Hydration and acetoxylation of monoterpenes catalyzed by heteropoly acid

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Abstract

The liquid-phase hydration and acetoxylation of limonene (**1**), β-pinene (**2**) and α-pinene (**3**) catalyzed by dissolved or silica-supported heteropoly acid $H_3PW_{12}O_{40}$ (PW) in acetic acid and acetic acid/water solutions have been studied. All three substrates give α-terpineol (**4**) as the main product along with α-terpenyl acetate (**5**). The reaction rate increases in the order: limonene < α-pinene < β-pinene. Synthetically useful homogeneous and heterogeneous acetoxylation and hydration of **1**, **2** and **3** into **4** and **5** have been developed. At room temperature under optimized conditions, **2** and **3** form a mixture of **4** and **5** with 85% selectivity at 90% substrate conversion. **1** gives **4** and **5** with 85% selectivity at 50% conversion, with the main product being ester **5** in acetic acid (**4/5** ≈ 30/70) and alcohol **4** in $HOAc/H_2O$ (90/10 v/v) solutions (**4/5** ≈ 85/15). Virtually no oligomerization of monoterpenes occurs under the optimized conditions. The catalyst can be separated without neutralization and may be reused. The PW shows a much higher catalytic activity than conventional acid catalysts such as H_2SO_4 and Amberlyst-15. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Limonene, β-pinene and α-pinene are low-priced naturally occurring monoterpenes used as substrates for the production of monoterpenoid flavors and fragrances [1]. We have, in recent years, been exploring the application of metal complex catalytic systems for the selective functionalization of various monoterpenes. It has been reported that allylic acetates, alcohols, aldehydes and esters can be obtained in good yields and in some cases with high stereoselectivity by catalytic oxidation or carbonylation of limonene, β-pinene and camphene [2–5]. Acid catalyzed hydration and acetoxylation of terpenes are also important synthetic routes to valuable terpenic alcohols and esters with many applications in perfumery and pharmaceutical industry [1]. Thus, α-terpineol, which is the most important of the monocyclic monoterpenic alcohols and one of the top 30 commonly used flavor compounds [6], is produced on an industrial scale by hydration of α-pinene or turpentine oil to the *cis*-terpin hydrate with aqueous mineral acid, followed by its

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partial dehydration to α-terpineol [7]. The process is complicated by acid catalyzed isomerization of the substrate and usually resulted in complex mixtures of monoterpenes, alcohols and hydrocarbons [8]. In addition, the disposal of mineral acids has become a serious environmental problem.

α-Terpineol can also be obtained by hydration [9–11] or bioconversion [12] of limonene. The acid catalyzed processes of limonene hydration commonly produce large amounts of diols besides terpineols [13]. The mixture of α- and β-terpenyl acetates was obtained from limonene and acetic acid with ferric sulfate as a catalyst [14]. The hydrolysis of the former product may give α-terpineol. In hydration of α-pinene, the application of solid acid catalysts such as cation exchange resins [15] and zeolites [16–19] has also been reported.

Heteropoly acids (HPA) of the Keggin series are promising acid catalysts for the synthesis of fine and specialty chemicals [20–23]. They are employed as catalysts in an industrial liquid-phase hydration of olefins [23] and have also been used for the olefin acetoxylation [24–26]. Being stronger acids, HPA generally exhibit much higher catalytic activities than conventional catalysts, such as mineral acids, ion-exchange resins, zeolites, etc. in both heterogeneous and homogeneous systems [20,21]. Furthermore, HPA catalysis lacks side reactions such as sulfonation, chlorination, etc. which occur with mineral acids. The HPA are highly soluble in water and polar organic solvents, such as lower alcohols and carboxylic acids, and insoluble in hydrocarbons. This provides an opportunity to perform liquid-phase reactions with the easy recovery of the HPA catalyst without neutralization by precipitating with a hydrocarbon solvent [21].

This work describes the application of $H_3PW_{12}O_{40}$ (PW), the strongest HPA in the Keggin series [20], as a catalyst for the liquid-phase hydration and acetoxylation of limonene (**1**), β-pinene (**2**) and α-pinene (**3**). Homogeneous and heterogeneous systems have been studied. Efforts have been made to achieve the highest selectivity towards the desired products, α-terpineol (**4**) and α-terpenyl acetate (**5**), by optimizing the reaction variables, such as catalyst concentration, temperature and solvent composition. Efficient methods to convert **1**, **2** and **3** into a mixture of **4** and **5** have been developed.

2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. *R*-(+)-limonene, (1*S*)-(−)-α-pinene and (1*S*)-(−)-β-pinene were distilled before use. The $H_3PW_{12}O_{40}·10H_2O$ from Aldrich was used as a source for the homogeneous PW catalysts. The silica-supported catalysts 20–40% $H_3PW_{12}O_{40}/SiO_2$ (PW/SiO$_2$) were prepared by impregnating Aerosil 200 (Degussa) with an aqueous PW solution, followed by drying at 130°C/0.2–0.3 mmHg for 1.5 h, as described elsewhere [26]. The BET surface area was $174\,m^2\,g^{-1}$ for 20% PW/SiO$_2$ and $132\,m^2\,g^{-1}$ for 40% PW/SiO$_2$. The integrity of HPA Keggin structure in the catalysts was confirmed by ^{31}P MAS NMR; both catalysts showed only a single peak at ca. −15.0 ppm (referenced to 85% H_3PO_4) characteristic of $H_3PW_{12}O_{40}$ [21].

The reactions were carried out in a glass reactor equipped with a magnetic stirrer and followed by gas chromatography (GC) using a Shimadzu 14B instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. Bornyl acetate was used as the internal standard. The products were identified by GC–MS on a Hewlett-Packard MSD 5890/Series II instrument operating at 70 eV.

The homogeneous reactions were performed by adding monoterpene ($0.3\,mol\,l^{-1}$) to a 0.003–0.012 $mol\,l^{-1}$ $H_3PW_{12}O_{40}$ solution in acetic acid or an HOAc/H$_2$O mixture pre-thermostatted at 15–60°C. At appropriate time intervals, aliquots were taken, diluted with hexane (1/10 v/v) to precipitate the heteropoly acid and then analyzed by GC.

The heterogeneous reactions were performed by contacting 2.0 g of a monoterpene/HOAc mixture (1/1.2 mol mol^{-1}) with 0.05 g of 20 or 40% PW/SiO$_2$ at 15–40°C for 2–3 h with intense stirring. In order to prevent PW leaching from the catalyst the monoterpene/HOAc molar ratio was chosen higher than 1/3 [26]. At higher concentrations of acetic acid, some PW leaching was observed. For this reason, contact of the catalyst with neat acetic acid must be avoided. To control the PW leaching, diluting the filtered mixture with hexane (ca. five-fold) was used as a test. Appearance of a white PW precipitate indicated a significant PW leaching. At appropriate time intervals, the stirring was stopped and after quick catalyst

settling the aliquots were taken, diluted with hexane and analyzed by GC. After the reaction, the catalyst was filtered off, washed with hexane and reused.

The GC mass balance typically made up 90–95% based on the substrate charged. The difference, 5–10%, was assigned to oligomers, which were not GC determinable. The oligomers were estimated semiquantitatively. In some homogeneous systems at high conversions the oligomers precipitated out and were determined gravimetrically. In heterogeneous systems, they adsorbed on the catalyst and were determined from the difference in the catalyst weight.

3. Results and discussion

3.1. Homogeneous reactions

The PW, acting as a Brønsted acid catalyst, not only promotes the addition of acetic acid or water to limonene, β-pinene and α-pinene but also many side reactions such as skeletal and/or double bond isomerization and oligomerization of the substrates. The reaction network may be reprisented by Scheme 1. For

all the three monoterpenes studied, the highly valuable α-terpineol, along with its acetate, was detected as the only monoterpenic alcohol formed. No diol formation was observed. The balance between various reaction pathways is very delicate and depends strongly on the reaction conditions. In order to develop selective processes, we have studied the effects of the reaction variables on the catalyst activity and product distribution.

3.1.1. Acetoxylation of monoterpenes

In acetic acid solutions containing PW, acetic acid easily adds to the exocyclic double bond of limonene yielding α-terpinyl acetate **5** (Table 1, runs 1–4). In addition, α-terpineol **4** is also formed as the reaction mixtures always contain water (added with the PW hydrate), which is a more efficient nucleophile than acetic acid. The relative amount of **4** increases with reaction time due to the hydrolysis of **5** catalyzed by PW. The reaction is strongly complicated by acid catalyzed oligomerization of limonene. As a result, the selectivity quickly decreases with increasing limonene conversion, and initially colorless reaction solutions turn yellow and then brown. For example, in run 1 (Table 1), the total selectivity for **4** and **5** decreases
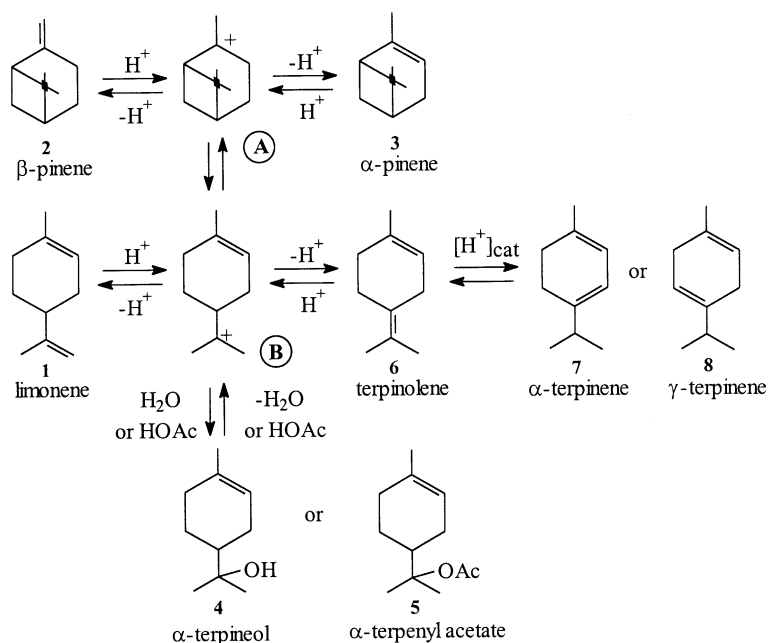
Scheme 1.

Table 1

Homogeneous hydration and acetoxylation of limonene catalyzed by $H_3PW_{12}O_{40}$ (PW)[a]

Run	[PW] × 10^3 (mol l^{-1})	t (°C)	Time (min)	Conversion[b] (%)	Selectivity[b,c] (%)	Product distribution[b] (%)			
						4	**5**	**6–8**	Oligomers
Solvent: acetic acid									
1	6	15	30	26	88	26	62	12	–
			180	63	58	20	38	16	26
2	6	25	40	60	43	20	23	14	43
3	6	40	25	50	44	13	31	12	44
4	12	15	70	50	87	24	63	13	–
			200	81	60	33	27	19	21
Solvent: acetic acid/H_2O = 95/5 (v/v)									
5	6	15	120	15	80	45	35	10	10
			1440	83	58	32	26	12	30
6	6	25	185	30	78	55	23	11	11
			1260	90	62	32	30	15	23
7	6	40	50	54	85	64	21	9	6
			110	85	45	35	10	32	23
Solvent: acetic acid/H_2O = 90/10 (v/v)									
8	6	25	150	7	93	50	43	7	–
			1560	57	81	55	26	13	6
9	6	40	80	40	82	55	27	9	9
			150	57	75	50	25	13	12
			240	75	70	54	16	19	11
10	6	60	15	36	90	70	20	10	–
			25	57	83	70	13	13	4
			45	71	70	62	8	20	10
11	3	40	120	30	66	44	22	11	23
			220	53	50	38	12	11	39
12	12	40	60	33	80	60	20	20	–
			120	63	70	44	26	30	–

[a] [Limonene] = 0.3 mol l^{-1}.

[b] Determined by gas chromatography.

[c] Selectivity for products **4** and **5**.

from 88% at 26% conversion (for 0.5 h) to 58% at 63% conversion (for 3.0 h). Apparently, the oligomerization occurs by the attack of carbenium ion **B** on the olefinic compounds present in the system.

Another side reaction, that occurs under the acetoxylation conditions, is the isomerization of the exocyclic double bond of limonene, yielding terpinolene (**6**), α-terpinene (**7**) and γ-terpinene (**8**) (Scheme 1). The double bond isomerization of olefins catalyzed by HPA in liquid phase has been reported earlier [26,27]. The acid catalyzed isomerization of limonene is rather fast and reversible [28], therefore, products **6–8** are recyclable together with the unconverted limonene. In an attempt to accelerate the reaction and improve its selectivity, we tried to raise the temperature and

catalyst concentration. However, the temperature increase led to a significant drop in selectivity (Table 1, runs 2 and 3 versus run 1), brown high-boiling products being precipitated. Maintaining a lower temperature (15°C) and using higher concentrations of PW allowed us to achieve excellent selectivity at relatively high conversions of limonene (Table 1, cf. runs 1 and 4). Substrate oligomerization did not occur until 50% conversion, with the selectivity for **4** and **5** being as high as 87% (run 4). α-Terpenyl acetate is the main addition product (**4**/**5** ≈ 30/70 mol mol^{-1}). About 13% of limonene reversibly isomerizes to products **6–8**, which, as mentioned above, can be recycled and then transformed to the desired products **4** and **5**. Thus, if we considered isomers **6–8** as unconverted substrates,

the real selectivities would be even higher than those given in Table 1. The selectivity could be almost 100% up to about 50% conversion of limonene, i.e. until the point when the reaction solution turned light brown indicating the formation of oligomerization products (ca. 20% at 80% conversion). It is worth noting that the catalyst can be easily recovered without neutralization by simply precipitating with a hydrocarbon solvent and, in principle, could be reused.

The data on the acetoxylation of β-pinene and α-pinene are presented in Table 2 (runs 1 and 2) and Table 3 (run 1), respectively. These two substrates did not show good selectivities in acetic acid solutions due to their fast oligomerization. Even at a low temperature (15°C), both **2** and **3** reacted almost completely in 20 min giving ca. 40% oligomers.

3.1.2. Hydration/acetoxylation of monoterpenes

The direct hydration of monoterpenes in a two-phase system, monoterpene/H_2O-PW, occurs slowly due to a very low solubility of monoterpenes in water, similar to that observed earlier for the hydration of dihydromyrcene [26]. To enhance the solubility, we have studied the reactions of monoterpenes **1–3** in acetic acid solutions containing 2.5–10 vol.% of water (Tables 1–3).

The data for limonene are presented in Table 1 (runs 5–12). The reaction, which is now a combined hydration/acetoxylation, results mainly in α-terpineol (**4**/**5** ≈ 85–75/15–25 mol mol^{-1}), as acetic acid seems to be a poorer nucleophile compared to water under the conditions used. The relative amount of α-terpineol increases with temperature and reaction time due to the hydrolysis of ester **5** catalyzed by PW. The effect of water addition to the reaction solutions on the catalyst activity and product distribution can be clarified by comparing the results within two sets of runs: 2, 6 and 8 (at 25°C) and 3, 7 and 9 (at 40°C). The limonene conversion drops significantly with an increase in water concentration. However, the addition of water, as expected [26], benefits the reaction selectivity by suppressing substrate

Table 2

Homogeneous hydration/acetoxylation of β-pinene catalyzed by $H_3PW_{12}O_{40}$ (PW)[a]

Run	[PW] × 10^3 (mol l^{-1})	t (°C)	Time (min)	Conversion[b] (%)	Selectivity[b,c] (%)	Product distribution[b] (%)			
						4	**5**	**6–8**	Oligomers
Solvent: acetic acid									
1	6	15	25	86	27	10	17	37	36
2	12	15	20	85	25	13	12	37	38
Solvent: acetic acid/H_2O = 95/2.5 (v/v)									
3	3	15	30	77	64	20	44	19	17
			200	87	69	27	42	14	17
4	6	15	50	91	80	26	54	17	3
5	3	25	12	78	58	22	36	38	4
			50	86	64	34	30	29	7
6	3	40	20	87	53	30	23	15	32
Solvent: acetic acid/H_2O = 90/10 (v/v)									
7	3	15	60	43	80	35	45	20	–
			140	71	83	41	42	12	5
8	3	25	30	75	78	37	41	22	–
			120	92	87	42	45	13	–
9	6	25	30	93	85	37	48	12	3
10	3	40	40	82	70	40	30	26	4
			140	86	69	50	29	25	6
11	6	40	20	89	84	46	38	16	–

[a] [β-Pinene] = 0.3 mol l^{-1}.

[b] Determined by gas chromatography. α-Pinene and limonene are considered as unconverted substrate.

[c] Selectivity for products **4** and **5**.

Table 3

Homogeneous hydration/acetoxylation of α-pinene catalyzed by $H_3PW_{12}O_{40}$ (PW)[a]

Run	[PW] $\times 10^3$ (mol l^{-1})	t (°C)	Time (min)	Conversion[b] (%)	Selectivity[b,c] (%)	Product distribution[b] (%)			
						4	**5**	**6–8**	Oligomers
Solvent: acetic acid									
1	12	15	20	93	24	12	12	40	36
Solvent: acetic acid/H_2O = 95/2.5 (v/v)									
2	6	15	80	90	75	23	52	14	11
Solvent: acetic acid/H_2O = 95/5 (v/v)									
3	3	25	180	89	86	36	50	12	2
Solvent: acetic acid/H_2O = 90/10 (v/v)									
4	3	25	90	44	56	29	27	30	14
5	6	25	90	73	85	44	41	15	–
			180	90	83	43	40	12	5

[a] [α-Pinene] = 0.3 mol l^{-1}.

[b] Determined by gas chromatography. Limonene is considered as unconverted substrate.

[c] Selectivity for products **4** and **5**.

oligomerization. Thus adding 5 vol.% water increased the selectivity from 44% in glacial acetic acid (run 3) to 85% (run 7) at the conversions about 50%, with only 6% of limonene being irreversibly converted to oligomers (versus 44% oligomers in run 3). Similar results were obtained at room temperature (cf. runs 2 and 8 at a 60% conversion). A further addition of water (HOAc/H_2O = 90/10) allowed to maintain a relatively high selectivity up to ca. 75% conversion (11% oligomers), however, significantly decelerated the reaction even at 40°C (run 9).

In order to optimize the process, we have studied the effects of temperature and catalyst concentration on the reactions in aqueous acetic acid solutions. The data obtained show that in the temperature regions of 15–40°C for HOAc/H_2O = 90/5 (runs 5–7) and 25–60°C for HOAc/H_2O = 90/10 (runs 8–10), the product distributions at the same conversions of limonene in each set of runs are rather close. Thus, the reaction selectivity hardly depends on the temperature, while it is strongly influenced by the concentration of water. It is also noteworthy that at higher temperatures, the relative amount of the desired product, α-terpineol **4** versus its acetate **5**, increases significantly: the molar ratio of **4** to **5** is 68/32 at 25°C (run 8), 77/23 at 40°C (run 9) and 88/12 at 60°C (run 10).

We have also found that the balance between the concurrent reaction pathways is affected by the catalyst concentration (runs 9, 11, 12). With an increase in PW concentration from 0.003 to 0.012 mol l^{-1} the amount of limonene converted to oligomers decreases from 39% (run 11) to nearly none (run 12) at ca. 60% conversion.

The best result on the hydration of limonene, in terms of catalyst activity and selectivity for α-terpineol, was achieved in the aqueous acetic acid solution (HOAc/H_2O = 90/10 v/v) at 60°C (Table 1, run 10). The selectivity for the addition products **4** and **5** (80–90 mol.% of **4**) reaches 90% at 36% conversion and 83% at 57% conversion, with only trace amounts of oligomers being formed. As mentioned above, isomers **6–8** (10–13%) can be recycled together with unconverted limonene and the catalyst can be easily separated from the reaction solutions.

The addition of water to acetic acid also produces a beneficial effect on the hydration/acetoxylation of β-pinene (Table 2, run 1 versus 3 and 7, run 5 versus 8). The reaction now occurs much slower than in glacial acetic acid (but much faster than with limonene under similar conditions), however, the amounts of the oligomerization products decrease dramatically. In HOAc/H_2O = 90/10 v/v, almost no oligomerization was observed and the reaction solutions remained colorless even at high substrate conversions. With the increase in water concentration, the selectivities for products **4** and **5** rise at the expense of both oligomerization and isomerization. It should be mentioned that under these reaction conditions,

β-pinene easily isomerizes to form initially α-pinene and limonene (which disappear rapidly) and then less reactive monoterpenes **6–8** containing internal double bonds. No products of the acetic acid/water addition to these substrates were detected. At longer reaction times and especially at higher water concentrations, **6–8** are also consumed due to the isomerization back to limonene, which then gives desired products **4** and **5** (runs 7 and 8). As a result, the selectivity for these products increases with time, e.g. in run 8, the selectivity of 87% is achieved at 92% conversion of β-pinene for 2 h, while 78% at 75% conversion.

To optimize the system we have varied the temperature and catalyst concentration. With 2.5 vol.% of water in acetic acid, the temperature increase from 15 to 25°C and then to 40°C (runs 3, 5 and 6) had practically no effect on the selectivity for **4** and **5**, influencing only the balance between the side reactions (isomerization versus oligomerization). At a higher catalyst concentration (0.006 mol l^{-1}) and 15°C, the selectivity of 80% was obtained at 91% conversion, with the oligomerization being almost negligible (run 4). The best results were obtained in the acetic acid solutions containing 10 vol.% of water. In an attempt to accelerate the conversion of isomers **6–8** into desired products, i.e. to increase the selectivity based on the amount of the substrate charged, we have again varied the temperature and PW concentration (runs 7–11). In various runs, excellent results in terms of both catalyst activity and selectivity have been achieved: ca. 85% selectivity at ca. 90% conversion for 0.5–2 h depending on reaction conditions (runs 8, 9 and 11). It is important that in these runs almost no oligomerization of monoterpene occurred. Isomers **6** and **8** are recyclable, moreover, they slowly transform into products **4** and **5** under the reaction conditions (cf. the product distributions at 30 and 120 min in run 8).

The data on the hydration/acetoxylation of α-pinene, are presented in Table 3 (runs 2–5). In the acetic acid solutions containing PW and water (2.5–10 vol.%), α-pinene can be smoothly converted to α-terpineol and its acetate. As with other monoterpenes, the reaction is strongly complicated by oligomerization and skeletal/double bond isomerization leading to limonene and then to its isomers with internal double bonds (**6–8**). On calculating the data in Table 3, limonene was considered as unconverted substrate, while **6**, **7** and **8** as the products because,

although they can be converted to the desired products **4** and **5** with time, it occurs slower than with limonene. The optimization of the reaction variables, whose effects are similar to those observed in the hydration/acetoxylation of limonene and β-pinene, has resulted in developing a rather fast and highly selective process occurring at room temperature. Thus in runs 3 and 5, the selectivity of ca. 85% was attained at ca. 90% conversion, with only trace amounts of the substrate being oligomerized (2–5%).

The relative reactivities of the monoterpenes studied under the same conditions can be seen from comparison between run 8 in Table 1, run 9 in Table 2 and run 5 in Table 3. The selectivities for products **4** and **5** in all three runs are near 85%. As can be seen, β-pinene reacts much faster then its isomer α-pinene, containing the endocyclic double bond. The latter is much more reactive than limonene, in which the more reactive double bond is the exocyclic one. It is worth noting again that PW can be easily recovered from the reaction mixture by precipitating with a hydrocarbon solvent, e.g. hexane.

The molar catalytic activities of PW in acetoxylation/hydration of limonene, α-pinene and β-pinene are approximately 80 times higher than those of H$_2$SO$_4$, as found from the initial reaction rates. For limonene, the initial rates with HPA and H$_2$SO$_4$ were found to be 0.156 and 0.0020 mol l^{-1} h^{-1}, respectively, at 40°C, [catalyst] = 0.0060 mol l^{-1}, [limonene] = 0.30 mol l^{-1} and HOAc/H$_2$O = 90/10. For α-pinene, they were 0.270 and 0.0040 mol l^{-1} h^{-1} at 25°C and for β-pinene 0.358 and 0.0050 mol l^{-1} h^{-1} at 15°C and otherwise the same conditions. This is in accordance with the relative acid strengths of PW and H$_2$SO$_4$ in acetic acid (pK_1 4.8 and 7.0, respectively [29]).

The transformations occurring with limonene, β-pinene and α-pinene in acetic acid solutions, in the presence of heteropoly acid, can be represented within the framework of a carbenium ion mechanism depicted in Scheme 1. The protonation of β-pinene and α-pinene originate carbenium ion **A**, which then isomerizes giving carbenium ion **B**. The latter also forms directly by the protonation of limonene and undergoes a nucleophilic attack by water or acetic acid to give α-terpineol **4** or its acetate **5**. Alternatively, carbenium ion **B** can lose a proton resulting in terpinolene **6**, which, in turn, can further isomerize

to α-terpinene **7** or/and γ-terpinene **8**. Apparently, all these processes are reversible. In addition, both carbenium ions **A** and **B** can react with another olefin molecule present in the reaction solution to give a C_{20} carbenium ion which could initiate an irreversible oligomerization process. Thus, the more efficient the nucleophile, the slower the isomerization and oligomerization occur. The significant increase in selectivity with the addition of water observed for all the substrates studied can be explained as a result of an efficient trapping of carbenium ion **B** by water molecules (stronger nucleophiles than acetic acid), which prevents its isomerization and oligomerization.

The PW catalyzed transformations of limonene, β-pinene and α-pinene apparently involve common carbenium ion intermediates. However, the reactivities of these substrates differ significantly. The reactivities observed parallel the standard enthalpies of formation of the substrates (ΔH°(liq) = -7.7; -16.4; and $-54.5\,\text{kJ mol}^{-1}$ for β-pinene, α-pinene and limonene, respectively [30]), the most stable substrate limonene exhibiting the lowest reactivity. This may indicate that the rate determining steps in Scheme 1 are the protonation of olefins.

3.2. Heterogeneous acetoxylation of monoterpenes

The data on the acetoxylation of monoterpenes with solid acid catalysts are presented in Table 4.

Silica has been used as a support for solid PW, because of its inertness towards heteropoly acids. The state and acidity of PW on silica have been reviewed elsewhere [20]. Bulk PW has been reported to exhibit a low activity in the acetoxylation of dihydromyrcene [26], which has been explained by the small surface area of the catalyst (1–$5\,\text{m}^2\,\text{g}^{-1}$) and also by possible deactivation of strong proton sites of the bulk PW due to adsorption of reaction products or substrates. Silica-supported HPA has weaker proton sites due to the interaction with surface silanol groups [20,31], and thus, less susceptible to deactivation. In this work, we have used 20 or 40% PW/SiO_2 as catalysts for the acetoxylation of limonene, α-pinene and β-pinene. The reactions with supported PW proceeded similarly to the homogeneous acetoxylation, with the formation of mainly α-terpenyl acetate along with smaller amounts of α-terpineol (**4**/**5** = 5–20/95–80 mol mol^{-1}). No significant oligomerization of monoterpenes occurred under the optimized conditions shown in Table 4, contrarily to what observed in homogeneous systems, especially for α-pinene and β-pinene. The PW/SiO_2 catalyst, initially a white powder, turned light brown during the reaction. In runs 2 and 5 after the reaction, the catalyst was filtered off, washed with hexane and used repeatedly (three times) almost without loss of activity (the activity decreased by only ca. 10% compared to the first run). In the forth run, only a half of the initial activity was observed probably because of blocking

Table 4
Acetoxylation of monoterpenes with solid acid catalysts[a]

Run	Substrate	Catalyst	t (°C)	Time (min)	Products **4** + **5**[b] (mol l^{-1})	Conversion (%)[c]
1	Limonene	20% PW/SiO_2	15	170	0.64	16.0
2	Limonene	20% PW/SiO_2	25	40	0.42	10.5
3	Limonene	20% PW/SiO_2	40	10	0.22	5.5
4	α-Pinene	20% PW/SiO_2	15	50	0.40	10.0
5	α-Pinene	20% PW/SiO_2	25	95	0.35	8.8
6	α-Pinene	20% PW/SiO_2	40	90	0.37	9.3
7	α-Pinene	40% PW/SiO_2	25	160	0.86	21.5
8	β-Pinene[d]	20% PW/SiO_2	15	10	0.78	19.5
9	β-Pinene[d]	20% PW/SiO_2	25	10	0.55	13.8
10	Limonene	Amberlyst-15	25	40	0.15	3
11	α-Pinene	Amberlyst-15	25	90	Traces	<1
12	β-Pinene	Amberlyst-15	25	10	0.06	1.4

[a] 2.5 wt.% of catalyst, monoterpene/HOAc mixture (1/1.2 mol mol^{-1})

[b] **4**/**5** ≈ 20/80 mol mol^{-1}.

[c] Reversibly formed isomers are considered as unconverted substrate.

[d] Bornyl acetate is detected (**4** + **5**/bornyl acetate = 70–90/30–10 mol mol^{-1}).

the active acid sites by oligomers. PW/SiO$_2$ showed much higher activity than Amberlyst-15 (Table 4, runs 10–12 versus runs 2, 5, 9), similar to what has been observed in the acetoxylation of dihydromyrcene [26].

No leaching of heteropoly acid from the catalyst surface took place in the reaction mixture at near stoichiometric substrate/HOAc ratios. As mentioned above, at high concentrations of acetic acid (monoterpene/HOAc < 1/3), some PW leaching occured.

As can be seem from the data presented in Table 4, limonene (run 1), α-pinene (run 7) and β-pinene (run 8) can be readily converted into **4** and **5**. The total concentration of the products in reaction mixture reaches 0.65–0.86 mol l^{-1} (10–13 wt.%), corresponding to a 16–21% substrate conversion. As in homogeneous reactions, β-pinene reacts much faster than limonene or α-pinene. The best results are obtained at low temperatures (15–25°C). At a higher temperature, **4** and **5** formed initially react further probably to give condensation products. The concentration of **4** and **5** passes a maximum, with the maximum yield decreasing as the temperature increases. Interestingly, in the case of β-pinene, we observed the formation of bornyl acetate (up to 30 mol.%), which is a useful product. This may be explained by a higher steady-state concentration of carbonium ion **A** (Scheme 1), which forms rapidly from β-pinene and is stabilized on the catalyst surface. **A** probably isomerizes not only to **B** but also, at a lower rate, to a bornyl-type carbenium ion that gives rise to the bornyl acetate.

4. Conclusions

Synthetically useful homogeneous and heterogeneous protocols for the hydration and acetoxylation of limonene, β-pinene and α-pinene into α-terpineol and α-terpenyl acetate in liquid phase have been developed, with the use of H$_3$PW$_{12}$O$_{40}$, the strongest heteropoly acid in the Keggin series, as the catalyst. The heteropoly acid shows a much higher catalytic activity than the conventional acid catalysts such as H$_2$SO$_4$ and Amberlyst-15. Under optimized conditions, all three substrates give the valuable product α-terpineol, along with α-terpenyl acetate with 85–90% total selectivity. Virtually no oligomerization of monoterpenes occurs under such conditions. The main by-products,

terpinolene, α-terpinene and γ-terpinene, that form reversibly, may be recycled together with the unconverted substrate. The uncommon solubility properties of HPA allow for easy and clean catalyst recovery from acetic acid solutions without neutralization by simply precipitation with a hydrocarbon solvent. The HPA catalyst, in principle, could be reused.

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