# Isomerization of α-Pinene, Limonene, α-Terpinene, and Terpinolene on Sulfated Zirconia

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**ABSTRACT:** Transformations of α-pinene, limonene, terpinolene, and α-terpinene were studied in liquid phase on sulfated zirconia having 15% $H_2SO_4$, with the aim of identifing the pathway of α-pinene isomerization. The principal products obtained in α-pinene isomerization were camphene, tricyclene, limonene, and terpinolene; the concentration maxima observed at 120°C and 180 min were 53, 6.1, 7.7, and 3.0%, respectively. The principal products formed in the limonene transformation after a 20-min reaction time were terpinolene, α-terpinene, and γ-terpinene; then the concentration of these products decreased. The terpinolene reaction yielded principally m-cymenene, whereas the α-terpinene transformation produced p-cymene. Studies of the initial rates of transformation of terpenes indicate a very high rate for α-pinene, intermediate for limonene and α-terpinene, and very low for terpinolene. The scheme proposed to interpret the results of the α-pinene isomerization reaction on sulfated zirconia is in agreement with reaction schemes proposed by A. Al-lahverdiev, S. Irandoust, and D.Y. Murzin (Isomerization of α-Pinene over Clinoptilolite, *J. Catal.* 185:352–362, 1999).

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**KEY WORDS:** Limonene, α-pinene isomerization, sulfated zirconia, terpenes, terpinolene.

Camphene is an important intermediate in the chemical industry; the main use is in camphor synthesis. Camphene is obtained as the principal reaction product when α-pinene isomerization is performed in a liquid phase in the presence of acid catalysts, as well as limonene, tricyclene, terpinolene, and other mono- and bicyclic compounds.

The commercial process for camphene production uses $TiO_2$ catalysts treated with acids, but the reaction rate on these catalysts is slow, and more active catalysts are desirable. Zeolites, clays, and different oxides have been used with this purpose (1–8). Our group reported previously the isomerization of α-pinene on sulfated zirconia with and without modifications by Fe and Mn, zirconia with molybdenum and tungsten, and kaolinitic and bentonitic clays (9,10).

The activity is associated with the catalyst acidity and the type of active sites, and the strength of the latter has an effect on the ratio of selectivities in bicyclic to monocyclic products.

Severino *et al.* (1) maintain that Lewis sites favor the formation of bi- and tricyclic products whereas Brönsted sites favor the formation of monocyclic products.

Ion-exchanged natural zeolites give two main groups of products: bicyclic and monocyclic. Camphene and bicyclic products are preferentially formed on Lewis sites from α-pinene, and monocyclic products are formed on Brönsted sites (2).

Reaction pathways using clays, zeolites, and resins for the isomerization of α-pinene are found in the literature (3–6). These mechanisms were deduced from experimental results of the α-pinene isomerization reaction.

Zirconium oxide, when modified with sulfate anion, forms a highly acidic or superacidic catalyst that exhibits superior catalytic activity for the catalysis of isomerization reactions. Catalysts of sulfated zirconia are active in α-pinene isomerization (7,9); in the present work, sulfated zirconia (15%) was selected to study the isomerization of α-pinene, limonene, and terpinolene to help understand the reaction pathway.

Our group reported previously on the isomerization of α-pinene on catalysts of sulfated zirconia (9). The aim of the present work was to study the pathway of α-pinene isomerization by studying the isomerization of α-pinene, limonene, terpinolene, and α-terpinene.

## EXPERIMENTAL PROCEDURES

The catalyst was prepared by impregnating zirconium hydroxide with the necessary amount of a solution of $H_2SO_4$ (1 N; Merck, Darmstadt, Germany) in methanol (Carlo Erba, Milano, Italy). The zirconium hydroxide was obtained by hydrolysis of zirconyl chloride ($ZrOCl_2 \cdot 6H_2O$; Fluka, Buchs, Switzerland). The nominal concentration of $H_2SO_4$ in the catalyst was 15%. The precursor was calcined up to 600°C for 4 h before its use in the reaction.

Transformation reactions of terpenes were carried out in a batch reactor, at constant temperature, with magnetic stirring. The analysis of the reaction components was performed by GLC with a capillary column DB1 (Supelco, Bellefonte, PA) of 60 m and the temperature was increased from 75 up to 200°C at a rate 3°C/min. The identification of products was made by comparison of retention times with terpene standards and confirmed by GC–MS.

The surface area of the support and catalysts and the distribution of pore sizes were determined by using the $N_2$ BET

method, in a Micromeritics Accusorb 2100E instrument. The crystalline structure of catalysts was determined by X-ray diffraction (XRD) studies on Rigaku D-Max III equipment with Cu Kα radiation (λ = 1.5378 Å, 40 K, 30 mA). The 2θ range analyzed was between 5 and 70°. FTIR spectra of the catalysts were obtained in a Bruker IFS66 FTIR instrument using KBr pellets. FTIR spectra of catalysts with adsorbed ammonia were used to determine the presence of Brönsted acidity. The adsorption was carried out at room temperature by passing pure ammonia (15 cm$^3$/min) for 30 min. Excess ammonia was eliminated by applying vacuum for 12 h.

## RESULTS AND DISCUSSION

*Characterization of the catalysts.* The zirconium oxide catalyst impregnated with 15% $H_2SO_4$ that was used in this study had a surface area of 130 m$^2$/g.

XRD peaks corresponding to a monoclinic as well as a tetragonal phase were observed, but the latter was found in larger proportion. The ratio of the monoclinic to the tetragonal phase from XRD data was 0.56.

From comparison of FTIR spectra performed on the catalyst with and without adsorbed ammonia, the appearance of a band at 1400 cm$^{-1}$ is observed with the former. This band is assigned to the asymmetric vibration of the $NH_4^+$ ion and indicates the presence of Brönsted sites.

*α-Pinene reaction.* To study the distribution of products of this reaction, experiments were performed over a temperature range of 90–140°C. The concentration of each product, calculated as chromatographic area × 100/total area, for different reaction times and temperatures is shown in Table 1. In experiments carried out at 90°C, the concentration of all reaction products increased with reaction time except for fenchene, which reached a maximum at 120 min and then fell. At 120°C, the concentrations of bornylene, fenchene, α-terpinene, γ-terpinene, and terpinolene reached a maximum with reaction time

(20 or 120 min) and then fell (180 min). Similar results were observed at 140°C; in this case, compounds that reached a maximum and then fell after 3 h were bornylene, fenchene, limonene, α-terpinene, γ-terpinene, terpinolene, and isoterpinolene. All compounds that exhibited a maximum concentration and then fell can be considered intermediates in the reaction pathway. Small amounts of low retention-time products and other products are produced, the sum of which does not exceed 3%.

Table 2 shows the concentration of the bicyclic and monocyclic compounds for the complete temperature range studied, as well as the ratio and averaged ratio between bicyclic and monocyclic compounds. From Table 2 one can see that the ratio of bicyclic to monocyclic compounds is constant with time. As the ratio is a constant (for this catalyst, equal to 3), these products are probably derived from a common intermediate (carbocation). The ratio of bicyclic to monocyclic compounds is constant over the reaction time and temperature range studied, suggesting that activation energies are similar for the formation of bicyclic and monocyclic compounds.

Figure 1 shows the concentration of all monoterpenes from this reaction (limonene, α-terpinene, γ-terpinene, terpinolene, *p*-cymene, and isoterpinolene) as a function of time for the experiment at 140°C. The *p*-cymene concentration increased continuously with time up to 8%, whereas the concentration of the other monoterpenes (limonene, α-terpinene, γ-terpinene, and terpinolene) reached a maximum and then leveled off or declined somewhat.

*Reaction of limonene, α-terpinene, and terpinolene.* To study the reaction pathway, limonene, terpinolene, and α-terpinene were used as reagents. Limonene isomerization at 120°C as a function of reaction time is shown in Figure 2. The principal products formed after 20 min were terpinolene (10%), α-terpinene (2.5%), and γ-terpinene (1.5%); the concentrations of these products passed through a maximum at or near this reaction time and then declined. The concentrations of *p*-cymene

**TABLE 1**
**Isomerization of α-Pinene**[a]

| Time | 90°C | | | 120°C | | | 140°C | | |
|------|------|------|------|------|------|------|------|------|------|
| (min) | 20 | 120 | 180 | 20 | 120 | 180 | 20 | 120 | 180 |
| LRTP | 0.0 | 0.5 | 0.6 | 1.0 | 1.6 | 1.1 | 1.7 | 2.2 | 2.1 |
| α-Pinene | 88.8 | 73.3 | 69.6 | 28.7 | 13.7 | 13 | 20.3 | 2.8 | 2.4 |
| Camphene | 6.6 | 15.7 | 19.6 | 41.9 | 51.2 | 53.8 | 45.6 | 56.8 | 56.6 |
| Tricyclene | 0.6 | 1.0 | 1.0 | 4.9 | 5.8 | 6.1 | 6.1 | 9.0 | 9.0 |
| Bornylene | 0.5 | 1.0 | 0.9 | 2.7 | 3.6 | 3.3 | 2.6 | 3.2 | 2.8 |
| α-Fenchene | 0.7 | 2.0 | 0.5 | 2.5 | 2.2 | 1.6 | 2 | 0.6 | 0.6 |
| α-Thuyene | 0.0 | 0.0 | 0.0 | 0.9 | 1.0 | 1.0 | 1.3 | 1.7 | 1.6 |
| Limonene | 1.7 | 4.0 | 4.9 | 5.9 | 7.7 | 7.7 | 6 | 5.3 | 5.2 |
| α-Terpinene | 0.4 | 0.6 | 0.6 | 3.7 | 1.8 | 1.4 | 4.5 | 4.4 | 3.9 |
| γ-Terpinene | 0.0 | 0.4 | 0.4 | 1.7 | 1.2 | 0.9 | 2.0 | 2.0 | 1.9 |
| Terpinolene | 0.7 | 1.5 | 1.9 | 3.9 | 3.7 | 3.0 | 4.1 | 4.5 | 4.3 |
| *p*-Cymene | 0.0 | 0.0 | 0.0 | 1.6 | 5.9 | 6.5 | 2.2 | 5.7 | 7.9 |
| Isoterpinolene | 0.0 | 0.0 | 0.0 | 0.6 | 0.6 | 0.6 | 1.0 | 1.2 | 1.1 |
| OP | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 0.6 | 0.6 |

[a]Percentage of compounds in the reaction mixture as a function of reaction time and reaction temperature. LRTP, low retention time products; OP, other products.

**TABLE 2**
**Percentage of Bicyclic and Monocyclic Compounds in the Reaction Mixture**

| Time (min) | Temperature (°C) | Bicyclic | Monocyclic | Ratio bi/mono | Average ratio |
|---|---|---|---|---|---|
| 20 | 90 | 8.4 | 2.8 | 3.0 | |
| 60 | 90 | 14.5 | 5.3 | 2.8 | 2.97 |
| 120 | 90 | 19.7 | 6.5 | 3.1 | |
| 20 | 120 | 52.9 | 17.4 | 3.0 | |
| 60 | 120 | 61.3 | 21.7 | 2.8 | 2.97 |
| 120 | 120 | 63.8 | 20.9 | 3.1 | |
| 20 | 140 | 57.6 | 19.8 | 2.9 | |
| 60 | 140 | 65.8 | 23.5 | 2.8 | 2.93 |
| 120 | 140 | 71.3 | 23.1 | 3.1 | |

and *m*-cymenene increased during the reaction time studied; at 180 min, *p*-cymene had the higher concentration. The concentration curve for limonene shows clearly that the reaction was nearly complete after 20 min; the change in limonene concentration between 20 and 180 min was negligible.

The *p*-cymene/*m*-cymenene ratio decreased during the 3-h reaction from 4 to 2; one may hypothesize that the *p*-cymene is dehydrogenated to form *m*-cymenene.

The limonene reaction was also studied at 140°C, and the results were similar to those at 120°C.

Terpinolene isomerization at 120°C as a function of reaction time is shown in Figure 3. The principal product is *m*-cymenene; *p*-cymene, limonene, and isoterpinolene are found in low concentrations. The other monoterpenes were produced in concentrations less than 0.5%. The *p*-cymene/*m*-cymenene ratio decreased from 0.8 to 0.2 as the reaction progressed (0–180 min). This decrease suggests two alternatives: (i) The rate of formation of *m*-cymenene from terpinolene is higher than that for *p*-cymenene; if this supposition correctly describes the pathway, the concentration of both products would increase with the reaction time. (ii) The *p*-cymene is transformed to *m*-cymenene; in this case, a maximum in the *p*-cymene concentration would appear. The observed behavior allows us to propose that the *m*-cymenene is obtained by terpinolene transformation.

Figure 4 shows the product concentrations during α-terpinene isomerization. A marked increase in *p*-cymene concentration is observed with time, whereas limonene and isoterpinolene remain almost constant.

Results of transformations of terpinolene and α-terpinene (Figs. 3 and 4) show clearly that terpinolene is transformed to *m*-cymenene and α-terpinene to *p*-cymene.

Initial rates at 120°C for the terpenes studied were 1.66 mol/g·h for α-pinene, 0.42 mol/g·h for limonene, 0.44 mol/g·h for α-terpinene, and 0.006 mol/g·h for terpinolene. The transformation rate of α-pinene was higher than for the remainder of the monoterpenes studied; the rates of transformation of limonene and α-terpinene were similar and on the order of four times lower than that of α-pinene; whereas the transformation rate of terpinolene was low and only 0.4% of that for α-pinene.

In the scheme proposed by Yadav *et al.* (5), the loss of a proton from the carbocation (*p*-menthenyl cation) can generate
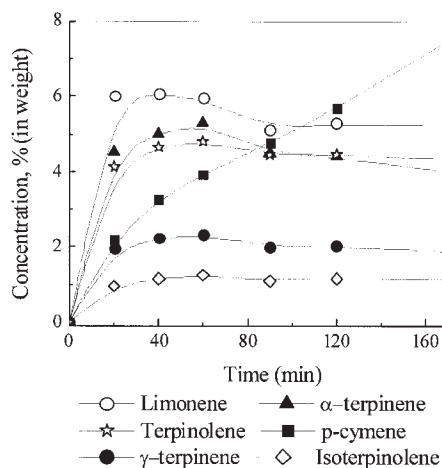
**FIG. 1.** α-Pinene isomerization at 140°C as a function of reaction time. Only monoterpenes obtained in the reaction are presented.
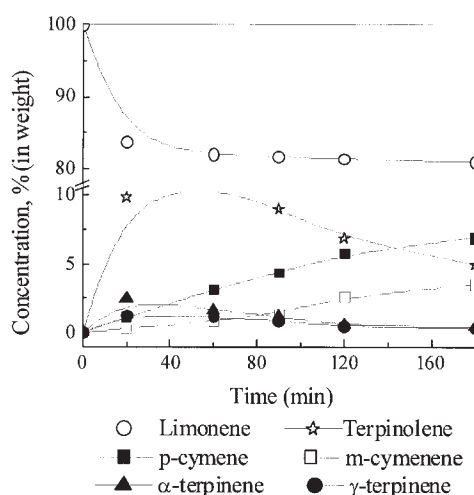
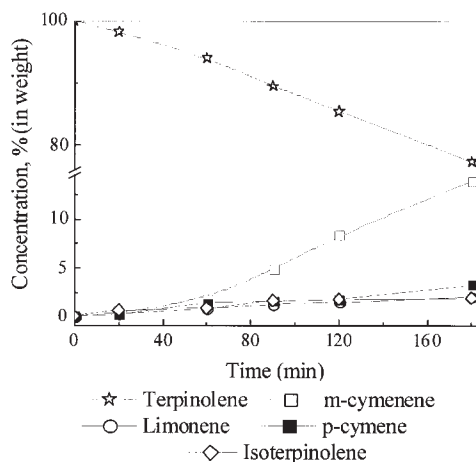**FIG. 2.** Limonene isomerization at 120°C as a function of reaction time.

**FIG. 3.** Terpinolene isomerization at 120°C as a function of reaction time.

limonene as well as terpinolene, this last then being converted into isoterpinolene. Results of this work suggest a different pathway: Limonene isomerization at 120°C gives terpinolene as the most important product.

Allahverdiev *et al.* (4) propose that α-pinene produces the pinanyl cation, which then is transformed into the *p*-menthenyl cation. The latter can also be generated from α-pinene. The pinanyl cation yields bi- and tricyclic compounds (camphene, fenchenes, bornylene, and tricyclene) whereas the *p*-menthenyl cation gives different monoterpenes. Lopez *et al.* (3) propose a scheme for α-pinene isomerization in which *p*-cymene is formed from terpinolene by a disproportion reaction. The *p*-cymene can be also formed from α-terpinene by a dehydrogenation reaction. We found that the *p*-cymene is formed from α-terpinene.

Chimal-Valencia *et al.* (6) studied the isomerization of α-pinene on a commercial exchange resin. Their scheme considers that monoterpenes are produced by one route and bi- and tricyclic terpenes by another route, a mechanism that is widely
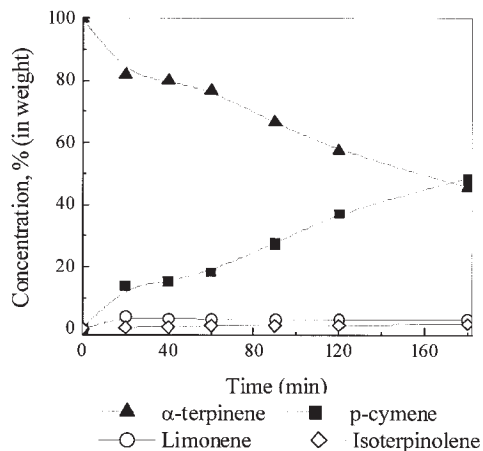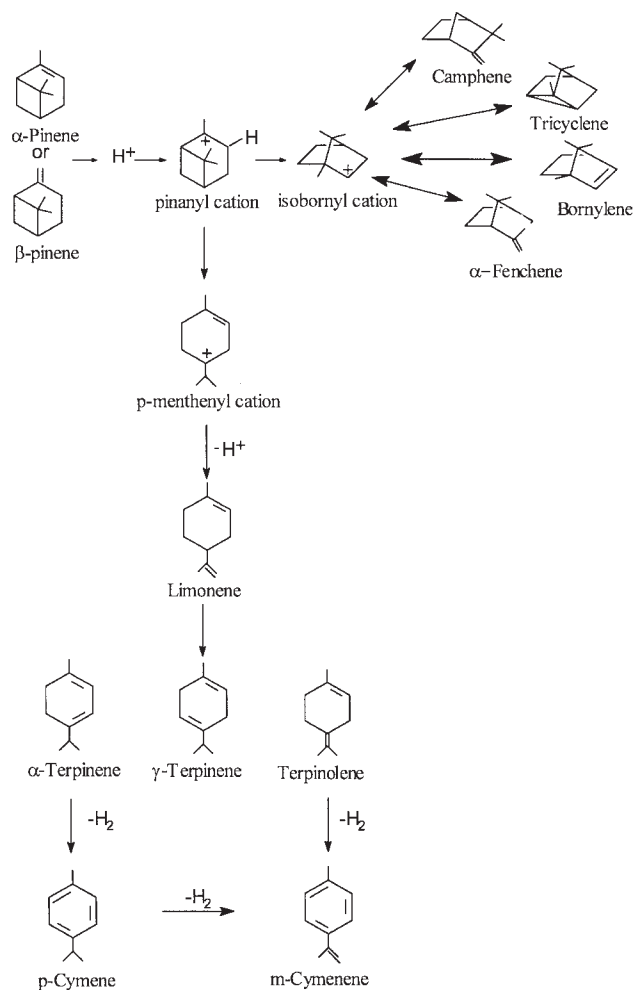


**FIG. 5.** Proposed reaction scheme for the isomerization of α-pinene.

accepted in the literature. These authors propose that bi- and tricyclic compounds are transformed to monoterpenes. In the present work, one can see that the ratio of bicyclic to monocyclic compounds is constant and equal to 3. This suggests that bicyclic compounds do not transform into monocyclic compounds. Results found in this study by using sulfated zirconia as catalyst do not show the pathway proposed by Chimal-Valencia *et al.* (6) for α-pinene isomerization on a commercial exchange resin.

The pathway proposed for the isomerization of α-pinene to camphene using sulfated zirconia as catalyst (Fig. 5) starts with the formation of the pinanyl cation. This carbocation, by transposition, generates the isobornyl and *p*-menthenyl cations. The isobornyl cation generates camphene, tricyclene, bornylene, and α-fenchene.

The *p*-menthenyl cation resulting from the loss of $H^+$ generates limonene. Limonene is then isomerized to yield α-terpinene, γ-terpinene, and terpinolene. α-Terpinene gives *p*-cymene by dehydrogenation, and terpinolene generates *m*-cymenene by dehydrogenation or isoterpinolene by isomerization.



**FIG. 4.** α-Terpinene isomerization at 120°C as a function of reaction time.

## ACKNOWLEDGMENTS

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