Oxidation of norbornene over vanadium-substituted phosphomolybdic acid catalysts and spectroscopic investigations

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Abstract

Oxidation of norbornene has been carried out over mono-, di- and tri-vanadium-substituted phosphomolybdic acid catalysts with aqueous hydrogen peroxide (aq. H_2O_2) as an oxidant in different solvents. Monovanadium-substituted phosphomolybdic acid catalyst was found to be better than other catalysts for the above reaction and acetonitrile was the suitable solvent. At the optimum temperature of 60 °C, the norbornene conversion was 70% and the selectivity for 2,3-epoxy norbornane was 58%. The side products were norborneols and 2-norbornanone. The lower selectivity of 2,3-epoxy norbornane with aq. H_2O_2 is attributed to the simultaneous formation of other products, norborneols and 2-norbornanone. The norborneols are formed from norbornene by acid-catalyzed reaction. Other oxidants like urea–hydrogen peroxide adduct (UHP) and *tert*-butyl hydrogen peroxide (TBHP) were also tested for norbornene oxidation reaction. With UHP, the conversion was almost same (69%) as that of aq. H_2O_2 reaction; however, 2,3-epoxy norbornane was the main product with >97% selectivity. Thus, the overall yield was 66.9% at 60 °C after 4 h. The high selectivity with UHP is attributed to the controlled release of H_2O_2, absence of water and less acidic nature of UHP. With TBHP the selectivity for the epoxide was >96%; however, the conversion was low (27%). A mechanism for the norbornene oxidation is believed to be proceeding via V(5+)-peroxo and V(4+)-superoxo intermediates. NMR, EPR and UV–vis spectroscopic techniques were employed to understand the reaction intermediates and reaction pathways.

1. Introduction

Epoxides are the essential precursors in the synthesis of various important substances like plasticizers, perfumes, epoxy resins, etc, and thus epoxidation reaction assumes significant importance. Amongst oxidizing agents employed for epoxidation reactions, hydrogen peroxide is the highly versatile oxidant as it is easy to handle, water is the only co-product and it also has high oxygen atom efficiency [1,2]. Many catalytic systems containing transition metal ions have been exploited for the oxidation of organic substrates. In recent years, transition metal-substituted polyoxometalates-based catalysts have gained considerable interest due to their multi versatilities for the oxidation of organic substrates [3]. Transition metal substituted polyoxometalates generally provide higher conversion and better selectivity, particularly with environmentally friendly oxidants such as hydrogen peroxide, air, etc [4]. Among the polyoxomolybdates, vanadium-substituted polyoxometalates are the most studied ones that have attracted the attention as catalysts for a variety of catalytic oxidation reactions. For example, hydroxylation of benzene with aqueous hydrogen peroxide, oxidation of toluene and nitrobenzene with aqueous hydrogen peroxide, oxidation of isobutyric acid to methacrylic acid, etc [5,6].

Norbornene and its derivatives like epoxy norbornane, diol, etc. have wide applications in polymers synthesis, pharmaceutical intermediates, general organic synthesis, etc [7]. Oxidation of norbornene has been carried out by many cat-

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alytic systems. In most of the cases, the selectivity and thus the yield to the epoxide is moderate [8]. Patel et al. have carried out oxidation of norbornene with *tert*-butyl hydroperoxide (TBHP) using a polymer-supported manganese catalyst at 40 °C [9]. After 24 h, a maximum selectivity of the epoxide observed was only 45%. Koner et al. [10] also carried out the oxidation of norbornene with TBHP over Cr(salen) catalyst immobilized in MCM-41, where exo and endo norborneols were the major products. There have been many reports on the epoxidation of norbornene using iodosylbenzene as the oxidant over different catalysts [11]. But, the epoxide yield was found to be less in most of the cases. Epoxidation of norbornene using CsCl-promoted Ag/Al$_2$O$_3$ catalyst was carried out with air as an oxidant with high selectivity, but at a temperature of 225 °C [12]. Epoxidation using Co(III) acetylacetonate [13] at temperature ranging from 60 to 130 °C under 10 kg cm^{-2} pressure of O$_2$ gave a selectivity of 43% to the epoxide after 18 h. Kamata et al. [14] have recently reported the epoxidation of various olefins including norbornene with hydrogen peroxide using a lacunary silicotungstate, [γ-SiW$_{10}$O$_{34}$(H$_2$O)$_2$]$^{4-}$, with high selectivity based on H$_2$O$_2$. However, the yield based on the substrate was low.

Our current interest is to exploit vanadium-substituted phosphomolybdate-based catalysts for the oxidation of higher alkenes and to understand their reaction mechanism. Herein, we report epoxidation of norbornene, using different oxidants under various experimental conditions, and spectroscopic studies.

2. Experimental section

2.1. Materials

Di-sodium hydrogen phosphate dodecahydrate, sodium molybdate dihydrate, sodium meta vanadate, phosphomolybdic acid and tetrabutyl ammonium bromide (Loba Chemicals), conc. H$_2$SO$_4$ were used as received for the preparation of vanadium-substituted phosphomolybdic acid. Norbornene, 30% aq. H$_2$O$_2$ and TBHP were purchased from Merck. Diethyl ether, acetonitrile, methanol and acetone (S.D. fine) were of analytical grade and used without further purification. UHP was prepared as per the reported procedure [15]. The exact strength of hydrogen peroxide was determined by redox titration with KMnO$_4$ solution.

2.2. Catalyst preparation

The mono-, di- and tri-vanadium-substituted phosphomolybdic acids (H$_4$[PV$_1$Mo$_{11}$O$_{40}$]·19H$_2$O, H$_5$[PV$_2$Mo$_{12}$O$_{40}$]·14H$_2$O, and H$_5$[PV$_3$Mo$_9$O$_{40}$]·14H$_2$O were prepared according to the method developed by Tsigdinos and Hallada [16]. Aqueous solutions of Na$_2$HPO$_4$·12H$_2$O, NaVO$_3$ and Na$_2$MoO$_4$·H$_2$O were mixed in appropriate molar ratios in acidic medium. The polyoxometalate formed was

extracted with diethyl ether and dried. The powder was recrystallized from water, air-dried and stored over conc. H$_2$SO$_4$ in a desiccator. The number of water molecules was estimated from TGA measurements. Tetrabutyl ammonium salt of H$_4$[PV$_1$Mo$_{11}$O$_{40}$]·19H$_2$O (Q$_4$[PV$_1$Mo$_{11}$O$_{40}$], Q = Bu$_4$N$^+$) was prepared as per the reported procedure [5c].

2.3. Characterization

The freshly prepared catalyst was characterized by IR, UV–vis, NMR and EPR spectroscopic techniques and by thermogravimetric analysis. The IR spectra of the sample were recorded on a Shimadzu FTIR 8201 PC instrument. The UV–vis spectra of the catalysts were recorded in acetonitrile on a Shimadzu UV-2550 PC UV–vis spectrometer in the region of 200–900 nm. Room-temperature EPR spectra were recorded on a Bruker EMX X-band spectrometer operating at 100 kHz field modulation at microwave frequency, 9.766 GHz. The microwave frequency was calibrated using a frequency counter of the microwave bridge ER 041 XG-D. Bruker Simfonia and WINEPR software packages were used in the spectral simulations and to calculate hyperfine coupling constant. The spectra were recorded by taking the polycrystalline samples in a quartz tube and the acetonitrile solution in a flat quartz aqueous cell. Thermal analysis was performed on a Seiko model instrument (TG DTA 32) and the thermograms recorded at a heating rate of 10 °C min^{-1} from 30 to 600 °C under nitrogen atmosphere.

2.4. Procedure for catalytic reaction

The liquid-phase oxidation of norbornene was carried out in a two-necked 50 ml round bottom flask immersed in a thermostated oil bath maintained at required temperature. A typical reaction mixture contains 0.012 mmol of catalyst, 0.94 g (10 mmol) of norbornene, 10 mmol of aq. H$_2$O$_2$ (30%) or UHP or TBHP and 8 g of acetonitrile. The reaction mixture was stirred with a teflon-coated magnetic bar. 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 samples were analyzed simultaneously by UV–vis, NMR and EPR to identify the possible active intermediate species and to understand the reaction pathways. The substrate:oxidant ratio of 1:1 was kept constant for all the reactions.

3. Results and discussion

3.1. Characterization

The Keggin structure of the catalyst was confirmed by IR spectroscopy. The major IR peaks were: 1060 cm^{-1}
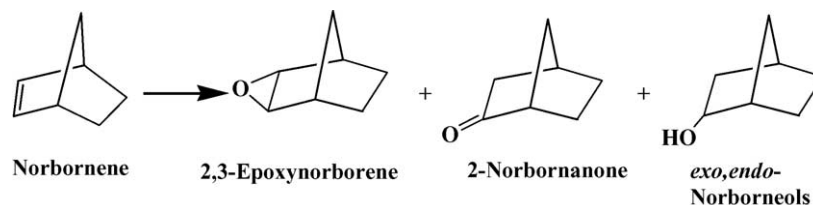
Scheme 1. Different possible products during norbornene oxidation reaction catalyzed by $H_4[PV_1Mo_{11}O_{40}]$ in the presence of aq. H_2O_2.

for $[\nu(P–O_I–Mo)]$, $960\,cm^{-1}$ for $[\nu(Mo–O_t)]$ and 807 and $783\,cm^{-1}$ for $[\nu(Mo–O_b–Mo)]$, where O_I, O_t and O_b are the inner, terminal and the bridging oxygen atoms, respectively, in the Keggin anionic framework [16]. The total water content of the catalyst was determined by thermogravimetric analysis.

The UV–vis spectrum of the catalysts in acetonitrile showed absorption maxima at 218 and 308 nm, which are typical for the Keggin structure. These bands are due to the ligand to metal charge transfer transitions associated with octahedrally coordinated Mo^{6+} unit [16]. Room-temperature EPR spectrum of a polycrystalline sample of vanadium-substituted phosphomolybdic acid, for example, $H_4[PV_1Mo_{11}O_{40}]$, shows a weak and broad hyperfine feature which is characteristic of $H_4[PV_1Mo_{11}O_{40}]$, where V ion is primarily in the 5+ oxidation state with a trace of V(4+) ion. The hyperfine feature is due to the interaction of unpaired electron of V(4+) ($S = 1/2$) and vanadium nucleus of nuclear quantum number, $I = 7/2$. Apparently, a trace of paramagnetic V(4+) species is usually present in most of the vanadium containing phosphomolybdates [17].

3.2. Catalytic study

Selective oxidation of norbornene has been carried out using mono-, di-, and tri-vanadium-substituted polyoxomolybdic acids as catalysts in different solvents. The reactions were carried out with three different oxidants, and as a function of catalyst concentration, temperature and reaction time. The product mixture was analyzed and estimated using GC analysis. The reaction products (Scheme 1) were identified by comparing with authentic samples.

3.2.1. Aqueous hydrogen peroxide as an oxidant

The mono-substituted vanadomolybdic acid, $H_4[PV_1Mo_{11}O_{40}]$, with varying amounts in the range of 0.005–0.018 mmol, was used as a catalyst for norbornene oxidation with aq. H_2O_2 as an oxidant. The reaction was carried out in acetonitrile solvent at $60\,°C$ for 4 h and the results are given in Fig. 1. It is clear from the figure that maximum conversion and selectivity was reached, when the catalyst amount was 0.012 mmol for 0.94 g (10 mmol) of substrate. At this catalyst concentration, norbornene oxidation experiments were carried out with all the three different vanadium-substituted vanadomolybdic acids catalysts namely $H_4[PV_1Mo_{11}O_{40}]$, $H_5[PV_2Mo_{10}O_{40}]$ and
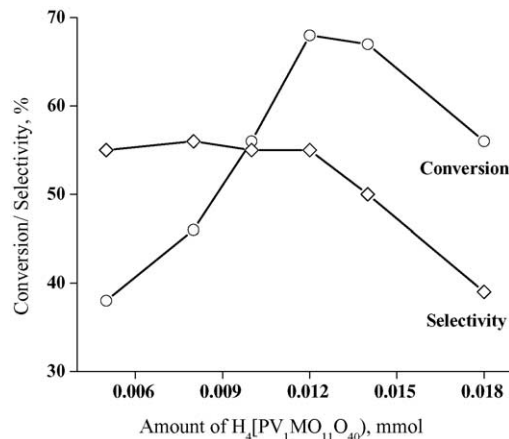

Fig. 1. Effect of amount of $H_4[PV_1Mo_{11}O_{40}]$ catalyst on the conversion and selectivity of norbornene oxidation. Experimental conditions: substrate:oxidant (mol/mol) = 1:1, norbornene = 10 mmol, acetonitrile = 8 g, temperature = $60\,°C$, time = 2 h.

$H_6[PV_3Mo_9O_{40}]$ with three different solvents, acetonitrile, acetone and methanol, to find out the better one among the three catalysts and also to find out the suitable solvent. The reactions were carried out for 2 h and the end results are depicted in Fig. 2. The results clearly indicate acetonitrile was the suitable solvent. However, among the three vanadium-substituted phospomolybdic acid catalysts, the norbornene oxide yield was better with $H_4[PV_1Mo_{11}O_{40}]$. So, the catalyst $H_4[PV_1Mo_{11}O_{40}]$ was used in acetonitrile
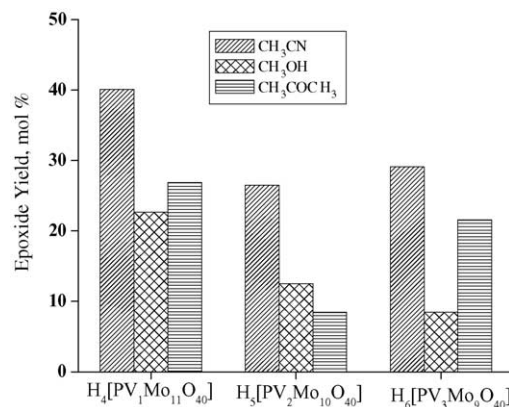

Fig. 2. Yield of 2,3-epoxy norbornane yield as a function of $H_4[PV_1Mo_{11}O_{40}]$, $H_5[PV_2Mo_{10}O_{40}]$ and $H_6[PV_3Mo_9O_{40}]$ and a function of solvents. Experimental conditions: substrate:oxidant (mol/mol) = 1:1, norbornene = 10 mmol, acetonitrile = 8 g, temperature = $60\,°C$, time = 2 h.
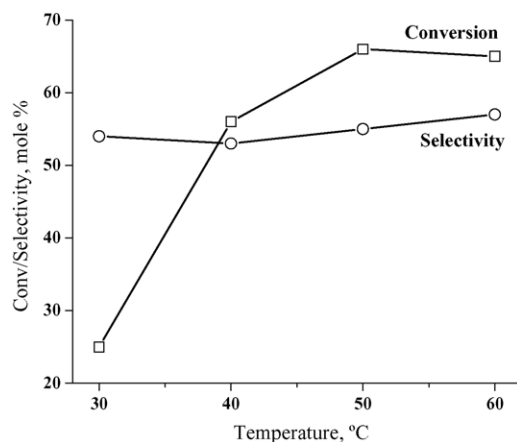
Fig. 3. Effect of reaction temperature on the norbornene oxidation reaction over $H_4[PV_1Mo_{11}O_{40}]$ catalyst with aq. H_2O_2. Reaction conditions: substrate:oxidant (mol/mol) = 1:1, acetonitrile = 8 g, catalyst = 0.012 mmol, time = 2 h.
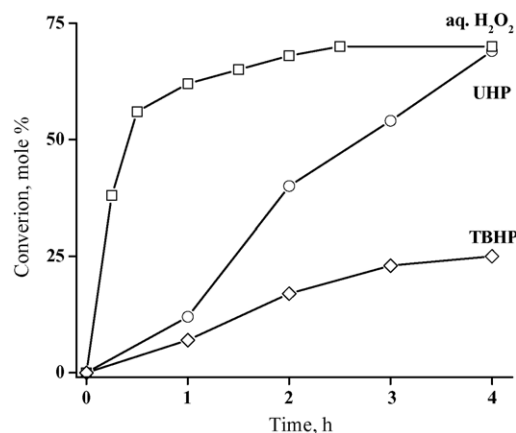

Fig. 4. Kinetics of oxidation of norbornene with different oxidants over $H_4[PV_1Mo_{11}O_{40}]$. Reaction conditions: substrate/oxidant (mol/mol) = 1:1, temperature = 60 °C, catalyst = 0.012 mmol, acetonitrile = 8 g.

solvent for all the further studies. To find the suitable temperature to obtain maximum yield, experiments were carried out at different temperatures in the range 30–60 °C for 2 h and the results are plotted in Fig. 3. While selectivity remains nearly constant 55 ± 2% throughout the reaction, the conversion of norbornene was steeper between 30 and 40 °C and reached maximum 50 °C and thereupon it became plateau; however, overall yield was slightly better at 60 °C.

Kinetic measurements on the norbornene oxidation with aq. H_2O_2 in acetonitrile were carried out at 60 °C and the products distribution and their selectivity at maximum conversion are summarized in Table 1. The conversion of norbornene is drawn as a function of time at this temperature and plotted in Fig. 4. It can be seen that with aq. H_2O_2, the conversion of norbornene was faster in the beginning as the oxidant is added in one lot and the rate of conversion of the substrate was slowed down thereafter (after 1.5 h) and there was no appreciable change in the conversion after 2 h. The selectivity to the desired product, 2,3-epoxy norbornene, was higher than the other products and it was more or less constant (58 ± 2%) during the entire course of the reaction. The other products of oxidation were norborneols (both exo and endo forms were formed) and 2-norbornanone (Scheme 1).

In the presence of aq. H_2O_2 and the vanadium-substituted phosphomolybdic acid catalyst, both oxidation as well as acid-catalyzed reactions have taken place. The oxidation reaction, addition of oxygen to the double bond of the substrate, to form epoxide is catalyzed by the vanadium center. An addition of water molecule to norbornene to form norborneol was catalyzed either by protons of $H_4[PV_1Mo_{11}O_{40}]$ or by protons formed during H_2O_2 activation in the presence of catalyst. To understand the origin of the proton mediated reaction and role of vanadium centers in the norbornene oxidation, reactions were carried out with vanadium-free phosphomolybdic acid catalyst, $H_3[PMo_{12}O_{40}]$. It was found that even after 4 h of reaction mixture, the conversion of the substrate was negligible. Titration of the reaction mixture with $KMnO_4$ indicates that added aq. H_2O_2 was mostly intact (more than 90%) and not activated. However, titration of the reaction mixture where $H_4[PV_1Mo_{11}O_{40}]$ was used as a catalyst indicates that the substrate conversion was 68% and more than 85% of added aq. H_2O_2 were utilized for the oxidation reaction. These observations indicate the following points:

(i) vanadium ions are active centers for the norbornene oxidation as there was no substrate conversion in the presence vanadium-free phophomolybdic acid;

(ii) formation of norborneols is not catalyzed by the protons of $H_4[PV_1Mo_{11}O_{40}]$ as there was no formation of

Table 1
Epoxidation of norbornene with different catalysts and different oxidants

Catalyst	Oxidant	Time (h)	Conv. (mol%)	Product distribution (mol%)		
				Epoxide	Norborneol	2-Norbornone
$H_3[PMo_{12}O_{40}]$	aq. H_2O_2	4	–	–	–	–
$H_4[PV_1Mo_{12}O_{40}]$	aq. H_2O_2	2	68	59	17	24
$H_4[PV_1Mo_{12}O_{40}]$	aq. H_2O_2	4	70	58	17	25
$H_4[PV_1Mo_{12}O_{40}]$	UHP	4	69	97	3	–
$H_4[PV_1Mo_{12}O_{40}]$	TBHP	4	25	96	2	2
$Q_4[PV_1Mo_{12}O_{40}]$	aq. H_2O_2	4	71	67	16	17
VO(acac)	aq. H_2O_2	2	55	64	15	21

Reaction conditions: norbornene/oxidant (mol/mol) = 1:1, catalyst = 0.012 mol, norbornene = 0.01 mol, solvent = acetonitrile (8 gram), $Q = Bu_4N^+$.

norborneols in the presence of $H_3[PMo_{12}O_{40}]$ which contains three protons; and

(iii) thus, the formation of norborneols from norbornene might have been catalyzed by protons formed during the activation of aq. H_2O_2 by vanadium containing catalyst, $H_4[PV_1Mo_{11}O_{40}]$.

To substantiate the points (ii) and (iii), two experiments were carried out with $(Bu_4N)_4$ $[PV_1Mo_{11}O_{40}]$ catalyst, where all the protons are replaced by tetrabutylammonium ions and with VO(acac) catalyst where there is no proton associated with the catalyst. The results are given in Table 1. From the table it is clear that the amount of both norborneols and norbornanone in the above case are substantial and similar to the results of $H_4[PV_1Mo_{11}O_{40}]$ catalyst, though the conversion and selectivity vary slightly.

3.2.2. Urea–hydrogen peroxide (UHP) and tert-butyl hydrogen peroxide (TBHP)

In many epoxidation reactions, a better selectivity has been observed when urea adduct of hydrogen peroxide (UHP) was used as an oxidant [18]. The better selectivity has been attributed to the controlled release of H_2O_2 into the solution. In the present study, UHP has been employed as another oxidant for norbornene oxidation reaction similar to the reaction with aq. H_2O_2 in acetonitrile solvent. The conversion of norbornene as a function of time at 60 °C is given in Fig. 4. The substrate conversion was gradually increasing unlike the reaction with aq. H_2O_2, where the conversion is faster in the beginning and reached 69% at 4 h [19]. The selectivity to the epoxide was more than 97% for the entire course of reaction time. The only other trace amount of product was norborneol (Table 1). Thus, the over yield of 2,3-epoxy norbornane was 67% compared to 44% with the aq. H_2O_2 oxidant. Selective epoxide formation with UHP is due to the absence of water and the presence of urea in the system; the latter acts both as a buffer and a weak base, thereby minimizing the chances of acid-catalyzed reactions that lead to the formation of norborneols. The reason for the gradual increase in conversion with UHP is due to the slow release of hydrogen peroxide during the reaction in a controlled manner, which allows the formation of the epoxide more selectively. To verify the above point, a simple U-tube manometer experiment had been carried out. The decomposed gaseous molecules were measured by reacting aqueous hydrogen peroxide and UHP over the catalyst at 60 °C. With the UHP, decomposition of H_2O_2 was very slow or barely noticed such that the oxygen content of UHP was fully available for selective epoxidation. However, with aqueous hydrogen peroxide fast decomposition of the oxidant was observed.

tert-Butyl hydrogen peroxide is yet another common oxidant generally employed for epoxidation of alkenes. Epoxidation of norbornene with TBHP in acetonitrile solvent at 60 °C was carried out and the results are given in Fig. 4. The trend was similar to that of UHP. Though the selectivity was nearly 95%, the conversion was very low (27%) compared

to the reactions with aq. H_2O_2 and UHP. Negligible amount of other products with TBHP is due to the absence of proton upon activation of TBHP, which can catalyze the norbornene to norborneols. Thus, this observation substantiate the earlier point that the formation norborneols is assisted by H^+ formed during H_2O_2 activation

3.3. UV–vis spectroscopy

A small amount of the reaction mixture was drawn periodically during the course of the reaction and was monitored by UV–vis spectroscopy in the region of 200–900 nm. Acetonitrile solution of the pure catalyst exhibits a characteristic band around 308 nm (Fig. 5a) with a long tail at higher wavelength, which is associated with the ligand–metal transfer transitions. The above broad band is deconvoluted into two bands (shown as dashed lines in Fig. 5): a strong band at 308 nm and a weak one at 355 nm, and the line-width of both the bands are about 50 nm. Upon addition of aq. H_2O_2 (trace, b) or norbornene + aq. H_2O_2 (trace, c) to the above catalyst, a distortion in the shape or line width could be noticed in the LMCT band, indicating the changes in the environment around heteropoly anion. However, the bands are not resolved enough to be noticed clearly to extract any further information. Similar was the case with the trace (d) and (e) in Fig. 5 corresponding to reaction mixtures at different reaction times.

Vanadium(4+) ion with d^1 configuration is expected to show a d–d band around 750 nm; however, vanadium(5+) ion with no electron in d-orbital does not show any such a band [20]. A broad band around 750 nm was seen for ace-
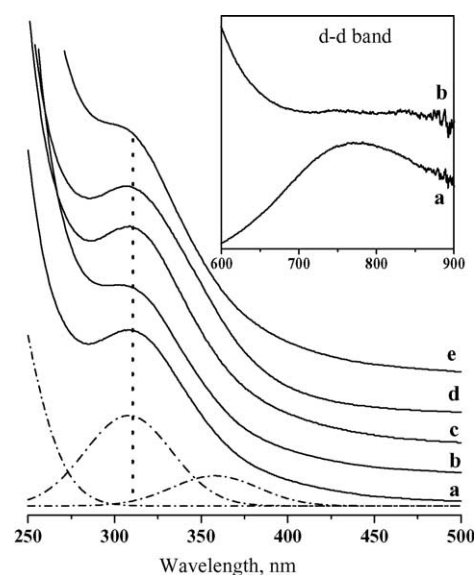

Fig. 5. UV–vis spectra of LMCT region for (a) $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile solution, (b) catalyst + aq. H_2O_2 in acetonitrile, (c) catalyst + norbornene in acetonitrile, reaction mixture at (d) 0.5 h and (e) 2 h. Deconvoluted bands of spectrum of (a) are given in dashed lines. Inset: d–d band region for (a) $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile solution, (b) $H_4[PV_1Mo_{11}O_{40}]$ + aq. H_2O_2 in acetonitrile.

tonitrile solution of the pure catalyst (Fig. 5, inset (a)), indicating that part of vanadium is in 4+ oxidation state as also evidenced by EPR spectroscopy (see below). However, it is interesting to note that upon addition of aq. H_2O_2 the broad d–d band vanishes (Fig. 5, inset (a)). Similar was the case for the reaction mixtures at different time intervals (not shown). This observation probably indicates that the V(4+) ions are oxidized to V(5+) during the reaction. However, not much information could be obtained from UV–vis studies about the vanadium–peroxide interaction.

3.4. NMR spectroscopy

NMR spectroscopy of ^{51}V and ^{31}P nuclei was used to gain further information on the possible catalytic intermediates formed during norbornene oxidation reaction. ^{51}V NMR spectra of pure $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile solution, aq. H_2O_2-treated $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile and the reaction mixture are shown in Fig. 6(a–c). The pure sample shows mainly a single peak at -540.1 ppm indicating all the five isomers of $H_4[PV_1Mo_{11}O_{40}]$ are not resolved in acetonitrile solvent [21]. There are other tiny peaks around -548 ppm most probably due to the presence of other isomers in small amount or any vanadyl species [5a]. However, upon addition of aq. H_2O_2, a set of three broad signals appeared in the up-field positions at -640.8, -651.3, -671.6 ppm (Fig. 6b). This large up-field chemical shift can be attributed to $PVMo_{11}O_{40}$ – peroxo compounds as discussed in the case of hydrogen peroxide-treated $PV_2Mo_{10}O_{40}$ species in acetic acid [21b], and no strong peaks were seen around -540 ppm except a

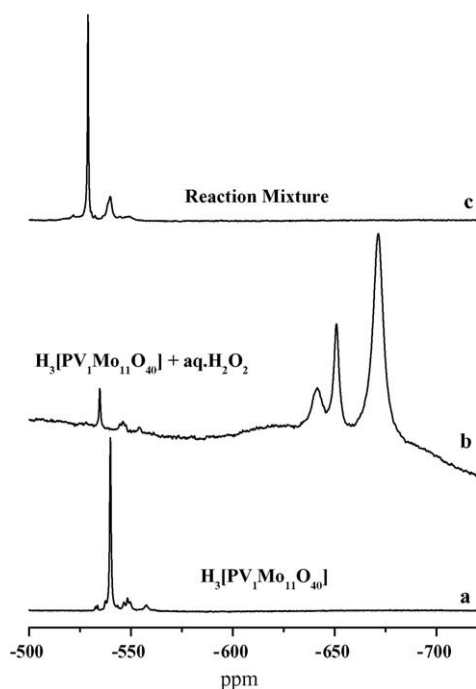Fig. 6. ^{51}V NMR spectra (25 °C) of (a) $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile solution, (b) $H_4[PV_1Mo_{11}O_{40}] + aq. H_2O_2$ in acetonitrile and (c) reaction mixture at 0.5 h.

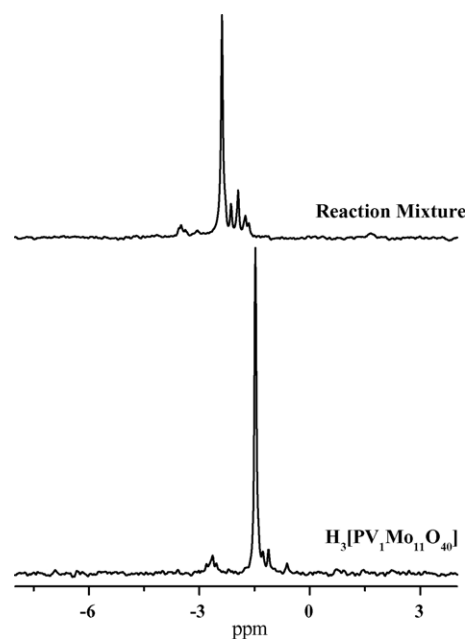

Fig. 7. ^{31}P NMR spectra (25 °C) of (a) $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile solution, and (b) reaction mixture at 0.5 h.

small peak at -534.5 ppm. However, for the reaction mixture ($H_4[PVMo_{11}O_{40}] + aq. H_2O_2 + $norbornene in acetonitrile), the up-field broad bands disappeared but exhibits a narrow signal at -529 ppm and a peak with lower intensity at -548.1 ppm. Disappearance of the broad up-field peaks on addition of norbornene (i.e. for the reaction mixture) and appearance of the narrow peak at around -548 ppm clearly indicates that the bound peroxide ion is released from Keggin unit and the heteropoly anion unit has retained its structure after completion of the reaction. The small down-field shift of ^{51}V NMR signal for the reaction mixture compared with that of pure catalyst sample may be an indication of small structural changes like changes in the number of water coordination.

Similarly, the ^{31}P NMR spectra were recorded for the pure sample, $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile as well as for the reaction mixture and are shown in Fig. 7. For the pure sample showed a main signal at -1.46 ppm and for the reaction mixture it appears at -2.39 ppm in addition to multiple peaks with very low intensity. Small down-field shift of ^{31}P NMR signal for the reaction mixture may be due the same reason as discussed above. Also, absence of any signal at 0 ppm characteristic of H_3PO_4 clearly indicates that there is no degradation of vanadium–heteropoly acid to phosphates with the present experimental condition.

3.5. EPR spectroscopy

EPR spectroscopy can be used to monitor V(4+) ion and any paramagnetic transient species formed during the course of the reaction. In an effort to understand the reaction intermediates and to throw light on the reaction mechanism, a
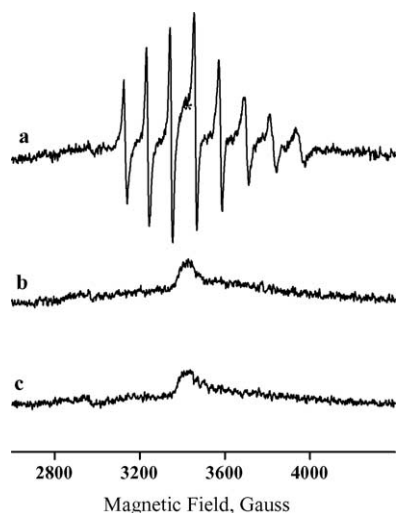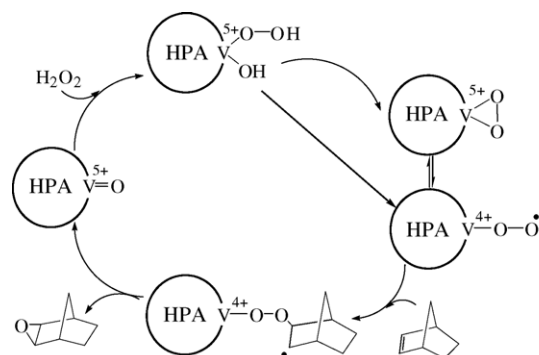
Scheme 2. A schematic representation of proposed reaction mechanism for the epoxidation of norbornene catalyzed by $H_4[PV_1Mo_{11}O_{40}]$ in the presence of aq. H_2O_2. The heteropoly anion framework is represented as HPA. The bonds, which undergo changes are alone shown for clarity.

Fig. 8. Room-temperature EPR spectra of (a) $H_4[PV_1Mo_{11}O_{40}]$ in acetonitrile, (b) $H_4[PV_1Mo_{11}O_{40}]$ + aq. H_2O_2 in acetonitrile and (c) the reaction mixture at 0.5 h. The (*) signal comes from the EPR cavity.

small amount of sample was drawn from the reaction mixture at different time intervals and EPR spectra were recorded after the sample was quenched at room-temperature. To gain a better understanding, the EPR spectra of acetonitrile solution of the catalyst before and after addition of aq. H_2O_2 and the substrate were also recorded. Representative spectra of such experiments are given in Fig. 8. The acetonitrile solution of the pure catalyst at room-temperature exhibits isotropic ^{51}V hyperfine lines (Fig. 8a) due to the presence of trace amounts of V(4+) species ion in the catalyst. The EPR spectrum contains eight hyperfine lines pattern due to the interaction of paramagnetic electron of V(4+) with its nucleus ($I = 7/2$). The Hamiltonian parameters of this species based on the computer simulation are: $g_{iso} = 1.97$ and $A_{iso} = 109$ G. A small difference between the eight different lines is noticed due to the second-order hyperfine effect, which is not discussed in the current paper. Addition of either aq. H_2O_2 or UHP to the above acetonitrile solution with or without the substrate leads to the disappearance of the V(4+) signal instantaneously (Fig. 8b and c). This observation probably indicates that V(4+) center is oxidized to V(5+). The vanadium ions generate V(5+)-peroxo species (I, Scheme 2) on interaction with H_2O_2, which may partly be in equilibrium with V(4+)-OO• (II, Scheme 2) [22]. Possibility for the presence of any other species like superoxo radical bound to V(5+) may be ruled out as its characteristic EPR signals with small hyperfine value are not observed in the present work [23]. It is noteworthy here that the EPR of the above solution was measured subsequently at various time intervals and it was found that the solution remains EPR silent even after 24 h.

3.6. Mechanism

Based on the catalytic studies, it is clear that the main product of norbornene oxidation reaction with the vanadium-substituted phosphomolybdic acid catalyst is the 2,3-epoxy norbornane, and the minor products are (endo, exo) norborneols, and norbornanone. The selectivity of the products depends on the oxidants used and other reaction conditions as discussed earlier. Formation of epoxide along with hydroxylated products and ketone indicates that more than one mechanistic pathways are involved or subsequent reactions have proceeded after epoxide formation.

Absence of characteristic EPR signal of V(5+)-OO• species and appearance of up-field shift in ^{51}V NMR for the H_2O_2 interacted vanadium-substituted heteropoly acid indicate that V(5+)-peroxo (Scheme 2) is the possible active intermediate species, which may partially be in equilibrium with V(4+)-OO• (Scheme 2). The V(5+)-peroxo species might have formed via unstable vanadium (V) hydroxy–hydroperoxy species (Scheme 2). A plausible reaction mechanism has been proposed in Scheme 2 [22]. The mechanism involves the formation of stable vanadium–peroxo species, as described in Scheme 2, which is partially in equilibrium with V(4+)-OO• radical transient species. This transient species then interacts rapidly with norbornene to form the metallo-peroxy-norbornene intermediate. In the subsequent step, breakage of bonds between the oxygen atoms in this intermediate species leads to the formation of epoxide.

A mixture of norborneols and 2-norbornanone are always seen as the side products in the oxidation reaction when aq. H_2O_2 is used as an oxidant (Table 1). The formation of mono-hydroxylated products is due to the acid-catalyzed hydration reaction with the norbornene (Scheme 3), where the acidity came from the protons formed upon H_2O_2 activation by the vanadium centers of the catalysts. The other minor product, 2-norbornanone, might have formed in two ways: either by the rearrangement of epoxide to ketone form, which is catalyzed by acidic nature of the reaction mixture, or by secondary oxidation, where a part of the norborneols might have converted to 2-norbornanone (Scheme 3). However, with UHP such acidic nature of the reaction mixture is reduced in the presence of urea. In fact, pH of UHP-added solution is found
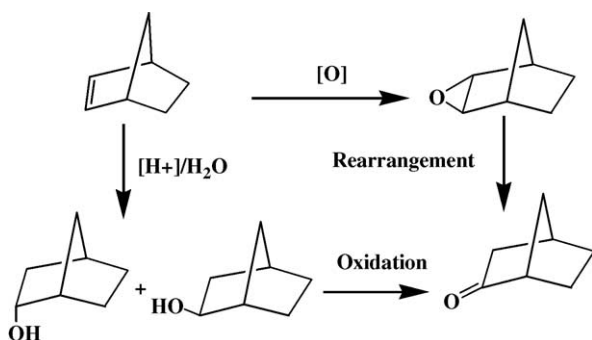
Scheme 3. Proposed reaction pathways leading to different products.

to be higher (pH = 4 at 40 °C) than that of the aqueous H_2O_2-added solution (pH = 3 at 40 °C). Thus, with UHP amount of norbonanone and norborneols are negligible. With TBHP also, there is no proton formation upon activation of TBHP by the catalyst unlike the H_2O_2 oxidant. Thus, the norbonanone and norborneols products formation are not facilitated.

4. Conclusions

Oxidation of norbornene has been carried out using vanadium-substituted phosphomolybdic acid catalysts with aqueous hydrogen peroxide, urea adduct of hydrogen peroxide and *tert*-butyl hydrogen peroxide. Though norbornene conversion was almost the same with H_2O_2 and UHP, selectivity of the 2,3-epoxy norbornane is only moderate with aq. H_2O_2, and the side products are norborneols and 2-norbornanone. However, with UHP the product is mainly of 2,3-epoxy norbornane with trace amounts of norborneols. The conversion was very low with TBHP oxidant though the selectivity was high. The hydroxylated products norborneols are formed by the hydration of norbornene with the help of protons formed during the activation of H_2O_2 by the catalyst. With UHP and TBHP, such a reaction was hindered as these oxidants make the solution less acidic. The epoxidation reaction is believed to proceed through the reactive intermediates, V(5+)-peroxo and V(4+)-superoxo species. NMR and EPR studies indirectly provide support for the formation of V(5+)-peroxo species as a reaction intermediate.

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[19] During the oxidation of norbornene with UHP a colourless oily substance starts sticking to the sides of the glass reactor. Within 2–3 h the light orange solution became colourless as the catalyst also starts

sticking to the sides along with the oily substance. We believe that the catalyst precipitates out from the solution along with the urea in UHP.

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