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Synthesis of terpineol from α-pinene by homogeneous acid catalysis

M. Román-Aguirre, L. De la Torre-Sáenz, Wilber Antúnez Flores,
A. Robau-Sánchez, A. Aguilar Elguézabal [*]

Centro de Investigación en Materiales Avanzados S.C., Miguel de Cervantes No. 120 Complejo Ind,
Chih, Chihuahua, Chih., CP 31109, Mexico

Abstract

Chloroacetic acid was used as catalyst for the hydration of α-pinene using water as hydroxyl donor, which is soluble in aqueous and organic solvents. The highest selectivity was 95.5 with a conversion of 10%, whereas the higher conversion was 99% with selectivity of 70% after 4 h of reaction at 70 °C. Organo-chlorinated compounds were not found in products as in the case of the use of HCl as catalyst, which indicates that the intermediate carbocation formed after alkene protonation is not susceptible to react with the chloroacetic anion.

Keywords: Pinene; Terpineol; Hydration

1. Introduction

Terpineol is a product widely used in the cosmetic industry as perfume and repellent of insects [1], in the pharmaceutical industry as antifungal [2] and disinfectant [3], in the cleaning industry as odorant and disinfectant and in mineral benefit industry as metal flotation agent. Lately, some functional copolymers were obtained using terpineol and styrene [4].

Hydration and isomerization of the α-pinene to several alcohol or terpenic hydrocarbons have been studied since the 1940s, when Mosher [5] studied the isomerization of the α-pinene in acid media using 1-chloro-4-naftalen sulfonic acid. There is a lack of solid catalysts able to carry out the reaction of hydration of the α-pinene to terpineol with high selectivity and conversion. Castanheiro et al. [6] used molybdophosphoric acid (HPMo) to hydrate α-pinene to terpineol, they supported their catalyst on poly-dimethyl siloxane and polyvinyl alcohol membranes as well as in Y type zeolites. Although they achieved 70% of selectivity with conversion of 90%, the reaction time was 150 h. This same research group, in a previous work [7] used dispersed zeolites in poly dimethyl siloxane to model the kinetic-diffusional effect of α-terpineol in the hydration of α-pinene.

Other groups have used homogenous catalysts, thus for example, Robles et al. [8] used $HPW_{12}O_{40}$ as catalyst and mixtures of acetic acid and water as solvent for hydrating limonene, β-pinene and α-pinene, obtaining selectivity to terpineol near to 30%, with 90% of α-pinene conversion after 3 h of reaction at 25 °C. Pakdel et al. [9] used aqueous solutions of sulfuric acid as catalyst in the presence of acetone to obtain terpineol from crude sulphated pine oil, they reported 67% of selectivity to terpineol although conversion was not reported. The systems before mentioned need the manufacture of catalytic supports; nevertheless, diffusivity is altered in the course of the reaction, or they present environmental problems by the disposition of the used homogenous catalysts. Junko et al. [10] patented a catalytic system using a solid Brönsted acid catalyst in the presence of chloro-substituted fatty acids for the hydration of the α-pinene. The same group [11] patented a catalytic system using rare earth in the presence of a chloro-substituted fatty acid for the same reaction. The objective of this work is to study the role of chloroacetic, oxalic and acetic acid catalysts to hydrate α-pinene to terpineol using water as the hydroxyl group donor.

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[*] Corresponding author.
E-mail address: alfredo.aguilar@cimav.edu.mx (A.A. Elguézabal).

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2. Experimental

The α-pinene was provided by COPAMEX. S.A. de C.V; where α-pinene is obtained as by-product from the processing of pine wood for the production of paper pulp. The content of α-pinene is 92% (w/w). The chloroacetic acid (CAA) and deionized water were J.T. Baker products. Oxalic acid (OA), hydrochloric acid (HCl) and acetic acid (AA) were Fisher Sci. products and acid was from Avocado Res. Chem. Ltd. The reagents were not purified before its use. The reactions were made in a glass reactor provided with magnetic stirrer, sampling port, temperature bath and condenser. A mixture of 0.25 mol of pinene with 0.60 mol of water was loaded into reactor. The mixture was stirred and warmed up to the desired temperature. Once the desired temperature was reached, the catalyst was loaded into the reactor in the amount shown in Table 1. The reaction products were analyzed by gas chromatography taking samples to the 30, 60, 120 and 240 min after adding the catalyst. The products were cooled at the end of the reaction and two phases, organic and aqueous were separated by densities difference. The final mass of the catalyst was measured in each phase by titration with a 0.1N NaOH solution to verify the absence of undesired reactions of catalysts. The compounds present in the samples were identified in a Thermofinigan GC Top 8000/Voyager MS gas chromatograph/mass spectrometer system. The column used was an All Tech AT-5 capillary column with 30 m of length and 0.25 mm of internal diameter. The temperatures of injector and transference line were maintained constant at 250 °C. The initial temperature of the furnace was maintained at 60 °C by 3 min, then it was increased at rate of 5 °C/min up to 150 °C, where stayed by 1 min. Finally, the temperature was increased at a rate of 10 °C/min up to 250 °C and this temperature was maintained 1 min. Once identified, the total content of each specimen was calculated from its concentration in both, aqueous and organic phase. These analyses were performed in a Perkin-Elmer Auto-System XL gas chromatograph instrument with a Perkin-Elmer PE-1 capillary column of 60 m × 0.25 mm of internal diameter and a hydrogen flame ionization detector. The temperatures of injector and detector were maintained constant to 270 °C. The initial temperature of the furnace was 80 °C during 1 min, thereafter temperature was increased at a rate of 10 °C/min up to 150 °C and this temperature was maintained 1 min, and again, temperature was increased at a rate of 15 °C/min up to 250 °C remaining at this temperature by 15 min. The FID response factors were determined experimentally taking the α-pinene as the reference compound.

Table 1
pK_a constant and solubility of the catalyst used for α-pinene hydration

Acid	pK_a	Solubility in organic phase[a] (% w/w)
HCl	$\ll 1$	–
CH_3COOH	4.2	>100
HOOCCOOH	1.3	0.64
$ClCH_2COOH$	2.8	>100

[a] Measured at 70 °C.

3. Results and discussion

3.1. Effect of catalyst

Acids catalyze the hydration reactions of alkenes in aqueous solution. The acid transfers a proton to double bond of the alkene, forming an intermediary carbocation that reacts with water to form a protonated alcohol. The loss of H^+ from the protonated alcohol generates the neutral product and the recovery of the catalyst. In the hydration of terpenes, a variety of products may be obtained depending on the catalyst and reaction conditions. To study the effect of acidity strength and organic/inorganic nature of several acids on the pinene hydration, reaction test were made at 70 °C with catalyst concentration of 6.4 mol/L with reaction time of 4 h. Table 2 shows the pK_a as well as the solubility in the organic phase of the studied acid catalysts.

Conversion and selectivity to terpineol curves, plotted against time for each catalyst are shown in Figs. 1 and 2, respectively. For the acetic acid, which is the weaker acid, conversion was negligible, despite the good affinity with pinene. It was observed that with HCl as catalyst, pinene conversion becomes near to 100% within the first minutes of reaction, nevertheless the production of terpineol is minimum, being bornyl chloride the main reaction product, followed by isomers of α-pinene, mainly γ-terpinene and limonene. This result is due to the high strength of the acid, since after the formation of carbocation, the halogen competes with the water to share the electronic pair and Cl^- bonds to carbocation. The selectivity to α-terpineol was lower than 10%.

For the oxalic acid the highest conversion is near to 40% with selectivity to α-terpineol of 60%, these values were obtained with reaction time of an hour, and further changes are minimal. The low solubility of oxalic acid limits the conversion due to the poor availability of protons in the organic phase, and hydration reaction is carried out mainly at water/pinene interphase. The products with the higher yield using oxalic acid as catalyst were non-oxygenated compounds like limonene, terpinolene and carenes. The formation of these compounds supports the above mentioned, and oxalic acid does not promote the water/pinene interaction, so protons at organic phase promote mainly pinene rearrangement isomerization like in the isomerization process of pinene to produce camphene.

As shown in Figs. 1 and 2, the conversion obtained using chloroacetic acid as catalyst was 91% and the selectivity to terpineol was 69%, this result is notable for industrial purposes, other advantages with this catalyst are the absence of chlorinated by-products, and the capability to recover catalyst by simple recrystallization. Chloroacetic acid is

Table 2
Reaction condition of pinene hydration tests with the selected catalysts

Exp. no.	T (°C)	Water (mol)	α-Pinene (mol)	Hydrochloric acid (mol)	Acetic acid (mol)	Oxalic acid (mol)	Chloroacetic acid (mol)	%	
								C[a]	S_{t}[b]
1	70	0.6	0.25	0.05	0	0	0	99.8	9.6
2	70	0.6	0.25	0.33	0	0	0	100	9.9
3	70	0.6	0.25	0	0.05	0	0	–	–
4	70	0.6	0.25	0	0.33	0	0	–	–
5	70	0.6	0.25	0	0	0	0.05	–	–
6	70	0.6	0.25	0	0	0	0.11	10.1	95.5
7	70	0.6	0.25	0	0	0	0.16	29.0	79.5
8	70	0.6	0.25	0	0	0	0.21	78.3	69.1
9	70	0.6	0.25	0	0	0	0.33	91.2	69.2
10	70	0.6	0.25	0	0	0	0.42	100	69.6
11	70	0.6	0.25	0	0	0.03	0	5.6	67.4
12	70	0.6	0.25	0	0	0.11	0	17.1	74.4
13	70	0.6	0.25	0	0	0.22	0	53.4	64.0
14	70	0.6	0.25	0	0	0.43	0	39.8	60.8
Ref.[c]	70	0.6	0.25	0	0	0	0.33	91.1	68.9

[a] C = α-pinene conversion.

[b] S_{t} = selectivity to terpineol.

[c] Ref. consists in the use of 0.34 g of Amberlist 35 wet ion exchanger resin as a co-catalyst with chloroacetic acid.

miscible with pinene and also soluble in water, due to these two factors, this catalyst, besides the formation of the proton to form the carbocation, favors the transfer of OH^- to organic phase and as a result, hydration yield is the highest of the studied catalysts.

3.2. *Effect of catalyst concentration*

The effect of catalyst concentration for oxalic and chloroacetic acids is shown in Figs. 3 and 4, respectively. Fig. 3 shows conversion and selectivity to α-terpineol, limonene and γ-terpinolene against acid concentration. Selectivity to α-terpineol remained almost constant independently of conversion. Apparently the conversion reached a chemical equilibrium, as if the catalyst were deactivated after some minutes, as is shown in Figs. 1 and 2 for conversion and selectivity versus reaction time. A possible explanation is the formation of chemical species which inhibit the migration of protons and OH^- groups from oxalic acid ionized in water phase to organic phase.

Fig. 4 shows the conversion and selectivity to terpineol, limonene and γ-terpinene against chloroacetic acid concentration. As was mentioned before, chloroacetic acid is completely soluble on the system at 70 °C and showed a sigmoidal growing tendency in conversion as acid concentration used for reaction increases, being 99% the maximum, with selectivity of 69%. The good performance of chloroacetic acid as catalyst must be due to the high affinity for both phases organic and aqueous, since this promotes the transfer of hydroxyl anion to organic phase in such a way, that the carbocation hydration reaction is faster than rearrangement reactions which produce α-pinene isomers. Junko et al. [10] patented a method to obtain terpineol from α-pinene using chloro-substituted fatty acids

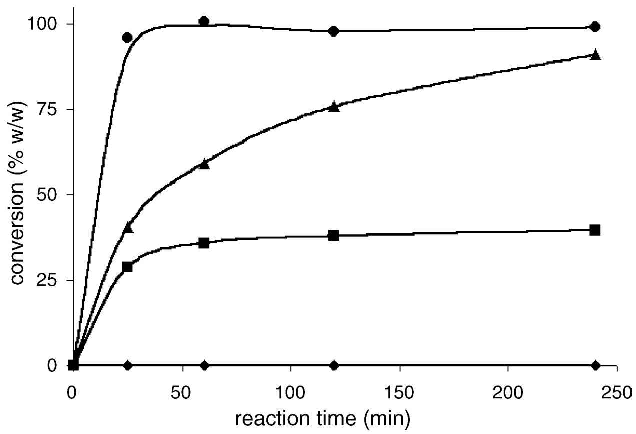


Fig. 1. α-Pinene conversion vs. reaction time curves for: (◆) acetic acid; (▲) chloro acetic acid; (■) oxalic acid and (●) hydrochloric acid. Temperature: 70 °C, catalysts concentration: 6.4 mol/L.

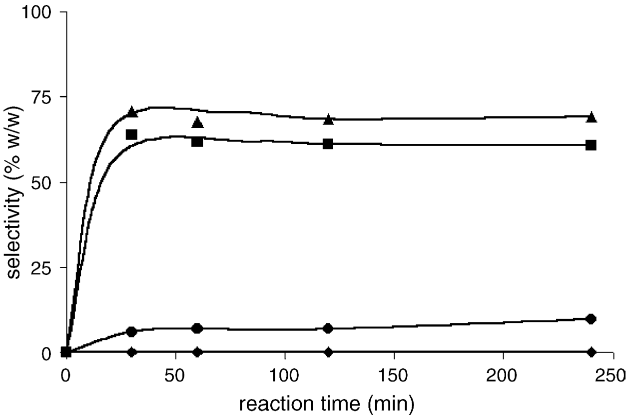


Fig. 2. Selectivity to α-terpineol vs. reaction time curves for: (◆) acetic acid; (▲) chloro acetic acid; (■) oxalic acid and (●) hydrochloric acid. Temperature: 70 °C, catalysts concentration: 6.4 mol/L.

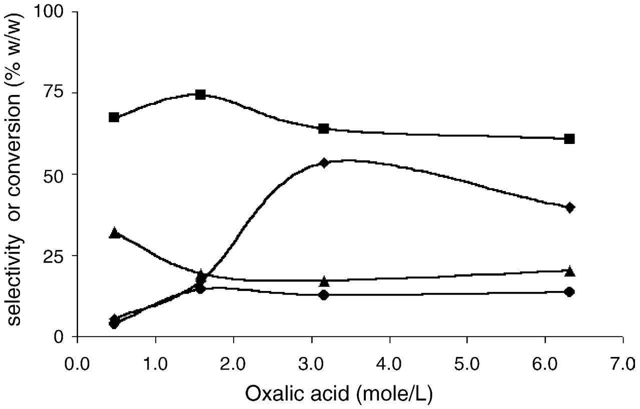


Fig. 3. Conversion and selectivity vs. oxalic acid concentration: (◆) α-pinene conversion, (■) selectivity to α-terpineol, (▲) selectivity to terpinolene and (●) selectivity to limonene. Temperature = 70 °C, reaction time = 240 min.

as a medium and Brönsted acid resins as a catalyst. On the other hand, Noburu et al. patented a process to obtain terpineol from α-pinene using ion exchange resins. In this work, a reference reaction using Amberlist 35 wet ion exchange resin with chloroacetic acid was made, and the same results of conversion and selectivity were found when reaction was made without exchange resin, which indicate that the proton is given by chloroacetic acid and the exchange resin is unnecessary.

It was observed in our study that the main product was terpineol, γ-terpinolene and limonene. Robles et al. [8], proposed a reaction scheme for the acid catalyzed hydration of α-pinene and β-pinene. They used molybdophosphoric acid as catalyst and obtained limonene, γ-terpinolene and α-terpineol as main products. Since the same main products are found in this work, a similar evolution as the one shown in Scheme 1 could be taking place in the reaction with oxalic and chloroacetic acid as catalysts.

Actually, the typical way to obtain terpineol is by hydration of α-pinene with aqueous sulfuric acid [12]. The separation of catalyst from the reaction products is too difficult and is an environmental problem. According to this work, oxalic acid is a good candidate for the industrial hydration of α-pinene, due to its easy separation from reaction products and low cost. On the other hand, chloroacetic acid catalyst is also easy to separate from reaction products and conversion and selectivity are better than the observed for oxalic acid catalyst.

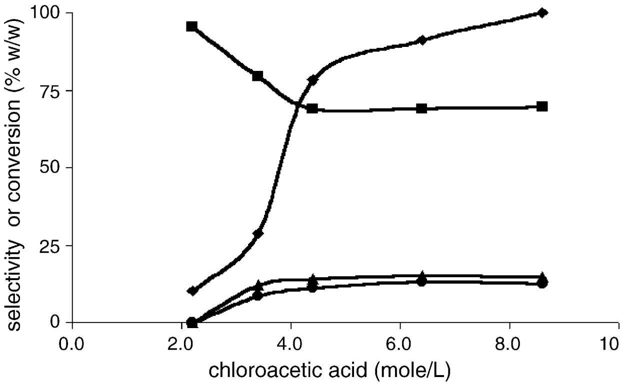
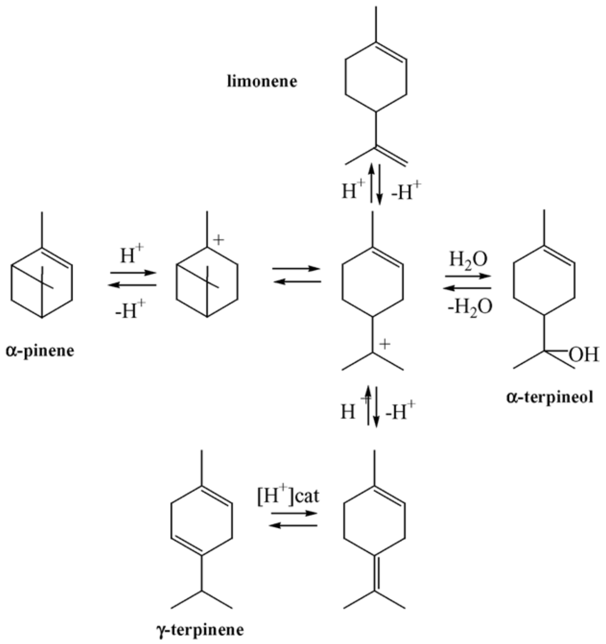


Fig. 4. Conversion and selectivity vs. chloroacetic acid concentration: (◆) α-pinene conversion; (■) selectivity to terpineol; (▲) selectivity to γ-terpinene and (●) selectivity to limonene. Temperature = 70 °C, reaction time = 240 min.



Scheme 1. Evolution of the chemical specimen present on the acid catalyzed hydration of α-pinene, Robles et al. [8].

4. Conclusions

Chloroacetic acid was found as good catalyst for the production of α-terpineol from pinene. The good results are due to strong acidity and high solubility and affinity with aqueous and organic phases during reaction. The obtained yield with this catalyst is interesting for industrial application, mainly due to the absence of chlorinated compounds and for the easy separation and purification of this catalyst from the reaction media if compared with sulfuric acid (chloroacetic acid become insoluble in water and pinene at 5–7 °C, and precipitates as crystals). No other co-catalyst as ion exchange resins is necessary to obtain good selectivity and high conversion on the hydration of α-pinene to terpineol with chloroacetic acid.

Oxalic acid is slightly soluble in pinene and conversion and selectivity were lower than the observed for the chloroacetic acid catalyst. Since pK_a is 1.3 for oxalic acid, it is expected that results can be improved if a co-solvent is added to reaction system to favor the interaction of α-pinene and oxalic acid catalyst. Any way, the low cost of oxalic acid and its easy separation and purification make it of industrial interest.

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