# Kinetics of limonene epoxidation by hydrogen peroxide on PW-Amberlite

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## Abstract

Selective limonene epoxidation was carried out over a heteropolyacid anchored on Amberlite IRA-900, using hydrogen peroxide as the oxidant. The effects of various parameters such as the concentration of catalyst, $H_2O_2$, limonene, and water on the rate of reaction have been studied. A mechanism similar to that proposed under the so-called Ishii–Venturello chemistry was used to develop a kinetic model based on the Langmuir–Hinshelwood formalism. This includes the adsorption of reactants and solvent on the catalyst. Although the kinetic model showed to be in agreement with the experimental results, water did not appear to adsorb on the catalytic sites. Furthermore, the influence of epoxide addition to the reaction mixture was examined. Epoxide deactivates the catalyst and the reaction practically stops when the amount of epoxide added is equivalent to about 160 turnovers. Notwithstanding, the catalyst is reactivated after being washed with acetone. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Citrus fruits are abundant in Colombia, and advantage could be taken from fruit peel waste for obtaining valuable products. Limonene extracted from citrus oil is usually epoxidized as an intermediate step for the elaboration of fragrances, perfumes, and food additives [1]. One of the most used epoxidation process is the stoichiometric peracid route. However, the selective oxidation of monoterpenes is hard to achieve with peracid due to their oxidizing strength, by which mono- and di-epoxides, as well as, cleaved products are simultaneously obtained. Besides, environmen-

tal and economic factors make the use of peracids increasingly unacceptable [2]. As a consequence, catalytic routes are becoming dominant.

Metal catalyzed epoxidation of olefins by aqueous hydrogen peroxide is the preferred one since this oxidant is cheap, safe and environmentally clean. Tungsten-based compounds are among the most effective epoxidation catalysts using aqueous hydrogen peroxide. The Ishii–Venturello system ($W^{VI}/P^{V}$/phase transfer catalyst, $PTC/H_2O/CHCl_3$) is able to catalyze the selective epoxidation of a variety of monoterpenes to give the corresponding mono- and di-epoxides in good yields under mild conditions. However, the Ishii–Venturello system has disadvantages since toxic and carcinogenic chlorocarbon solvents ($CCl_4$, $CHCl_3$, $CH_2Cl_2$) are required for high epoxide yield [3,4]. Besides, the catalyst is rapidly deactivated, likely due to catalyst decomposition by interaction with epoxides.

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More recently, a heterogeneous reusable catalyst, PW-Amberlite, was developed [5]. PW-Amberlite was prepared by ion exchange of a preformed peroxo PW-anion onto the nitrate form of a commercial macroreticular resin, Amberlite IRA-900, in the presence of $H_2O_2$ [5–8]. High yields were obtained with this catalyst for the selective epoxidation of a series of terpene–olefins with hydrogen peroxide at $38\,°C$. For limonene epoxidation, the best cosolvent was acetonitrile and the catalytic activity increased with the amount of cosolvent and $H_2O_2$ concentration. Adding enough cosolvent to reach a one-liquid phase system, 80 mol product per mole of exchanged $PW_4O_{24}{}^{3-}$ are produced. The selectivity for epoxides exceeds 90% and catalyst reusability proved satisfactory with respect to conversion and selectivity [8].

Although the PTC system has been extensively investigated [3], few studies of the kinetics and mechanism have been carried out. Duncan et al. [3] found that the oxidation rate of 1-octene in the biphasic system was first order with respect to both the active site (Ishii–Venturello) polyperoxophosphometalate anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and to the alkene. More recently, it was reported [9] that the reaction of styrene using the PTC can be represented by pseudo-first-order kinetics where the order in styrene concentration is unity. However, the order of reaction with respect to hydrogen peroxide has not been documented in the literature for these systems.

The scope of the present paper is to investigate the effect of different reaction parameters on the kinetics of limonene epoxidation over the heterogeneous PW-Amberlite catalyst. First a reaction mechanism is proposed and then, an expression for the rate is obtained based on the analysis of initial rate experiments.

## 2. Experimental

### 2.1. Materials

All commercial products were of the highest grade available and were used as such. Hydrogen peroxide was a 30% aqueous solution (J.T. Baker). Limonene was extracted by steam distillation of Colombian orange peel, as follows: chopped orange peel (8 kg) was placed in a 20 l round-bottom flask and subjected to a flow of steam ($96\,°C$) at a pressure of 0.84 atm for 5 h. The condensed volatiles were decanted and dried over anhydrous sodium sulfate. More than 99% limonene was obtained as determined by GC.

### 2.2. Catalyst preparation

The complex $PW_4O_{24}[(C_4H_9)_4N]_3$ was prepared according to literature procedures [10,11] and heterogenized on Amberlite IRA-900 taking care to preserve the peroxo groups of the complex [5–8]. The IR spectra (Matson FTIR 5000, KBr pellet technique) exhibits the main absorption bands of the peroxotungstophosphates [3,11–13] as previously found by IR and confirmed with Raman spectra [8]. The following IR bands typical of peroxotungstophosphates are observed: $1095\,cm^{-1}$ (P–O), $927\,cm^{-1}$ (W=O), $862\,cm^{-1}$ (O–O) and $538\,cm^{-1}$ ($W(O_2)_{s,as}$). The presence of bands corresponding to symmetric and asymmetric vibrations of metal with peroxo $W(O_2)$ indicates that the peroxo was kept intact. A band at $1384\,cm^{-1}$ in the IR spectra of PW-Amberlite-$NO_3{}^-$ proves that after exchange, a great part of the capacity continues to be occupied by $NO_3{}^-$ ions. The P-content determined by elemental analysis, using the vanadomolibdophosphoric complex method [14] is 0.59 mmol/g of dry material. This result agrees within experimental error of previous electron microprobe analysis (EPMA) showing that PW-Amberlite contains 0.55 mmol $PW_4$ per gram of dry material [8]. The atomic P/W ratio of 4, obtained by EPMA, confirms that the complex was not modified by exchange with the resin.

### 2.3. Catalytic experiments

The oxidation of limonene was carried out between 25 and $50\,°C$ in a 25 ml round-bottom flask equipped with a condenser and a thermocouple connected to a temperature controller. The system was magnetically stirred and heated with an electric mantle. In a typical reaction, 40 mg of PW-Amberlite, 2 mmol of limonene, 3.0 ml of acetonitrile (cosolvent), and 0.46 g of hydrogen peroxide (30 wt.% in water) were mixed in the flask and stirred, while heated to the reaction temperature. The reaction rate was followed, by collecting small aliquots at different reaction times.

Reactants and products were separated from the catalyst and analyzed in a Varian Star 3400 gas chromatograph equipped with a capillary column (DB-1, 50 m length) and a FID detector. The regioselectivity of the products was determined with an HP-5890 Series II gas chromatograph equipped with a FID, a MSD (HP 5972) and a capillary column (HP-5MS, 30 m length). The concentration of $H_2O_2$ was determined by cerimetry [15] using a 775 Dosimat (Metrohm). Blank experiments were also carried out under the same reaction conditions without catalyst and with the resin support only. No epoxide formation was detected. Thus, the activity of the catalytic system is due to the exchanged peroxophosphotungstate complex.

## 2.4. Solubility experiments

The objective of this part of the study was to make a preliminary examination of the effects of acetonitrile on the solubility of limonene in water. Thus, 140 mg of (R)-(+)-limonene (97%, Aldrich) and 270 mg deionized $H_2O$, were mixed and varying amounts (240–1116 mg) of acetonitrile (HPLC grade, Aldrich) were added. Mixtures were laid off in chromatographic syringes at $33 \pm 0.1\,°C$. Samples of the organic and aqueous layers were periodically analyzed by gas chromatography. After about 11 days, the phase compositions became constant. The values of the measured equilibrium limonene concentrations in the aqueous phase are listed in Table 1. As can be observed, the addition of acetonitrile increases the volume of the aqueous phase which becomes richer in limonene up to 0.33 mmol/ml. Beyond this point, further addition of acetonitrile lead to a dilution of limonene in the aqueous phase.

## 3. Kinetics of the oxidation of limonene

### 3.1. General considerations

From GC to MS analyses the main products from limonene oxidation were the epoxides (>96%). The $cis(1,2):trans(1,2)$ and the $(1,2):(8,9)$ epoxide ratios were 1:3 and 111:1, respectively. Therefore, the parallel reaction scheme of limonene epoxidation with $H_2O_2$, may be represented as follows:

$$H_2O_2 + C_{10}H_{16} \rightarrow C_{10}H_{16}O + H_2O \tag{1}$$

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2(g) \tag{2}$$
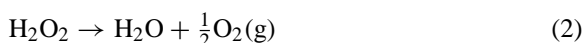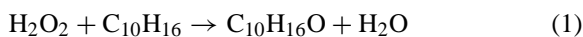
where $C_{10}H_{16}$ and $C_{10}H_{16}O$ are limonene and limonene epoxide, respectively.

Designating the conversion of $C_{10}H_{16}$ as $f_B$, the partial conversions of $H_2O_2$ through reactions (1) and (2) as $X_1$ and $X_2$, respectively, the number of moles of reactants $H_2O_2$ (A), $C_{10}H_{16}$ (B) and product $C_{10}H_{16}O$ (D) at any reaction time in the batch reactor will depend on the limiting reactant:

If B is chosen as the limiting reactant, then

$$N_B = N_{B0}(1 - f_B) \tag{3}$$

$$N_A = N_{A0} - N_{B0}f_B - N_{A0}X_2 \tag{4}$$

$$N_D = N_{B0}f_B \tag{5}$$

Thus, the partial conversion $X_2$ is

$$X_2 = \frac{N_{A0} - N_{B0}f_B - N_A}{N_{A0}} \tag{6}$$

If A is the limiting reactant:

$$N_A = N_{A0}(1 - X_1 - X_2) \tag{7}$$

$$N_B = N_{B0} - N_{A0}X_1 \tag{8}$$

Table 1
Limonene solubility in the aqueous phase, in the presence of $CH_3CN$ at $33\,°C$[a]

| Global limonene concentration (mmol/ml) | Limonene concentration in aqueous phase (mmol/ml) | Aqueous phase volume (ml) |
| --- | --- | --- |
| 0.55 | 0.29 | 1.92 |
| 0.59 | 0.33 | 1.63 |
| 0.70 | 0.27 | 1.32 |
| 0.85 | 0.19 | 1.05 |
| 1.4 | 0.06 | 0.54 |

[a] Conditions: laid off time 11 days, $33\,°C$; limonene, 140 mg; $H_2O$, 270 mg. Various amounts of cosolvent.

$$N_D = N_{A0} X_1 \tag{9}$$

Thus, the partial conversions $X_1$ and $X_2$ are expressed in the following equations:

$$f_B = \frac{N_{B0} - N_B}{N_{B0}} \tag{10}$$

$$X_1 = \frac{f_B N_{B0}}{N_{A0}} \tag{11}$$

By ceric sulfate titration, the total conversion of $H_2O_2$, $f_A$, is calculated:

$$f_A = X_1 + X_2 \tag{12}$$

$f_B$ can be obtained from GC analysis. $N_{B0}$ and $N_{A0}$ are calculated from the initial amounts of each component in the reaction mixture.

The $H_2O_2$ selectivity is defined as:

$$S = \frac{N_D}{N_{A0} - N_A} = \frac{N_{B0} f_B}{N_{A0}(X_1 + X_2)} \tag{13}$$

### 3.2. Reaction mechanism

By analogy with the previously proposed mechanism for the Ishii–Venturello system under biphasic conditions [3], the mechanism of the limonene epoxidation on PW-Amberlite in the presence of $H_2O_2$ is illustrated schematically in Fig. 1. It is important to recall that the heterogeneous catalyst contains the preformed peroxo PW-anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$, the active site in the Ishii–Venturello system [3]. Therefore, as shown in Fig. 1, the peroxo PW-anion (site [S]) interacts with one molecule of $H_2O_2$, to form a polyperoxophosphotungstate (site [$S_1$]). Limonene diffuses within the resin and is then adsorbed on $S_1$. In the next step, an oxygen atom is transferred to limonene from $S_1$ sites. The epoxide desorption generates an S site that may react with $H_2O_2$ to restore the $S_1$ site. The steps of the global reaction for the heterogeneous epoxidation of limonene with $H_2O_2$ may be represented as follows:

$$S + H_2O_2 \overset{K_1}{\Leftrightarrow} S_1 \tag{14}$$

$$S_1 + C_{10}H_{16} \overset{K_2}{\Leftrightarrow} C_{10}H_{16}\text{–}S_1 \tag{15}$$

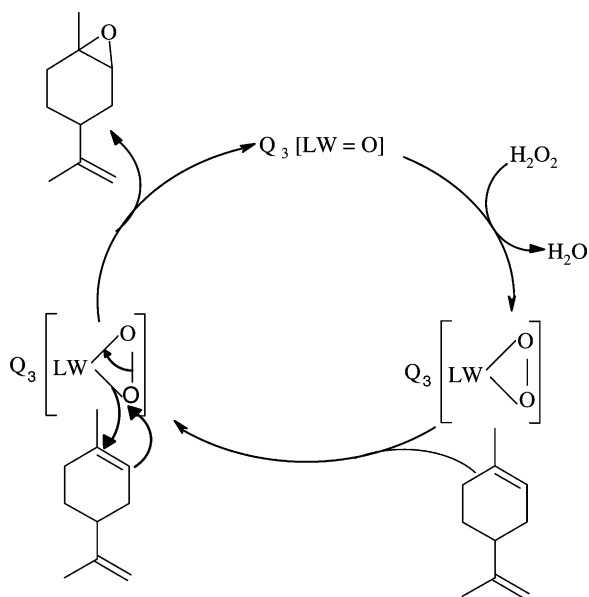$$C_{10}H_{16}\text{–}S_1 \overset{k}{\rightarrow} S + \text{Product} \tag{16}$$
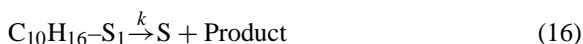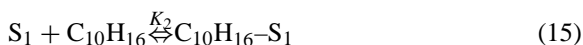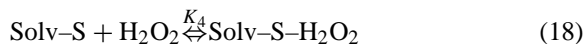


Fig. 1. Mechanism of limonene epoxidation on PW-Amberlite.

Considering that the solvent may also compete for adsorption sites, their adsorption equilibrium equations are as follows:

$$S + \text{Solv} \overset{K_3}{\Leftrightarrow} \text{Solv–S} \tag{17}$$

$$\text{Solv–S} + H_2O_2 \overset{K_4}{\Leftrightarrow} \text{Solv–S–}H_2O_2 \tag{18}$$

Following the Langmuir–Hinshelwood model and assuming that the surface chemical reaction is the controlling step, the kinetic expression is:

$$r = \frac{kK_1K_2[S]_0[H_2O_2][C_{10}H_{16}]}{1 + K_3[\text{Solv}] + [H_2O_2]} \tag{19}$$
$$\quad (K_1 + K_1K_2[C_{10}H_{16}] + K_3K_4[\text{Solv}])$$

where $[S]_0$ is the initial concentration of active sites in the catalyst, which is directly proportional to the amount of catalyst used. $[H_2O_2]$, $[C_{10}H_{16}]$ and $[\text{Solv}]$ are the concentrations of hydrogen peroxide, limonene, and solvent, respectively, $k$ the kinetic rate constant and $K_i$ are the equilibrium adsorption constants for the reaction steps given above.

### 4. Results and discussion

In order to determine whether Eq. (19) represents the kinetics of limonene epoxidation on

PW-Amberlite-$NO_3$ we applied the initial rate kinetic method. The initial rate of reaction was measured at low conversions (below 16–20%). Thus, very little epoxide was formed. First the initial concentrations of hydrogen peroxide, limonene and acetonitrile were kept constant and the amount of catalyst was varied. Under these conditions Eq. (19) can be reduced to:

$$r_0 = m[S]_0,$$
$$m = \frac{kK_1K_2[H_2O_2]_0[C_{10}H_{16}]_0}{1 + K_3[Solv] + [H_2O_2]_0 \quad (20)}{(K_1 + K_1K_2[C_{10}H_{16}]_0 + K_3K_4[Solv])}$$

Fig. 2a shows that at a given time limonene conversion increased with the amount of catalyst. Fig. 2b gives the initial rates calculated at different active site concentrations. As can be observed in Fig. 2b, the reaction is first order with respect to the amount of active sites.

In order to determine the order of reaction with respect to limonene, the initial rate of reaction was measured by using an excess of $H_2O_2$. The concentration of acetonitrile and catalyst were kept constant, and the initial concentration of limonene was varied. Under these conditions, it can be assumed that [Solv], [catalyst] and [$H_2O_2$] are constant. Thus, Eq. (19) can be reduced to:

$$r_0 = \frac{a[C_{10}H_{16}]_0}{b + c[C_{10}H_{16}]_0},$$
$$a = kK_2K_1[H_2O_2]_0[S]_0,$$
$$b = 1 + K_3[Solv] + [H_2O_2]_0(K_1 + K_3K_4[Solv]),$$
$$c = K_2K_1[H_2O_2]_0 \quad (21)$$

According to Eq. (21), the reaction order with respect to limonene can be zero or one, depending on the relative values of the adsorption constants for limonene, solvent and their interaction with $H_2O_2$. Typical conversion versus time profiles for different initial concentrations of limonene are shown in Fig. 3a. The conversion decreases with the increase in limonene concentration. However, when limonene is too diluted the reaction rate is slow and starts at a longer time. It is likely that diffusion and/or counter-diffusion effects are involved at lower limonene concentrations. The initial rates versus the initial concentration of limonene are plotted in Fig. 3b. From this figure, the reaction appears to be first order with respect to limonene. However, for limonene concentrations of
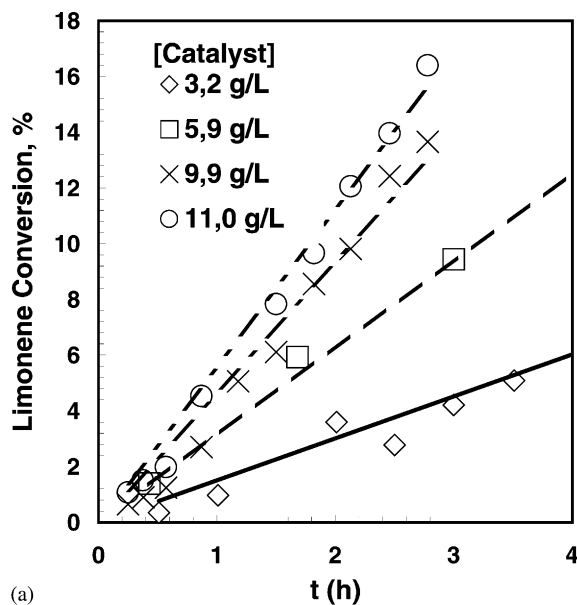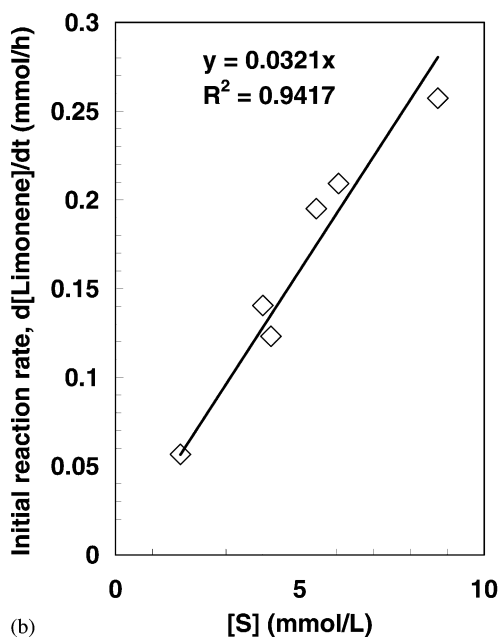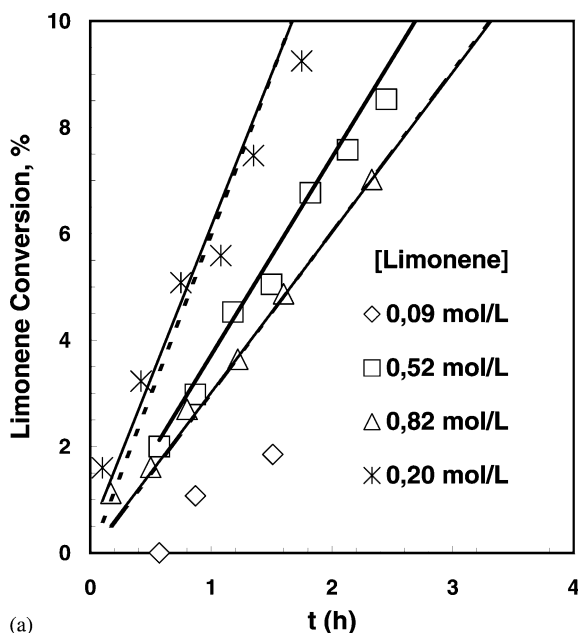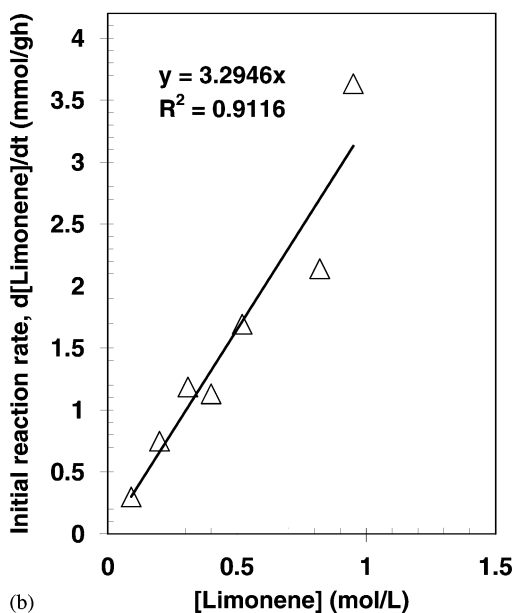


Fig. 2. Influence of catalyst concentration on (a) limonene conversion over PW-Amberlite and (b) initial reaction rate of limonene epoxidation over PW-Amberlite. Reaction conditions: $T = 33\,°C$; [limonene]$_0$ = 0.53 mol/l; [$H_2O_2$]$_0$ = 1.10 mol/l; [acetonitrile] = 610 g/l.

Fig. 3. (a) Limonene conversion as a function of the initial concentration of limonene over PW-Amberlite. (b) Initial reaction rate of limonene epoxidation over PW-Amberlite as a function of the initial concentration of limonene. Reaction conditions: $T = 33\,°C$; [cat] = 11 g/l; $[H_2O_2]_0 = 1.0\,mol/l$; [acetonitrile] = 647 g/l.

Table 2
The effect of water on the initial reaction rate of limonene epoxidation over PW-Amberlite[a]

| $[H_2O]$ (mol/l) | $r_0$ (mmol/g h) |
| --- | --- |
| 5.89 | 1.71 |
| 6.16 | 2.26 |
| 6.30 | 2.28 |
| 6.61 | 2.00 |

[a] Reaction conditions: $T = 33\,°C$; [cat] = 11 g/l; $[C_{10}H_{16}]_0 = 0.52\,mol/l$; $[H_2O_2]_0 = 1.1\,mol/l$; [acetonitrile] = 600 g/l.

0.82 and 0.95 mol/l, a deviation from the straight line is observed. This can be explained by a decrease in limonene solubility as its concentration in the reaction mixture is increased, so mass transfer problems due to different liquid phases are likely. Results from Table 1 confirm this explanation.

To obtain the kinetic order with respect to the concentration of $H_2O_2$, the reaction was carried out under an excess of limonene. The concentrations of acetonitrile and catalyst were kept constant and the initial concentration of hydrogen peroxide was varied. Under these conditions, Eq. (19) becomes:

$$r_0 = \frac{d[H_2O_2]_0}{e + f[H_2O_2]_0},$$
$$d = kK_1K_2[C_{10}H_{16}]_0[S]_0,$$
$$e = 1 + K_3[Solv],$$
$$f = K_1 + K_2K_1[C_{10}H_{16}]_0 + K_3K_4[Solv] \qquad (22)$$

Fig. 4a shows that the conversion of limonene increased with the amount of oxidant. The initial rates of reaction obtained at different initial concentrations of $H_2O_2$ are shown in Fig. 4b. As can be observed in this figure the reaction is first order with respect to $H_2O_2$.

The effect of solvent was also studied by adding different amounts of water to a typical reaction mixture that contained 5.89 mol/l of water. Recall, that the hydrogen peroxide used was about 30% aqueous. Fig. 5 shows that water enhances the conversion of limonene. However, no significant differences are observed in that figure when the concentration of water was changed between 6.16 and 6.61 mol/l. This result may be ascribed to the hydrophobic character of PW-Amberlite, which favors the adsorption of the organic substrates over the more polar water molecules. Table 2 shows that the rate is almost constant with increasing water concentration.
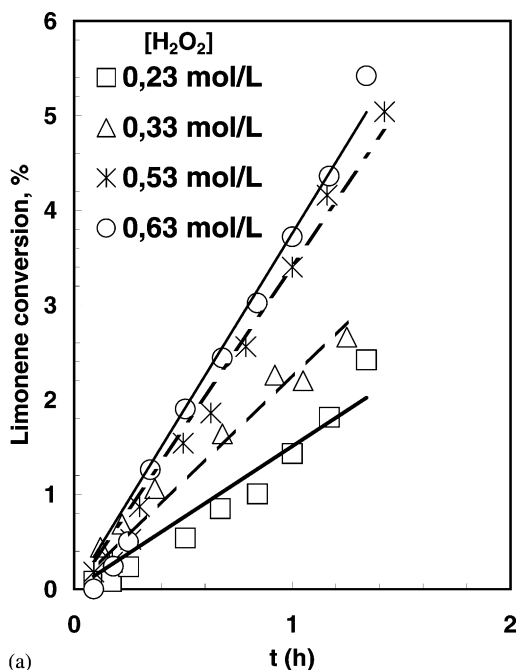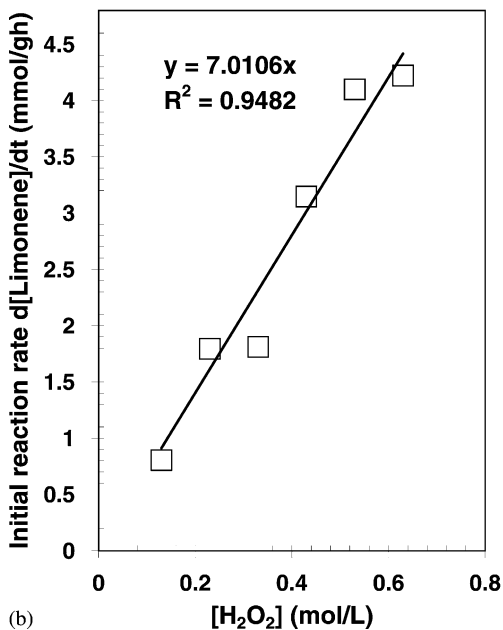
Fig. 4. (a) Limonene conversion over PW-Amberlite and (b) initial reaction rate of limonene epoxidation over PW-Amberlite as a function of the initial concentration of hydrogen peroxide. Reaction conditions: $T = 33\,°C$; [cat] = 11 g/l; $[C_{10}H_{16}]_0 = 1.0$ mol/l; [acetonitrile] = 641 g/l.
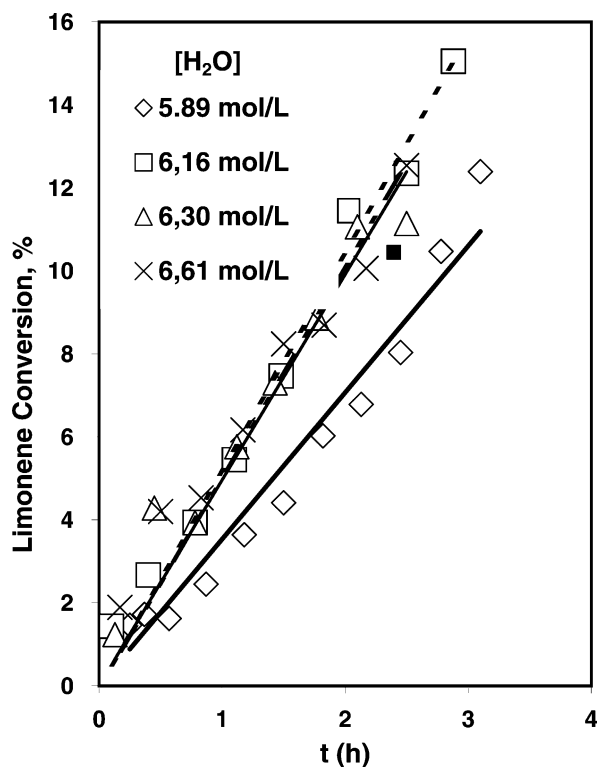


Fig. 5. The effect of water on the initial reaction rate of limonene epoxidation on PW-Amberlite. Reaction conditions: $T = 33\,°C$; [cat] = 11 g/l; $[C_{10}H_{16}]_0 = 0.52$ mol/l; $[H_2O_2]_0 = 1.1$ mol/l; [acetonitrile] = 600 g/l.

### 4.1. The effect of product epoxide

Since rapid inactivation of the Ishii–Venturello epoxidation catalyst under typical biphasic reaction conditions was observed by Duncan et al. [3], we studied the effect of the product on the reaction rate of limonene epoxidation over PW-Amberlite. Thus, different amounts of epoxide were added to the reaction mixture, while the concentration of catalyst, limonene, oxidant and acetonitrile were kept constant.

The influence of epoxide concentration on conversion and on the initial reaction rate of limonene epoxidation is shown in Fig. 6a and b, respectively. As can be observed in Fig. 6 a the addition of epoxide delays the time of reaction exhibiting an induction period. From Fig. 6b it can be seen that the reaction rate decreases linearly with the increase in epoxide addition. Thus, epoxide poisons the catalyst. The reaction being
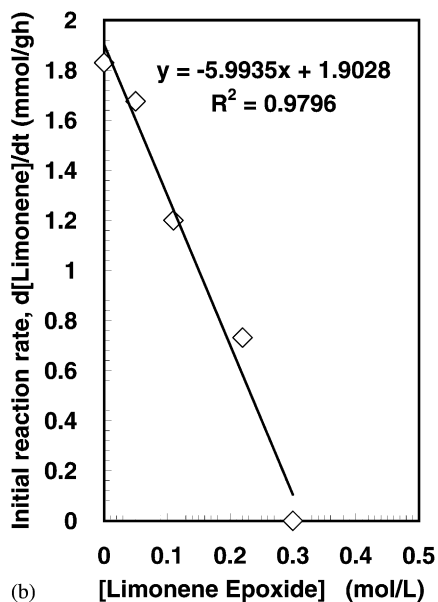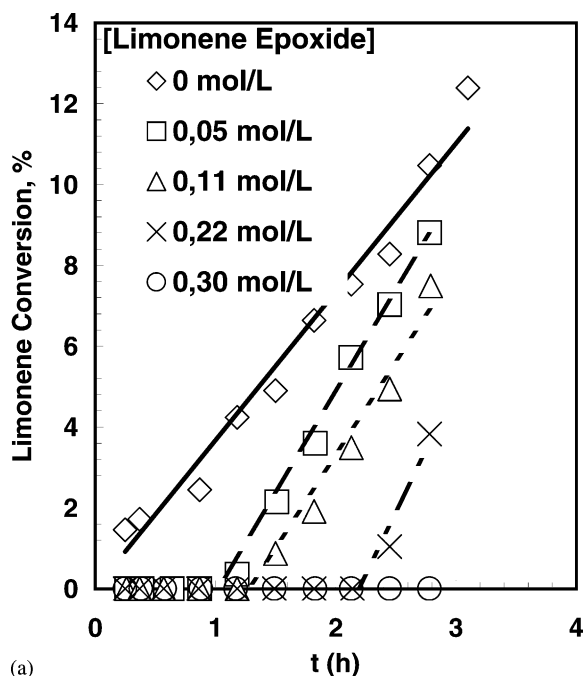
Fig. 6. The effect of epoxide on (a) limonene conversion and (b) initial reaction rate of limonene epoxidation over PW-Amberlite. Reaction conditions: $T = 33\,°C$; [cat] = 11 g/l; $[C_{10}H_{16}]_0 = 0.53$ mol/l; $[H_2O_2]_0 = 1.1$ mol/l; [acetonitrile] = 586 g/l.
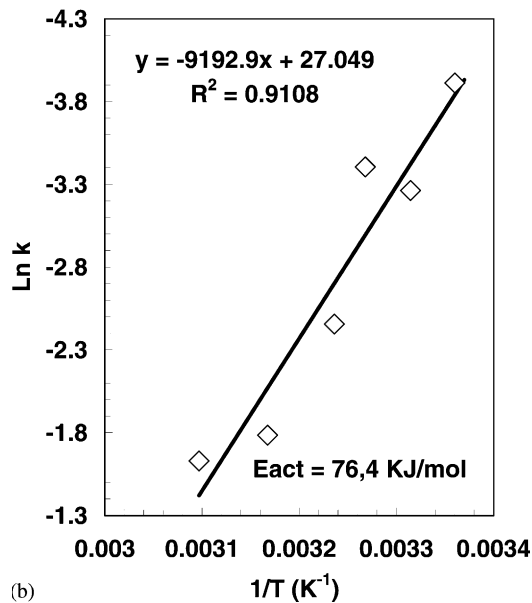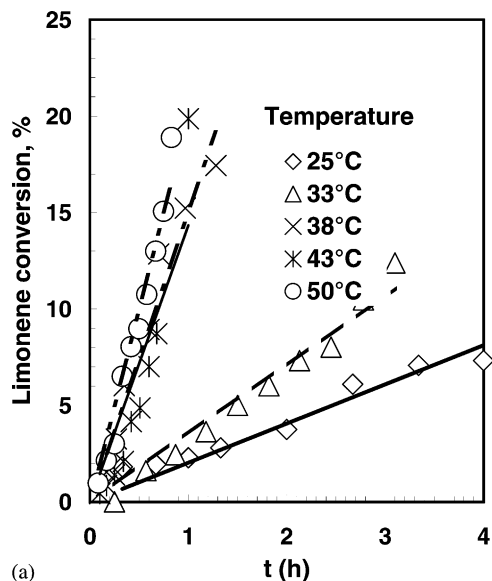
Fig. 7. (a) Influence of reaction temperature on the kinetics of limonene epoxidation over PW-Amberlite. Reaction conditions: $[limonene]_0 = 0.53$ mol/l; $[H_2O_2]_0 = 1.1$ mol/l; [acetonitrile] = 653 g/l. (b) Arrhenius plot of pseudo-first-order rate kinetics constants of limonene epoxidation over PW-Amberlite.

totally inhibited when the added epoxide is equivalent to about 160 turnovers. This value is much more lower than that observed under biphasic reaction conditions [3] in which catalysis nearly stops after 500 turnovers. Therefore, the removal of formed epoxide is required. It is interesting to point out that the activity was recovered after washing the catalyst with acetone. This result is valuable since the catalyst could be recycled.

### 4.2. Influence of reaction temperature

The effect of reaction temperature on limonene epoxidation over PW-Amberlite was studied from 25 to 50 °C. Fig. 7a shows that limonene conversion increases with temperature. The apparent first-order kinetic constant was calculated from Fig. 7a and the results have been fitted to the Arrhenius equation as shown in Fig. 7b. The apparent activation energy obtained is 76.4 kJ/mol.

### 4.3. Conversion and selectivity of hydrogen peroxide

Even though hydrogen peroxide conversion and selectivity plots are not shown in this paper, in general we observed that the conversion and the selectivity of hydrogen peroxide increased by increasing the temperature and the concentration of catalyst, limonene and hydrogen peroxide. However, the addition of epoxide to the reaction mixture leads to a higher level of oxidant decomposition to water and oxygen. This suggests that in fact epoxide may poison the catalytic sites avoiding their interaction with hydrogen peroxide to restore the polyperoxophosphotungstate complex.

## 5. Conclusions

The reaction rate equation obtained from Langmuir–Hinshelwood model gave good approximation to experimental data for limonene concentrations up to about 0.53 mol/l. The reaction rate is first order with respect to limonene, oxidant, and catalyst concentration. Water appears to slightly increase the reaction rate but, it does not appear to compete with limonene for the active sites. The epoxide product poisons the catalyst and totally inhibits the reaction at about 160 turnovers. However, full activity is recovered after washing the catalyst with acetone. Finally, the apparent activation energy for limonene epoxidation over PW-Amberlite is 76.4 kJ/mol.

## References

[1] J.M. Derfer, M.M. Derfer, Encyclopedia of Chemical Technology Kirk-Othmer, Vol. 22, 3rd Edition, Wiley, New York, 1978, p. 709.
[2] J.H. Clark, D.J. Macquarrie, Soc. Rev. (1996) 303.
[3] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681.
[4] I.V. Kozhevnikov, G.P. Mulder, M.C. Steverink-de Zoete, M.G. Oostwal, J. Mol. Catal. A 134 (1998) 223.
[5] A.L. Villa de P., B.F. Sels, D.E. De Vos, P.A. Jacobs, J. Org. Chem. 64 (1999) 7267.
[6] B.F. Sels, A.L. Villa de P., D. Hoegaerts, D.E. De Vos, P.A. Jacobs, Top. Catal. 13 (2000) 223.
[7] A.L. Villa de P., D.E. De Vos, B.F. Sels, C. Montes de Correa, P.A. Jacobs, in: J.M. Órfao, J.L. Faria, J.L. Figueiredo (Eds.), Proceedings of the Actas do XVII Simposio Ibero-americano de Catálise, Porto, Portugal, 2000.
[8] A.L. Villa de P., Epoxidation of monoterpenes by homogeneous and heterogeneous catalytic systems, Ph.D. Thesis, K.U. Leuven, Leuven, September 2000.
[9] G.D. Yadav, A.A. Pujari, Org. Process Res. Dev. 4 (2000) 88.
[10] C. Venturello, E. Alneri, M. Ricci, J. Org. Chem. 48 (1983) 3831.
[11] C. Venturello, R. D'Aloisio, J. Org. Chem. 53 (1988) 1553.
[12] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem. 30 (1991) 4409.
[13] L. Salles, C. Aubry, F. Robert, G. Chottard, R. Thouvenot, H. Ledon, J.-M. Brégeault, New J. Chem. 17 (1993) 367.
[14] J. Beltrán, Análisis Químico de Suelos, Ediciones Omega, S.A., Barcelona, 1964, p. 212.
[15] A.I. Vogel, Quantitative Inorganic Analysis, 2nd Edition, Longmans, London, 1964, p. 318.