to 0.0015 g and hence catalyst amount 0.0010 g (1.04 µmol) was considered as optimized catalyst amount.

The effect of oxidant amount i.e. aq. 30% H_2O_2 was measured by varying its amount. For this purpose, three different oxidant amount *viz.* 5, 10 and 15 mmol were chosen and reactions were carried out by taking 1.04 µmol of catalyst, 1 mmol of promoter (i.e. $NaHCO_3$) and 5 mL of CH_3CN at 60 ^{o}C. The

Table 1. Oxidation of cyclohexene (0.41 g, 5 mmol) using $VOTPPCl_8$ as a catalyst in 6 hour time scale under different reaction conditions.

Entry No.	Catalyst (mg, µmol)	30 % H_2O_2 (g, mmol)	$NaHCO_3$ (g, mmol)	CH_3CN (mL)	Temp. (°C)	Conv. %	Product Selectivity		
							-Oxide	-Ol	-One
1	0.5, 0.52	1.13, 10	0.084, 1	5	60	61	25	55	20
2	1.0, 1.04	1.13, 10	0.084, 1	5	60	73	28	47	25
3	1.5, 1.57	1.13, 10	0.084, 1	5	60	77	29	40	31
4	1.0, 1.04	1.69, 15	0.084, 1	5	60	78	21	34	45
5	1.0, 1.04	0.57, 5	0.084, 1	5	60	59	23	58	19
6	**1.0, 1.04**	**1.13, 10**	**0.168, 2**	**5**	**60**	**82**	**22**	**42**	**36**
7	1.0, 1.04	1.13, 10	0.252, 3	5	60	85	19	46	35
8	1.0, 1.04	1.13, 10	0.168, 2	7	60	68	28	33	39
9	1.0, 1.04	1.13, 10	0.168, 2	3	60	81	15	60	25
10	1.0, 1.04	1.13, 10	0.168, 2	5	70	86	20	49	31
11	1.0, 1.04	1.13, 10	0.168, 2	5	50	51	26	38	36
12	1.0, 1.04	1.13, 10	0.168, 2	5	30^a	35	16	64	20
13	1.0, 1.04	1.13, 10	–	5	60	58	19	42	39
14	–	1.13, 10	0.168, 2	5	60	16	11	58	31
15	–	1.13, 10	–	5	60	5	9	56	35

cyclohexene conversion was lowest (59 %) for 5 mmol of 30% H_2O_2 and comparable conversions were obtained while increasing H_2O_2 amount up to 10 mmol (77 %) and 15 mmol (78 %). Considering these observations, 10 mmol of 30% H_2O_2 was concluded best for the maximum oxidation of cyclohexene (entry 2, Table 1).

The amount of promoter $NaHCO_3$ also affects the oxidation of cyclohexene. This effect has been examined by conducting experiments with three different $NaHCO_3$ amounts (1, 2 and 3 mmol) while maintaining other reaction parameters (1.04 µmol of catalyst, 10 mmol of 30% H_2O_2, 5 mL of CH_3CN, temperature 60 °C) consistent. An increase in the conversion from 73% to 82% was achieved by increasing the amount of sodium bicarbonate from 1 mmol to 2 mmol. Using 3 mmol of sodium bicarbonate didn't increase the conversion significantly (85% conversion, as presented in Table 1) and therefore, 2 mmol $NaHCO_3$ amount was optimized for further optimization (entry 6, Table 1).

The solvent (CH_3CN) amount is also an important factor in terms of percentage conversion of cyclohexene. The effect of different amounts of solvent is shown in Table 1 under above optimized conditions i.e. catalyst (0.0010 g, 1.04 µmol), 30% H_2O_2 (1.31 g, 10 mmol), $NaHCO_3$(0.168 g, 2 mmol) at 60 °C reaction temperature. While using 5 mL of acetonitrile 82% of cyclohexene conversion was obtained which was reduced to 68% for 7 mL of CH_3CN possibly due to the dilution effect. The conversion was slightly decreased (81%) when 3 mL of solvent amount was employed. Considering all these facts, 5 mL of CH_3CN was chosen as optimal solvent amount for cyclohexene oxidation.

To understand the dependence of cyclohexene oxidation over reaction temperature, reactions have been carried out at different temperatures *i.e.* room temperature (30 °C), 50, 60 and 70 °C temperature under the optimized conditions for 6 hours. The oxidation of cyclohexene was found to be slowest at room temperature (30 °C) with only 35 % conversion. The catalytic activity of the catalyst $VOTPPCl_8$ increased significantly on increasing temperature from room temperature to 70 °C. A conversion of 51 % was obtained for 50 °C which was also further increased up to 82 % and 86 % for 60 °C and 70 °C, respectively (Table 1).

Details of all experimental conditions are presented in Table 1. Thus, the optimized reaction conditions for the oxidation of 5 mmol of cyclohexene are (entry no. 6, Table 1): catalyst [$VOTPPCl_8$] (0.0010 g, 1.04 µmol), 30% aqueous H_2O_2 (1.13 g, 10 mmol), CH_3CN (5 mL) and temperature 60 °C. The selectivity of different oxidation products under the optimized reaction condition is: 22% cyclohexene epoxide (**1**), 42% 2-cyclohexen-1-ol (**2**) and 36% 2-cyclohexen-1-one (**3**). To investigate the effect of both catalyst ($VOTPPCl_8$) and promoter ($NaHCO_3$) on the oxidation of cyclohexene, three types of controlled experiments were performed under the optimized conditions (Table 1): (i) The control experiment in the absence of catalyst ($VOTPPCl_8$) but with promoter $NaHCO_3$ under optimized conditions gave 16% of conversion (entry no. 14), (ii) The control experiment in the absence of promoter $NaHCO_3$ but with catalyst ($VOTPPCl_8$) under optimized conditions gave 58% of conversion (entry no. 13) and, (iii) The control experiment in the absence of both promoter $NaHCO_3$ and catalyst ($VOTPPCl_8$) under optimized conditions gave only 5% of conversion after 6 hours of reaction time (entry no. 15).

Table 2. Product distribution for the oxidation of cyclohexene (5 mmol) using $VOTPPCl_8$ as catalyst (1 µmol) and 10 mmol of 30% H_2O_2 as an oxidant under different reaction conditions.

Entry No.	Solvent (mL, v/v)	$NaHCO_3$ (g, mmol)	Temp. (°C)	Time (h)	Conv. %	TOF (h^{-1})	Product selectivity		
							-Oxide (**1**)	-Ol (**2**)	-One (**3**)
1	CH_3CN (5)	0.168, 2	60	6	82	653	22	42	36
2	CH_3CN (5)	–	60	6	58	462	13	58	29
3	**CH_3CN/H_2O (3/2)**	**0.168, 2**	**60**	**0.5**	**100**	**9560**	**99**	**–**	**–**
4	CH_3CN/H_2O(3/2)	0.168, 2	30^a	2	51	1219	30	44	26
5	CH_3OH (5)	0.168, 2	60	6	80	637	3	11	86
6	CH_3OH (5)	–	60	6	56	446	1	43	57
7	CH_3OH/H_2O(3/2)	0.168, 2	60	0.5	97	9273	7	52	41
8	CH_3OH/H_2O(3/2)	0.168, 2	30^a	2	45	1076	18	42	40

These control experiments demonstrate that the catalyst itself is moderately efficient in catalytic oxidation of cyclohexene using 30% H_2O_2 as an oxidant with adequate conversion of 58% even in the absence of any promoter. But the product selectivity for cyclohexene epoxide decreased from 22% to 13% (Table 2, entry no. 2), whereas, only 5% of cyclohexene was converted in the absence of both catalyst and promoter showing their catalytic roles in the oxidation (entry 15, Table 1). However, 16% of cyclohexene conversion was observed using $NaHCO_3$ alone in the reaction. Surely the use of $NaHCO_3$ as promoter activated the oxidant H_2O_2 and resulted in the increased catalytic efficiency of the catalyst ($VOTPPCl_8$) towards oxidation of cyclohexene in respect of both the conversion and selectivity of epoxide.[18-19,21-22]

Such type of activation of H_2O_2 with bicarbonate ion has been demonstrated by Drago and co-workers[29] and Richardson *et al.*[30] in sulfide oxidations using a solvent mixture of alcohol/water. Richardson *et al.*[22] have reported that HCO_3^-, which is an essential component in such systems, forms a peroxymonocarbonate ion, HCO_4^- and exists as following equillibria and is more active (more nucleophilicity) oxidant than H_2O_2.

$$H_2O_2 + HCO_3^- \rightleftharpoons HCO_4^- + H_2O$$

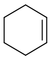
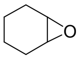
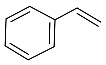
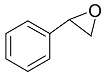
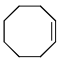
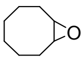
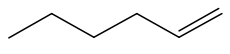
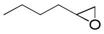
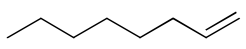
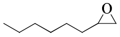
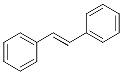
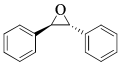
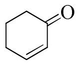
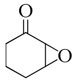
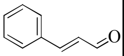
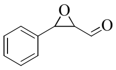
Later, this bicarbonate-activated peroxide (BAP) system, was adopted for olefin epoxidation using H_2O_2 as terminal oxidant in CH_3CN solvent[18,19] and in water/co-solvent mixture.[22] All these facts and our previous results showing respectable amount of selectivity towards epoxide (i.e. 22 %, Table 2, entry no. 1) under the optimized conditions led us to investigate that how the solvent mixture of water with CH_3CN or CH_3OH (as we have stated previously that comparable results were obtained with methanol) affects the cyclohexene conversion and epoxide selectivity?

To understand the effect of these solvent mixtures, the experiments were conducted under above stated optimized condition. The use of CH_3CN/H_2O (3 mL/2 mL, v/v) at 60 °C mixture dramatically improved the catalytic efficiency of the catalyst ($VOTPPCl_8$) and almost all cyclohexene was converted into epoxide (99% selectivity) within half an hour of reaction time (Table 2, entry no. 3). Using CH_3CN/H_2O (3mL/2mL, v/v) mixture at room temperature yielded 51% of conversion in 2 hours of reaction time with reduced 30% selectivity for cyclohexene epoxide (**1**) and increased 44% and 26% selectivity for the allylic oxidation products 2-cyclohexen-1-ol (**2**) and 2-cyclohexen-1-one (**3**), respectively. Similarly, in methanol/water (3 mL/2 mL, v/v) mixture 97% conversion was obtained in 0.5 hour time scale at 60 °C but with poor cyclohexane epoxide (**1**) selectivity i.e. 7% (Table 2, entry no.7) and a maximum of 45% conversion was obtained at room temperature with 18% selectivity towards epoxide. The similar trend of epoxide selectivity for acetonitrile and methanol was observed throughout the series of experiments (i.e. the epoxide selectivity is always higher if CH_3CN is used as solvent alone or with water).

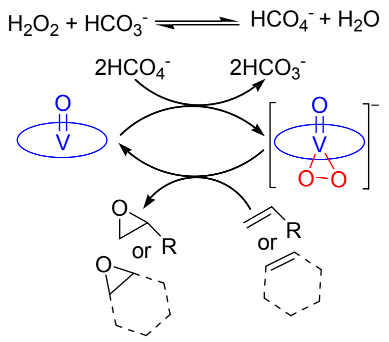
Finally, an optimized condition both in the respect of percentage conversion and epoxide selectivity was achieved for the cyclohexene oxidation as follows: catalyst ($VOTPPCl_8$) (0.0010 g, 1.04 µmol), 30% aqueous H_2O_2 (1.13 g, 10 mmol), CH_3CN/H_2O (3 mL/2 mL, v/v) and temperature 60 °C. Under this optimised condition, we have carried out the epoxidation reactions of various olefins and the results are summarized in Table 3.

Table 3. Oxidation of different olefins using 1.04 µmol of $VOTPPCl_8$ as catalyst, 30% H_2O_2 as terminal oxidant and sodium bicarbonate as promoter using CH_3CN/H_2O solvent mixture under the optimized reaction conditions.

$$\text{Olefins} \xrightarrow[\text{0.4 equiv. } NaHCO_3,\ CH_3CN/H_2O,\ 60\ ^{o}C]{\text{0.002 mol\% } VOTPPCl_8,\ \text{2 equiv. 30\% } H_2O_2} \text{Epoxides}$$

Entry No.	Substrate (5 mmol)	Product	Time (h)	Conv. %	% Selectivity	TOF (h^{-1})
1			0.5	100	99	9560
2			0.5	92	98	8884
3			0.5	98	100	9463
4			0.5	85	100	8208
5			0.5	100	99	9560
6			0.5	91	100	8787
7			0.5	73	98	7049
8			0.5	68	99	6566

Catalytic Mechanism



Scheme 1 Plausible catalytic mechanism for the conversion olefins to epoxides using $VOTPPCl_8$ catalyst.

We tried UV-Visible spectral titration of $VOTPPCl_8$ in presence of H_2O_2/$NaHCO_3$ in CH_3CN/H_2O mixture and found no spectral changes are observed. So, we have carried out ^{51}V NMR experiments in order to ascertain the intermediate formed during the catalytic reaction. H_2O_2 and HCO_3^- are used together to increase the activity of H_2O_2 by the *in situ* generation of HCO_4^- which is more nuleophilic than H_2O_2 and thus attributes to the enhanced oxidizing activity of the metal complexes and to speed up the reaction.[18-22] Hence, in the presence of H_2O_2 and $NaHCO_3$, the solution of $VOTPPCl_8$ in DMSO-d_6 is converted into oxidoperoxidovanadium(V), $[VO(O_2)TPPCl_8]^-$ with a resonance at -618.4 ppm and remains stable for two days as shown in the Figure 6. The addition of cyclohexene decreases the peak intensity at -618.4 ppm by heating to 50 °C for 5 minutes (Figure 6c). Further, the peak at -618.4 ppm is completely diminished by adding excess of cyclohexene and heating at 50 °C for 10 minutes (Figure 6d). The peak appeared at -618.4 ppm in ^{51}V NMR indicates the formation of oxidoperoxidovanadium(V) species.[18,19,31-35] In general, oxidoperoxidovanadium(V) species,[18,19,31,33-35] $[VO(O_2)TPPCl_8]^-$ is more stable as compared to oxidohydroperoxidovanadium(V), $[VO(O\text{-}OH)TPPCl_8]$ species[32,33] in which hydroperoxide ion binds in side-on mode.[18,19,31-35] Hence, the 100% selectivity for epoxide formation in good yields (70-100%) from olefin to epoxide by $VOTPPCl_8$ catalyst is possibly due to the formation of oxidoperoxidovanadium(V) intermediate, $[VO(O_2)TPPCl_8]^-$ which converts olefin to expoxide selectively.[18,19] Further, we have carried out MALDI-TOF mass analysis to identify the catalytic intermediate. $VOTPPCl_8$ (0.02 mol%) was heated in presence of H_2O_2 (2 equiv.) and $NaHCO_3$ (0.4 equiv) in CH_3CN at 60 °C for 30 minutes. Then the reaction mixture was cooled to RT and subjected to MALDI-TOF mass analysis using HABA matrix. The peak at m/z 989.3 clearly indicates the formation of oxidoperoxidovanadium(V) species (Figure S7 in the ESI). Cyclohexene (0.410 g, 5 mmol) was added to the reaction mixture containing oxidoperoxidovanadium(V) species and heated to 60 °C for 30 minutes. In MALDI-TOF mass analysis, the disappearance of peak at m/z 989.3 indicates the consumption of oxidoperoxidovanadium(V) species (Figure S8 in the ESI). This experiment further proves the existence of oxidoperoxidovanadium(V) species as reaction intermediate in addition to ^{51}V NMR studies.

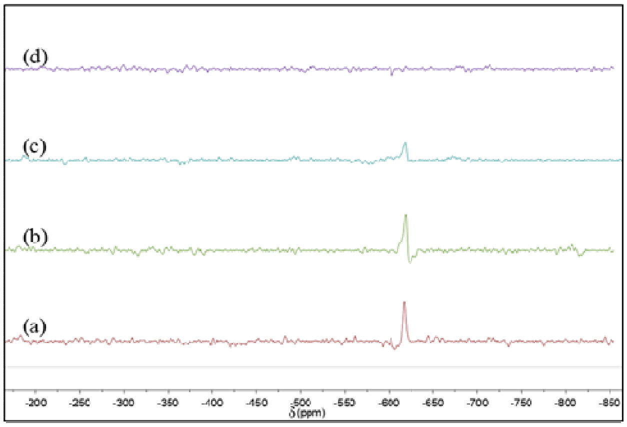


Figure 6. ^{51}V NMR spectra of $VOTPPCl_8$ (5.2 μmol) in DMSO-d_6 in the presence of: (a) 0.36 mmol of 30% aq. H_2O_2 and 0.3 mmol of $NaHCO_3$, 10 mins after addition, a peak appeared at -618.4 ppm; (b) after 48 hours; (c) 1.2 mmol of cyclohexene was added and heated for 5 mins at 50 °C; (d) large excess of cyclohexene was added and heated for 10 minutes at 50 °C.

The reason for very high TOF numbers (6566-9650 h^{-1}) is due to high thermal and chemical stability of $VOTPPCl_8$ which resist for thermal as well as chemical oxidative degradation and further bulkiness prevents the bimolecular attack. At the end, the obtained epoxide product was distilled off and catalyst was recovered. The isolated yields are approaching close to GC yields. For example, the isolated yields of 1-octene epoxide, *trans*-stilbene epoxide and *cis*-cyclooctene epoxide were found to be 94%, 84% and 93%, respectively. The UV-Vis absorption spectral features of $VOTPPCl_8$ didn't change before and after catalytic reaction indicating its high thermal and chemical stability as shown in Figure S9 in the ESI.

Conclusions

We have synthesized $VOTPPCl_8$ in good yield and characterized by various spectroscopic techniques. DFT optimized structure of $VOTPPCl_8$ in CH_3CN exhibited severe nonplanar saddle shape conformation and the oxidation state of metal ion (V^{IV}) was confirmed by EPR spectroscopy. CV studies revealed the electron deficient nature of porphyrin π-system by showing remarkable anodic shift in redox potentials as compared to VOTPP. $VOTPPCl_8$ showed very high thermal stability till 390 °C due to electron deficient nonplanar porphyrin core. Further, $VOTPPCl_8$ was utilized for the selective epoxidation of various olefins in good yields in presence of H_2O_2/$NaHCO_3$ in CH_3CN/H_2O mixture. The formation of oxidoperoxidovanadium(V) intermediate during catalytic cycle was probed by ^{51}V NMR studies and MALDI-TOF mass analysis. This porphyrin catalyst ($VOTPPCl_8$) has higher thermochemical stability and recyclability. However, anchoring of these catalysts in polymers or mesoporous materials (heterogenization) in high concentrations would be important for the commercial applications. Currently, we are working on the said topic and the results will be reported in the near future.

Experimental Section

Chemicals and materials

CH_3CN and DMF employed in the present work were of analytical grade and distilled before use. $VOSO_4$ and $NaHCO_3$ were obtained from HiMedia, India and used as received. Various alkenes used in this study were purchased from Alfa Aesar and used as received. Silica gel (100 - 200 mesh) used for column chromatography was purchased from Rankem, India and used as received. $TBAPF_6$ was obtained from Alfa Aesar, India and recrysatallized twice from ethanol followed by drying under vacuum at 60 °C for 10 h.

Instrumentation and methods

UV-Vis absorption spectra were measured in distilled CH_2Cl_2 using Agilent Cary 100 spectrophotometer. IR spectra were recorded in the mid IR range of 4000-400 cm^{-1} on a Perkin-Elmer spectrophotometer by making KBr pellets. Elemental analysis was carried out using Elementar Vario EL II instrument. ^{51}V NMR spectra were recorded on JEOL ECX 400 MHz spectrometer using DMSO-d_6 as a solvent containing 0.03% TMS (v/v). MALDI-TOF-MS spectra were measured using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer using HABA as a matrix. Cyclic voltammetric measurements were carried out using CHI 620E instrument in triple distilled CH_2Cl_2 containing 0.1 M $TBAPF_6$ as supporting electrolyte under argon atmosphere. A three electrode assembly was used consisting of a Pt disk working electrode, Ag/AgCl as a reference electrode and a Pt-wire as a counter electrode. Electron paramagnetic resonance spectra were obtained on a Bruker EMX EPR spectrometer in toluene solvent at 120 K. The spin Hamiltonian parameters were obtained from simulated EPR spectrum. Thermal analyses were performed with SII EXSTAR 6300 instrument. DFT studies were carried out using B3LYP functional with LANLD2Z basis set. The oxidation products were quantified using a Shimadzu 2010 plus gas-chromatograph equipped with an Rtx-1 capillary column (30 m × 0.25 mm × 0.25 µm) and an FID detector. GC-MS analyses were carried out using Perkin-Elmer GC-MS (Clarus 500).

Synthesis of 2,3,7,8,12,13,17,18-octachloro-*meso*-tetraphenylporphyrinato vanadium(IV) ($VOTPPCl_8$):

H_2TPPCl_8 (0.18 g, 0.202 mmol) was dissolved in 40 mL of DMF. To this, 10 equiv. of $VOSO_4$ (0.518 g, 2.02 mmol) was added and refluxed for 16 hours under argon atmosphere. At the end of this period the reaction mixture was cooled to room temperature and then 120 mL of distilled water was added. Porphyrin was precipitated out and filtered through G-4 crucible. The crude product was purified on silica column using $CHCl_3$ as eluent. Yield was found to be be 0.152 g (0.16 mmol, 79%).

UV-Vis (CH_2Cl_2): λ_{max} (nm) (logε) 354 (4.01), 452 (5.15), 578 (4.00), 618 (sh); IR (KBr, cm^{-1}) 1003 ($\nu_{V=O}$); MALDI-TOF-MS (m/z): found 954.95 $[M]^+$, calcd. 954.96; elemental analysis calcd. for $C_{44}H_{20}N_4Cl_8VO$: C, 55.32%; H, 2.11%; N, 5.87% and found: C, 55.23%; H, 2.28%; N, 5.98%.

Catalytic activity studies

The catalytic efficiency of $VOTPPCl_8$ was tested for the oxidation of various alkenes. In a typical catalytic experiment, 5 mmol (0.410 g) cyclohexene, 10 mmol 30 % H_2O_2 (1.13 g), 1 mmol $NaHCO_3$ (0.084 g) and 5.23×10^{-4} M (0.0005 g) of $VOTPPCl_8$ were added into a 5 mL of CH_3CN in a round bottom flask fitted with a condenser. The flask was placed in an oil bath and the temperature was kept 60 °C throughout the reaction time with 500 RPM mechanical stirring. After the reaction was finished, reaction mixture was filtered and its 1 mL portion was subjected to multiple heptane extraction. The extract was concentrated and its 0.2 µL was injected to the GC/GC-MS. The oxidation products were quantified using a Shimadzu 2010 plus gas-chromatograph equipped with an Rtx-1 capillary column (30 m × 0.25 mm × 0.25 µm) and an FID detector. The product identities were confirmed by a Perkin-Elmer GC-MS (Clarus 500).

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