

Chapter 4:
Alkene epoxidation catalyzed by
vanadium heteropoly acids dispersed on
hydrated titania

4.1 Introduction

Epoxides are one of the essential precursors for the synthesis of various important substances like plasticizers, perfumes, epoxy resins, etc, thus epoxidation reactions assume significant importance in the chemical industries. Many catalytic systems containing transition metal ions have been exploited for the epoxidation of alkenes in the past. In recent years, transition metal-substituted polyoxometalates based catalysts have gained considerable interest due to their multi versatilities for the oxidation of organic substrates [1-3]. Transition metal substituted polyoxometalates (TMSP) generally provide higher conversion and better selectivity for epoxides [4-7]. Amongst the TMSP, vanadium-substituted polyoxometalates are the most studied ones that have attracted the attention as catalysts for a variety of catalytic oxidation reactions like hydroxylation of benzene, oxidation of toluene and nitrobenzene with aqueous hydrogen peroxide, oxidation of isobutyric acid to methacrylic acid with molecular oxygen and so on [8-15].

Although, the activity of vanadomolybdophosphoric acids is well documented, most of the current examples demonstrate their catalytic applications as a homogenous catalyst [16-18]. Alternatively, they are heterogenized by anchoring them onto amine-functionalized SBA-15 and other mesoporous materials [19-20] or by impregnation on inert supports like silica, alumina or zirconia and further calcination at high temperatures [21-23]. The former strategy is generally applied for oxidation reactions while latter one is generally applied for acid catalyzed reactions. Both these methods have their own drawbacks like multi step synthesis of catalyst materials and time as well as energy consuming calcination steps respectively. So the simple strategy applied here was the wet impregnation of vanadomolybdophosphoric acids on a support and carry out the reactions in non-polar or hydrophobic solvents, so as to minimize the dissolution of these polar molecules and maintain the heterogeneity of the catalyst. Thus, in the current system vanadomolybdophosphoric acids were wet impregnated on two important support materials namely, $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ or $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$. After drying, these supported catalysts were tested for their activities in alkene epoxidation. Interestingly, amongst the two supports, titania supported vanadomolybdophosphoric acids showed a higher activity than the zirconia analogue. This higher activity of the former may be explained on the basis of the synergistic effect between heteropoly acid and the titania support, as we shall see further.

The mere wet-impregnation step of heteropoly acids on titania, however deprived us from using *aq.* H₂O₂ and *aq.* TBHP as oxidants, since the water component of these oxidants dissolves the heteropoly acids easily, thereby losing the heterogeneous behavior of these catalysts. Thus the oxidant used here was TBHP extracted in dichloroethane, or other hydrophobic solvents. This has refrained in having a comparative data of the catalytic activity with different oxidants for this system. Although the use of hydrophilic solvent like acetonitrile increased the catalytic activity as compared to the activity in dichloroethane, most of the heteropoly acid was lost due to its dissolution in the former. As a result the subsequent catalytic activity reduced drastically in further runs for such hydrophilic solvent systems. The dissolution of heteropoly acids in hydrophilic solvents may be the reason behind the initial higher activity displayed in the same. Although the additives like TBHP dissolve the heteropoly acid to some extent even in the dichloroethane solvent system, it is observed that there is not much loss in activity for next two subsequent runs, as shall be seen further. Importantly, in all the cases the major product was always the corresponding epoxide.

4.2 Experimental

4.2.1 Materials

Phosphomolybdic acid (PMA), phosphotungstic acid (PTA), titanium *t*-butoxide and zirconyl nitrate were purchased from Loba Chemie India Ltd. 1,2-dichloroethane, acetonitrile, methanol, ether and other solvents were procured from Merck India Ltd. All the alkenes were obtained from Aldrich, while 70% aqueous TBHP was obtained from Fluka. Sodium molybdate and sodium metavanadate were availed from S.D. fine chemicals India Ltd. All the chemicals were used as received without further purification. TBHP/DCE was prepared by shaking appropriate volumes of 70% *aq.* TBHP and 1,2 dichloroethane in a separating funnel and collecting the dichloroethane (DCE) layer, and drying it over anhydrous sodium sulfate.

4.2.2 Preparation of vanadomolybdophosphoric acids

Mono, di and tri vanadomolybdophosphoric acids (hereafter denoted by V_xHPA, where x = 1, 2 and 3 respectively) were synthesized by a reported procedure and their formation was checked by FT-IR and elemental analysis [24, 25].

4.2.2.1 Monovanadomolybdophosphoric acid, $H_4PMo_{11}VO_{40}$ (V_1HPA)

Sodium phosphate dibasic dodecahydrate (1.77 gm, 5 mmol), was dissolved in 25 ml water and mixed with sodium metavanadate (1.52 gm, 12.5 mmol) that was dissolved in 25 ml boiling water. The mixture was cooled and acidified to red color with 1.25 ml concentrated sulfuric acid. To this colored solution was added sodium molybdate dihydrate (33.25 gm, 137.42 mmol) in 50 ml of water. Finally 21.25 ml of concentrated sulfuric acid was added. Color of the solution became light red. After cooling the solution was extracted with four fractions each of 25 ml diethyl ether to isolate the heteropoly acid in a separating funnel. In this extraction the heteropoly etherate was present as the middle layer. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that separated was dissolved in water, concentrated to the first appearance of crystal in a vacuum desiccator over concentrated sulfuric acid and then allowed to crystallize further. The orange crystals that formed were dried, crushed and used for further studies.

4.2.2.2 Divanadomolybdophosphoric acid, $H_5PMo_{10}V_2O_{40}$ (V_2HPA)

Sodium metavanadate (4.06gm, 33.29 mmol) was dissolved by boiling in 16.6 ml water and then mixed with a solution of sodium phosphate dibasic dodecahydrate (1.18 gm, 3.29 mmol) in 16.6 ml water. To the cooled solution was added 0.83 ml of concentrated sulfuric acid. The resulting solution developed a red color. Addition of sodium molybdate dihydrate (20.16 gm, 83.32 mmol) in 50 ml water was then done. While the solution was stirred vigorously 14.16 ml of concentrated sulfuric acid was added slowly and then the hot solution was cooled to room temperature. The title compound was then extracted with four fractions each of 20 ml diethyl ether in a separating funnel. The heteropoly acid was present as the etherate in the bottom layer. This layer was isolated and dried in order to make it ether free. Orange colored solid was obtained after complete drying. Pure complex was obtained after recrystallization in water. The crystals that formed were dried and crushed for further use.

4.2.2.3 Trivanadomolybdophosphoric acid, $H_6PMo_9V_3O_{40}$ (V_3HPA)

Sodium phosphate dibasic dodecahydrate (1.77 gm, 4.95 gm) was dissolved in 12 ml water. Sodium metavanadate (9.15 gm, 75.04 mmol) was made soluble by boiling in 50 ml water. The sodium phosphate solution was mixed with the sodium

metavanadate solution. The resulting solution was cooled, followed by the addition of 1.25 ml of concentrated sulfuric acid. This red colored solution was then added to a solution of sodium molybdate dihydrate (13.62 gm, 56.3 mmol) in 37.5 ml water. This solution was stirred vigorously and simultaneously 21.25 ml of concentrated sulfuric acid was added. The hot solution was cooled to ambient conditions. The heteropoly acid formed was extracted with four fractions, each of 25 ml diethyl ether in a separating funnel. The heteropoly acid is present as the etherate in the middle fraction. The middle layer was then isolated, dried to free of ether. The resulting red colored solid obtained was dissolved in water, concentrated to first crystal formation and allowed to crystallize further. The red crystals that formed were dried and powdered prior to further use.

4.2.3 Sample Preparation

Hydrated titania ($\text{TiO}_2 \cdot x\text{H}_2\text{O}$) was prepared by hydrolysis of 1M titanium *t*-butoxide solution (in ethanol) with distilled water and hydrated zirconia ($\text{ZrO}_2 \cdot x\text{H}_2\text{O}$) was prepared by treating 1M zirconyl nitrate solution (aqueous) with 1:1 ammonia solution. Both the supports $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ and $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ were dried at 110°C prior to use. 15 wt% HPA/ MO_2 samples were prepared by wet impregnation method. Here HPA stands for heteropoly acids and MO_2 stand for hydrated titania or hydrated zirconia. In a typical procedure 0.15 g of the heteropoly acid was dissolved in 4 ml of methanol, and to the same solution 0.85 g of hydrated titania or hydrated zirconia was added and stirred at room temperature overnight (approximately 12 h). Excess of solvent was removed on a rota-vapor and the solid samples were dried at 110°C.

4.2.4 Characterization

The room temperature powder X-ray diffraction patterns of the samples were collected on a Philips X' Pert Pro 3040/60 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), nickel filter and X'celerator as detector. Solid state UV-visible spectra were recorded on Perkin-Elmer lambda-350 UV visible spectrophotometer. FT-IR spectra were recorded on Shimadzu FTIR 8201 PC instrument. ICP analysis was done on Perkin Elmer Plasma 1000 Emission Spectrometer.

4.2.5 Catalytic activity

The liquid phase epoxidation reactions were carried out in a two-necked 50 ml round bottom flask immersed in a thermostated oil bath maintained at desired temperature between 40-80°C. Prior to use the HPA/MO₂ catalysts were activated at 110°C. A typical reaction mixture consisted of 0.1 g of activated catalyst, 10 mmol of substrate, 20 mmol of 30% TBHP and 10 ml of dichloroethane. The reaction mixture was stirred with a Teflon-coated magnetic bar for a stipulated time interval of 5 h every time. Progress of the reaction was monitored by drawing small aliquots of the reaction mixture at regular intervals and subjecting them to GC analysis (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m × 0.32 mm 5% phenyl methylsilicone capillary column). The products were unambiguously identified by GC-MS (Shimadzu gas chromatograph, G-17A fitted with QP-500 MS Mass spectrometer) as per requirement.

4.3 Results and Discussion

4.3.1 Catalyst Characterization

Experimental data showed that the 15 wt% V₂HPA/TiO₂ was exceptionally active as catalyst for various epoxidation reactions, hence only this catalyst was studied in detail. The 15 wt% V₂HPA/TiO₂ was characterized using powder XRD, FTIR and UV-visible spectroscopy and the results of which are discussed in this chapter. The 15 wt% V₂HPA/TiO₂ catalyst along with the neat V₂PMA and TiO₂.xH₂O dried at 110°C were subjected to powder XRD, and the XRD patterns can be seen in Figure 1. No additional peak of divanadomolybdophosphoric acid (V₂PMA) was seen in the XRD pattern of 15 wt% V₂PMA/TiO₂ indicating that the supported compounds are amorphous or their size is too small and cannot be detected by XRD.

To show the presence of V₂PMA on the surface of titania, the catalyst (15 wt% V₂PMA/TiO₂), the support (TiO₂.xH₂O) and the neat V₂PMA acid were also subjected to solid state UV-visible spectroscopy and the spectra can be seen Figure 2. The absence of any peaks in the visible region (400-800 nm) for TiO₂.xH₂O, but the sharp bands seen at 470 nm for 15 wt% V₂PMA/TiO₂ corresponding to V₂PMA indicate that the presence of the V₂HPA on the surface of TiO₂.xH₂O. The minimal shift in the bands from neat V₂PMA to the impregnated one may be due to change in

environment, degree of hydration or additional interactions with the hydroxyl groups of the support. The bands corresponding to V₂PMA and TiO₂ overlap with each other in the ultraviolet region (200-400 nm).

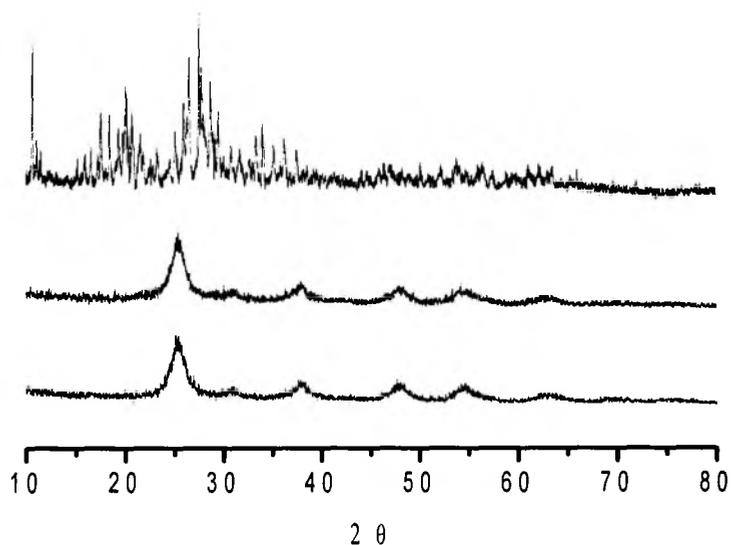


Figure 1: Powder XRD patterns of (a) neat V₂PMA (top), (b) 15% V₂PMA/TiO₂ (center) and (c) TiO₂.xH₂O dried at 110°C (bottom)

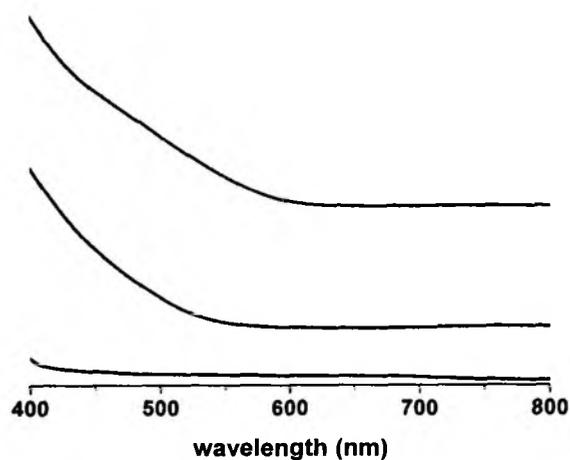


Figure 2: Solid state UV-visible spectra of (a) neat V₂PMA (top), (b) 15% V₂PMA/TiO₂ (center) and (c) TiO₂.xH₂O dried at 110°C (bottom)

Additional evidence to show the presence of divanadomolybdophosphoric acid on the support hydrated titania is given by FTIR. As seen in figure 3, the first line shows the FTIR spectrum of divanadomolybdophosphoric acid. The characteristic peaks of 1063 cm^{-1} for $\text{P-O}_t\text{-Mo}$, 961 cm^{-1} for Mo=O_t and 870 cm^{-1} and 785 cm^{-1} for $\text{Mo-O}_b\text{-Mo}$, where O_t , O_t and O_b are the inner, terminal and the bridging oxygen atoms respectively in a Keggin unit, can be seen clearly in the same [25]. Similarly the third line shows the FTIR spectrum of hydrated titania. In this spectrum no intense peak is observed in the region from 1200 to 400 cm^{-1} . Although the second line, which corresponds to $15\text{ wt}\% \text{ V}_2\text{HPA/TiO}_2$, also does not show any bands in the above seen region, very small peaks at 1063 and 961 cm^{-1} are clearly seen in this line. These peaks correspond to divanadomolybdophosphoric acid as shown in line 1 (Fig 3). This gives sufficient evidence to show that divanadomolybdophosphoric acid is present on the surface of titania, and that it has maintained its Keggin structure even after impregnation on hydrated titania and also during its activation, at 110°C .

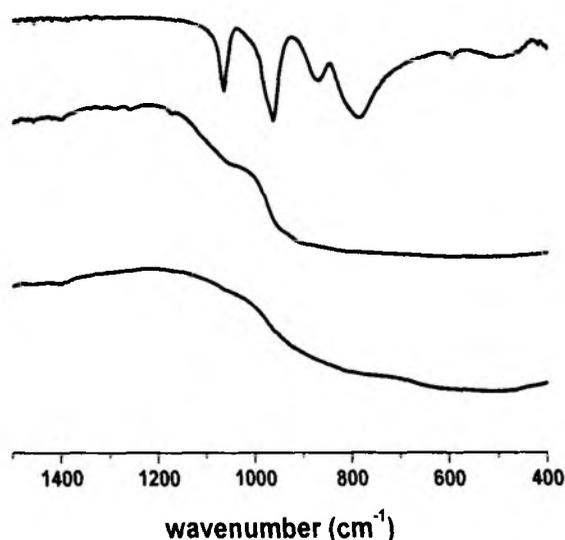


Figure 3: FT-IR spectra of (a) neat V_2PMA (top), (b) $15\% \text{ V}_2\text{PMA/TiO}_2$ (center) and (c) $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ dried at 110°C (bottom)

4.3.2 Effect of solvent on the reaction

The solvents used for the reaction were either dichloroethane or acetonitrile and in both the cases the oxidant used was 30% TBHP/DCE. Thus cyclooctene gave 94% conversion in dichloroethane solvent after 5 h of reaction time and 98% conversion in acetonitrile solvent after 3 h of reaction time, at 80°C reaction temperature for both the solvent systems. Hence, acetonitrile is a better solvent for the above reaction. However, when the reaction was stopped after 1.5 h and continued again after filtering off the catalyst, for both the solvent systems, it was observed that there was not much increase in the conversion for dichloroethane (*ca* 6%), but for acetonitrile, the conversion continues to increase steeply and steadily with time and the total increase in conversion was *ca* 37% as can be seen in Figure 4.

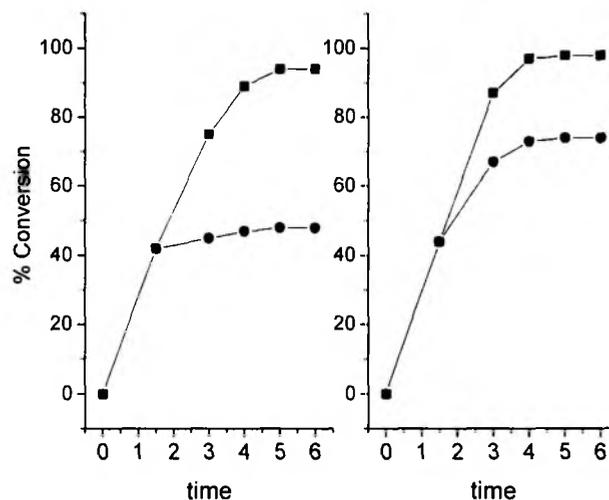


Figure 4: Leaching test for cyclooctene epoxidation over 15% V₂PMA/TiO₂ in 1, 2 dichloroethane (left) and acetonitrile (right) solvents. *Reaction conditions:* catalyst: 0.1 g, alkene: 10 mmol, TBHP/DCE: 20 mmol, Solvent: 10 ml, temperature: 80°C. (■: without filtration, ●: after filtration)

Thus, it was seen that substantial amount of divanadomolybdophosphoric acid had leached into the reaction mixture in acetonitrile as compared to dichloroethane, owing to the high solubility of heteropoly acids in the former. To substantiate this point, the above filtrates were subjected to ICP analysis and it was found that 7.1% of the total vanadium and 6.8% of the total molybdenum present in the reaction mixture had leached in the case of dichloroethane; however for acetonitrile 41.4% vanadium

and 42.2% molybdenum were observed to have leached. This obviously led us to check the recycling behavior of the catalyst in dichloroethane solvent. It was found that the conversion of cyclooctene had slightly decreased from 94% to 91% in the second run, and further to 86% in the third run. Thus, although the conversion had decreased, the magnitude was very small (8%). Similarly, recycling behavior of the catalyst (15 wt% $V_2\text{HPA}/\text{TiO}_2$) was investigated for some other alkenes *viz.* norbornene and limonene in dichloroethane solvent. Even for these two alkenes, there was not much drop in conversion up to first three runs (7% and 5% respectively). The minimal leaching of divanadomolybdophosphoric acid, in the case of dichloroethane solvent system is attributed to the slight dissolution of the heteropoly acids in the additives *viz.* TBHP and *t*-butanol formed during the course of reaction from TBHP. Importantly, no leaching of divanadomolybdophosphoric acid (from 15 wt% $V_2\text{HPA}/\text{TiO}_2$) was observed in neat dichloroethane, even at refluxing conditions. Further, consistency in the catalytic activity of 15 wt% $V_2\text{HPA}/\text{TiO}_2$ for three consecutive runs reiterates the fact that heteropolyacids do not decompose when TBHP is used as the oxidant. It is known that heteropolyacids decompose very rapidly when aqueous hydrogen peroxide is used as the oxidant.

4.3.3 Epoxidation of cyclooctene with different 15 wt% HPA/ MO_2

Epoxidation of cyclooctene was performed with different 15 wt% HPA/ MO_2 catalysts. Amongst them 15 wt% $V_2\text{HPA}/\text{TiO}_2$ was a better catalyst for the reaction as can be seen in Table 1. In order to investigate its higher activity over other 15 wt% HPA/ MO_2 catalysts, an attempt was made to explore the role of vanadium, titanium and other transition metal ions in the system. So few controlled experiments were conducted with different 15 wt% HPA/ MO_2 catalysts using TBHP/DCE as the oxidant and dichloroethane as the solvent, and the results are presented in Table 1. It can be seen from the results (Table 1) that even 15 wt% PMA/ TiO_2 (where PMA stands for phosphomolybdic acid) was also active for this reaction but showed a poor activity. Thus for the same reaction with TBHP/DCE as the oxidant, only 32% Cyclooctene conversion was seen 15 wt% PMA/ TiO_2 as against 94% conversion observed for 15 wt% $V_2\text{HPA}/\text{TiO}_2$ at the same set of reaction conditions, since vanadium substituted phosphomolybdic acids are better catalysts than neat phosphomolybdic acid [26]. Further, phosphomolybdic acid is a better catalyst than

phosphotungstic acid in oxidation reactions [26], thus 15 wt% PTA/TiO₂ (where PTA stands for phosphotungstic acid) failed to show any activity for the same reaction, with TBHP/DCE as oxidant. Although, phosphotungstic acid is known to have an excellent catalytic activity for oxidation reactions with aqueous H₂O₂ [27], it failed to show any activity with TBHP. TBHP/DCE was chosen as an oxidant over aqueous TBHP because the latter is typically immiscible with dichloroethane. Among the three vanadomolybdophosphoric acid catalysts, only 15 wt% V₂HPA/TiO₂ showed higher activity (94% conversion) in the oxidation of cyclooctene. The other two catalysts i.e. 15 wt% V₁HPA/TiO₂ and 15 wt% V₃HPA/TiO₂ gave only 44% and 89% conversion, respectively under the same reaction conditions. It is already known from the literature that as the number of vanadium substituents in phosphomolybdic acid increases from one to two, the catalytic activity of the heteropoly acid also increases [18, 28]. However, on increasing the number of vanadium substituents in phosphomolybdic acid from two to three, not much change in activity is observed. Similar to the role of vanadium, it was also checked whether titanium from the support is also playing any role or not. So two samples containing 15 wt% V₂HPA/TiO₂ and 15 wt% V₂HPA/ZrO₂ were prepared in similar manner and their activities were checked in oxidation of cyclooctene under similar conditions. The 15 wt% V₂HPA/TiO₂ catalyst showed *ca.* 94% conversion to give cyclooctene epoxide while 15 wt% V₂HPA/ZrO₂ catalyst gave only 20% conversion as seen in Table 1. It may also be seen in the table that the neat supports (neat 110°C dried TiO₂.xH₂O and ZrO₂. xH₂O) do not catalyze the reaction at all. Thus, it is assumed that the higher activity of 15 wt% V₂HPA/TiO₂ catalyst is due to the synergistic effect between the heteropoly acid and titania support. Such synergistic effect between titania and heteropoly acids has earlier been observed in photo catalytic reactions [29].



Table 1: Selective oxidation of cyclooctene over various 15% HPA/MO₂ with 30% TBHP/DCE

Entry	Catalyst	% Conversion	% Selectivity (epoxide)
1.	PMA/TiO ₂	32	>99
2.	V ₁ PMA/TiO ₂	44	>99
3.	V ₂ PMA/TiO ₂	94	>99
4.	V ₃ PMA/TiO ₂	89	>99
5.	V ₂ PMA/ZrO ₂	20	>99
6.	PTA/TiO ₂	<1	-
7.	TiO ₂ .xH ₂ O	<1	-
8.	ZrO ₂ .xH ₂ O	<1	-

Reaction Conditions: 0.1 g of catalyst, 10 mmol of cyclooctene and 20 mmol of 30% TBHP and 10 ml of 1,2-dichloroethane, temperature: 80°C, time: 5 h.

4.3.4 Effect of temperature and substrate: oxidant ratio on cyclooctene epoxidation

The oxidation of cyclooctene with the oxidant of TBHP/DCE over 15 wt% V₂HPA/TiO₂ catalyst was carried out with cyclooctene: TBHP/DCE mol ratio of 1:2 in the temperature range 40–80°C. The cyclooctene conversion increased with increase in temperature. Thus after 5 h of reaction, only 31%, 41% and 52% conversion of cyclooctene were observed at 40°C, 50°C and 60°C of temperatures, respectively, as against 94% conversion achieved at 80°C in the same time interval. Interestingly cyclooctene epoxide was the only product obtained at all these temperatures.

Kinetic measurements for cyclooctene oxidation were carried out as a function of temperature and the results are plotted in Figure 5 and the data showed the reaction to be first order with respect to cyclooctene concentration. The rate constants at different reaction temperature between 40°C and 60°C were obtained by subjecting the data to linear regression as shown in Figure 5. Arrhenius equation was used with above rate constant data to estimate the activation parameters for the cyclooctene epoxidation reaction (inset, Figure 5). The activation energy was 7.21 ± 0.32 kcal/mol and the enthalpy of activation was 6.61 ± 0.39 kcal/mol. The obtained activation energy although seems to be low, is typical for oxygen transfer reactions [30].

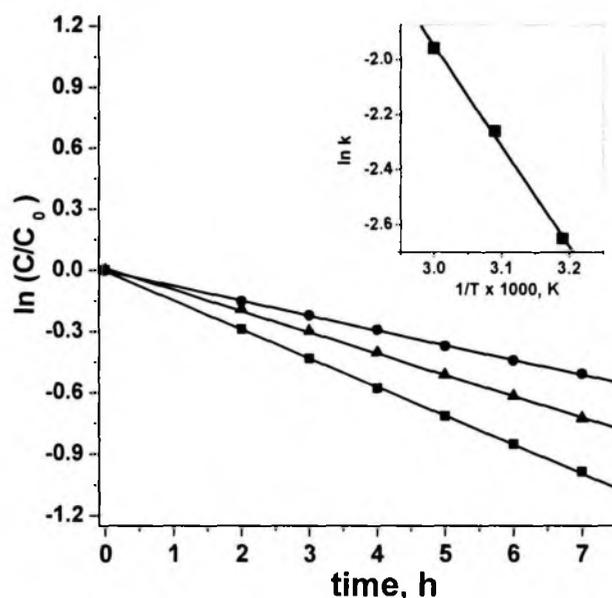


Figure 5: Kinetic profiles of cyclooctene epoxidation reaction as a function of temperature and their linear fittings (■: 60°C, ▲: 50°C, ●: 40°C). Reaction condition: catalyst: 0.1 g, alkene: 10 mmol, 30% TBHP/DCE: 20 mmol. (Inset: a plot of the measured rate constants as a function of temperatures in an Arrhenius plot)

In an attempt to optimize the amount oxidant TBHP/DCE needed for maximum cyclooctene conversion, experiments were carried out under similar reaction conditions and the results are shown in Figure 6. With cyclooctene: TBHP/DCE mol ratio of 1:1, the maximum conversion was 46% after 5 h. With cyclooctene: TBHP/DCE mol ratio of 1:2, it was 94% in the same time interval, and with 1:3 mol ratio, the cyclooctene conversion was nearly the same as that of 1:2 mol ratio. Thus it was indicated that the cyclooctene: TBHP/DCE mol ratio of 1:2 was optimum to obtain a satisfactory yield of the corresponding epoxide with this catalyst. Thus the substrate: TBHP/DCE mol ratio of 1:2 was employed in further epoxidation reactions.

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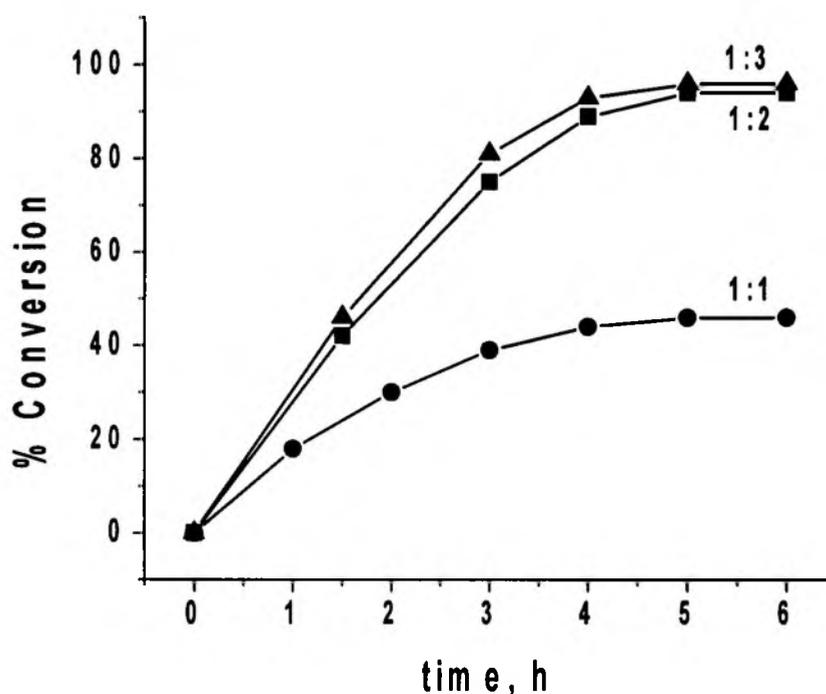
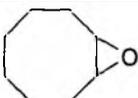
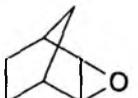
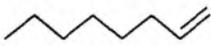
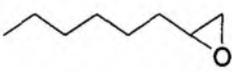
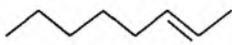
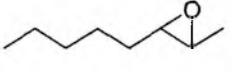
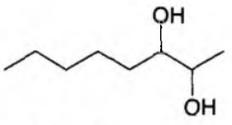
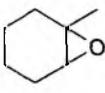
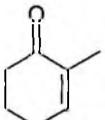
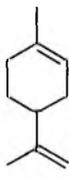
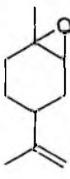


Figure 6: Epoxidation of cyclooctene with different substrate: oxidant ratios. Reaction conditions: Reaction condition: catalyst: 0.1 g, alkene: 10 mmol, 30% TBHP/DCE: 20 mmol

4.3.5 Epoxidation of other alkenes

Apart from cyclooctene, the epoxidation behavior of yet another industrially important alkene viz. norbornene was investigated, over 15 wt% V_2PMA/TiO_2 catalyst, with TBHP/DCE as oxidant and dichloroethane as the solvent at 80°C. In this case also, almost 100% selectivity for the corresponding epoxide was obtained at 87% conversion after 5 h, as can be seen in Table 2. Similarly, epoxidation of some more alkenes like 1-octene, trans-2-octene, and 1-methyl-1-cyclohexene was studied over 15 wt% V_2PMA/TiO_2 catalyst. The results are presented in Table 2. It was observed that an increase in the number of substitutions on the carbon-carbon double bond enhanced the reactivity of the alkenes. Thus, for 1-octene which is a mono-substituted alkene with respect to the olefinic bond, the conversion was 11% after 5 h, however, for a di-substituted alkene like trans-2-octene it was 21% and for a tri-substituted alkene like 1-methyl-1-cyclohexene was 40%, after the same time interval.

Table 2: Selective oxidation of various alkenes over 15% V₂HPA/TiO₂ with 30% TBHP/DCE

Entry	Substrate	% Conversion	Product	% Selectivity
1.		94		>99
2.		87		>99
3.		11		>99
4.		21		87
				13
5.		40		75
				25
6.		73		54
				29
				17

Reaction Conditions: 0.1 g of catalyst, 10 mmol of alkene and 20 mmol of 30% TBHP and 10 ml of 1,2-dichloroethane, temperature: 80°C, time: 5 h.

For all these alkenes, epoxide was always the major product (> 75 %). The by-product of glycol in the case of *trans*-2-octene possibly formed further from the epoxide, under the virtue of acidity present in heteropoly acid part of the catalyst system. The by-product of ketone in the case of 1-methyl-1-cyclohexene might have formed owing to the allylic oxidation. Similar by-products were also observed by others [30]. The activity was further extrapolated to limonene, a diene with one di-substituted and one tri-substituted double bond. Here, the two individual mono-epoxides along with some di-epoxide were obtained and as seen above the selectivity for epoxidized tri-substituted double bond was more than the di-substituted counterpart.

4.4 Summary and Conclusion

The results clearly indicate that divanadomolybdophosphoric acid wet-impregnated on hydrated titania ($\text{TiO}_2 \cdot x\text{H}_2\text{O}$) makes an excellent catalyst system for alkene epoxidation, with TBHP extracted in dichloroethane as the oxidant. The catalysts can be recycled without much loss in activity at least three times by choosing appropriate solvent for the reaction. For all the alkenes seen here the major product is always the corresponding epoxide. The controlled experiments unambiguously indicate that the vanadium substitutions in the heteropoly acid as well as the titanium species from the support have a role to play. Thus a simple catalytic system, which is free of high temperature calcination steps and tedious multi-step procedures, normally encountered in heterogenization of heteropoly acids, is demonstrated hereby.

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