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Ring-Opening Reactions of α- and β-Pinenes in Pressurized Hot Water in the Absence of Any Additive

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Supporting Information

ABSTRACT: Reactions of α- and β-pinenes in pressurized hot water were examined in a batch reactor made of a SS316 1/2-in. tube at temperatures of 250−400 °C, pressures of 4−30 MPa, and reaction times of 1−30 min in the absence of any additive under an argon atmosphere. The maximum yields of limonene from α-pinene were ca. 70% in 20 min at 300 °C or 1 min at 400 °C. Limonene was obtained from β-pinene in ca. 16% yield for 30 min at 300 °C and 1 min at 400 °C. Reversible production of myrcene in 14% yield and formation of unidentified C_{20} dimer fractions were noted for 1 min at 370 °C from β-pinene. The conversion of α-pinene to limonene took place under anhydrous conditions, albeit at slightly lower yield of 65% compared to processes conducted in the presence of water, where increased limonene yield of 70% was observed for 1 min at 400 °C. The conversion of β-pinene to limonene under anhydrous conditions was limited to 6.1% in contrast to 11.9% in the presence of water for 7 min at 370 °C. In the presence of oxygen, *p*-cymene was formed in 23% and 24% yield at the expense of limonene from α- and β-pinenes, respectively, for 30 min at 400 °C.

■ INTRODUCTION

α- and β-Pinenes are typical monoterpenes distributed in large amounts in pine and other coniferous trees and released to the atmosphere, by logging operations, and from kraft pulp mills. They occur in wood turpentine obtained by the steam-distillation of chopped tree trunks and dead wood, crude sulfate turpentine (CST) obtained from wood pulp, as a waste product in the manufacture of cellulose *via* the sulfate process, black liquor usually burned to help save the fuel, and finally in wastewater. Worldwide annual productions of turpentine in which pinenes are the major components have been estimated at around 330,000 tons.[1]

In view of its wide distribution in nature, chemical conversions of pinenes have been studied as early as in the nineteenth century.[2,3] No significant pyrolysis of α- and β-pinenes takes place for a short contact time at 250−300 °C.[4] However, myrcene is formed from the latter with a maximal overall yield of 77% in gas phase reactions with a contact time of 0.5−2.5 s at 300−600 °C.[5,6] This method of the pyrolysis of β-pinene has been used for the commercial production of myrcene at 550−600 °C. Effective pyrolysis in the gas phase is usually carried out over solid catalysts such as copper chromite,[7,8] amorphous zirconium phosphate,[4] and Pd powder in the presence of hydrogen.[9,10] Limonene and dipentene are always formed with various other products, and the selectivity is low. In the last example, high yield (65%) of *p*-cymene is achieved when gaseous pinenes are passed through a tube (i.d. 6 mm) filled with Pd at 300 °C.[9,10] Since the liquid phase isomerization and polymerization of α-pinene by heterogeneous catalysis was reported in 1915,[11] a large variety of acidic substances, primarily clays, minerals, and inorganic salts, have been studied as catalysts, the objectives having been to increase the yield of camphene and reduce polymer formation.[12,13] The yield of limonene decreases and that of allo-ocimene increases with increasing temperature.[7,8] Upon heterogeneous catalytic reactions in the liquid phase over a calcinated clay or cobalt molybdite, α-pinene decomposes rapidly to camphene and limonene in nearly equal amounts, followed by slower reaction to other monoterpenes, dimers, and polymers at the reflux temperature of 156−172 °C. α-Terpineol is synthesized by treating α- and β-pinenes with dilute acids such as aqueous sulfuric acid,[14] formic acid, or phosphoric acid[15] to give terpin hydrate, which in turn is dehydrated with more concentrated acids.

In contrast to the acid- or base-catalyzed treatment of the bicyclic hydrocarbons, we became interested in their behavior in hot pressurized water to see if the development of such a conversion process without addition of any catalyst might be possible. Physicochemical properties of water change drastically near or above its critical points (T_C = 374.15 °C, P_C = 22.12 MPa) and provide water with various merits as alternative reaction media. Its high specific dielectric constant (ε_r) of 78 at room temperature drops continuously to about 28 at 250 °C (cf. ε_r = 28 of ethanol and 33 of methanol at 25 °C) and ca. 2 at 450 °C (cf. ε_r = 2.3 for benzene at 25 °C under atmospheric pressure) as the hydrogen bond is broken at higher temperature.[16,17] Thus, near the critical point, as vapor and

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liquid phases become indistinguishable, organic compounds are soluble in water and inorganic compounds such as salt become insoluble. The ionic dissociation of water is endothermic and therefore enhanced as the temperature is raised in accordance with Le Chatelier's principle. Since the dielectric constant decreases as the temperature approaches the critical point, the ion product of water reaches a maximum of $\mathrm{p}K_{\mathrm{W}} = 11.2$ at ca. 200 °C under its saturated vapor pressure,[18,19] thereby facilitating various acid- or base-catalyzed organic reactions. All these properties are temperature-dependent and can be tuned to optimize the reaction conditions. If successful, it might be possible to attain acidic or basic conditions without adding a strong acid or base, and yet require no additional workup processes of neutralization with base or acid, respectively, after the reactions. Dielectric properties would allow us to carry out the reactions under homogeneous condition and yet the organic layer and water separate after the reaction under ambient conditions. Other than the above factors favoring reactions in hot water, the rate of any reaction with a positive activation enthalpy should be accelerated at the expense of the selectivity at higher temperature. However, the manufacturing of the high-pressure reactors and the electricity required for carrying out such high-temperature reactions have to be taken into account if the merits of the above potential economic and environmental improvements are claimed seriously.

There are a number of examples for the application of pressurized hot water to the treatment of biomass. They are mostly focused on decomposition of woods and hydrolysis/gassification of lignocellulose.[20,21] The resulting glucose is reported to undergo retro-aldol condensation, dehydration, tautomerization, and hydration. The formation of furfural in 13% yield for 0.8 min at 400 °C and 80 MPa is an example.[22] Our attention was paid to the processing of fine chemicals under these conditions as generally reviewed in references.[23−27] Limonene most probably produced efficiently from *α*- and/or *β*-pinenes should be used as fragrance and for the synthesis of *d*-carvone, a fragrant present in spearmint oil. Myrcene will serve as a starting material for the industrial production of *l*-menthol. *p*-Cymene is a mild antiseptic and used for the synthesis of thymol and other chemicals.

■ RESULTS AND DISCUSSION

Batch reactions in pressurized hot water were carried out in a reactor made of a SS316 1/2-in. tube of an effective inner volume of ca. 10 cm^3 that was dipped into a preheated salt bath as detailed in the Experimental Section.

I. Reactions of *α*-Pinene, *β*-Pinene, and Myrcene in Near-Critical and Supercritical Water under Argon. *α*-Pinene disappeared gradually in pressurized hot water with half-lives of ca. 20 and 1.5 min at 250 and 300 °C, respectively. No unconverted *α*-pinene was detected after 1 min at 400 °C (see Table S1). Limonene was the main product and its maximum yield was ca. 70% in 20 min at 300 °C and in 1 min at 400 °C. Limonene had never been obtained in yields as high as 70% from *α*-pinene without using a catalyst, and this yield of limonene under near-critical and supercritical water is comparable to the reported highest yields of limonene from *α*-pinene using acidic catalyst in the literature.[4,7,8] The lack of formation of significant amounts of dimers and polymeric materials from *α*-pinene as judged from GC-FID chromatogram (Figure S2) appears to be unique to the pressurized hot water reaction. As the temperature was decreased from 400 °C, it took longer reaction times before the maximum limonene yield of ca. 70% was reached (Figure 1). It is clearly seen that the yield decreased with time at temperatures higher than 300 °C. Secondary decomposition/fragmentation reactions of limonene seemed to set in sooner at higher temperature as suggested by a number of minor peaks in GC-FID chromatogram.

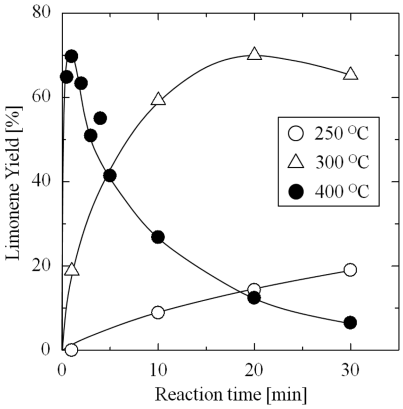


Figure 1. Effect of temperature (250−400 °C) and reaction time (1−30 min) on limonene yield from *α*-pinene under argon.

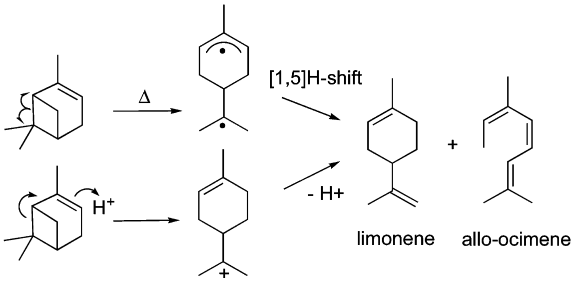
Allo-ocimene (= 2,6-dimethylocta-2,4,6-triene) was obtained in 16.2% in 10 min at 300 °C (Table 1, Scheme 1). A chromatographic peak that appeared at ca. 0.7 min later than that of allo-ocimene was negligible at the reaction time of 3 min and grew in at 20 min (see Figure S2). The latter peak was tentatively assigned to the formation 2,6-dimethyl-1,3,5-octatriene at the expense of allo-ocimene.

Table 1. Effect of Reaction Time (1−30 min) on *α*-Pinene Conversion and Limonene and Allo-Ocimene Yields at 300 °C under Argon[a]

reaction time /min	unconverted *α*-pinene /%	limonene produced /%	allo-ocimene produced /%
1	64.8	18.9	8.1
10	0.63	59.3	16.2
20	0.15	70.0	13.5
30	0.14	65.3	8.6

[a]See also Table S1.

Scheme 1. Reaction Course of *α*-Pinene



During preliminary experiments, *α*-pinene was subjected to flow reactor conditions in which limonene was obtained in 63% yield under contact time of 15.0 s with the molar ratio of *α*-pinene to water of 1:100 at 400 °C and 30 MPa. No other monoterpene nor diterpene was detected under this short contact time.[30]

Conversion of β-pinene was slightly slower than the α-isomer in water with half-lives of ca. 46 and 8 min at 250 and 300 °C, respectively. Myrcene and limonene were produced at similar levels of 14−16% from β-pinene at 370 °C and 21 MPa (Table S2). Similarly to the case of α-isomer, the yield of limonene decreased with time at temperatures higher than 300 °C (Figure 2). The yield of myrcene did not increase substantially compared to pyrolysis studies in the literature.[5,28,29] As shown in a typical GC-FID chromatogram given in Figure S3, β-pinene always gave other products: many small peaks in the C_{10} and several peaks in the diterpene C_{20} regions remained to be identified. In preliminary experiments, β-pinene was subjected to a flow reactor in which limonene and myrcene were obtained in 24.3% and 9.4% yield, respectively, under contact time of 1.9 s with the molar ratio of β-pinene to water of 1:300 at 370 °C and 21 MPa. The GC peaks in the diterpene C_{20} region increased considerably in the contact time of 20 s.[31,32]

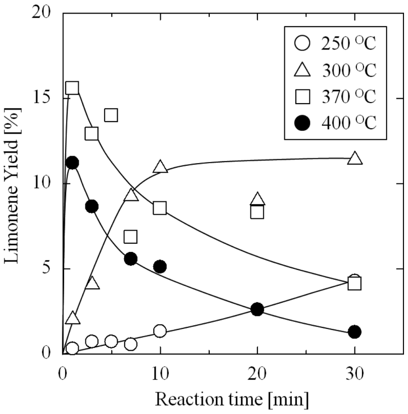


Figure 2. Effect of temperature (250−400 °C) and reaction time (1−30 min) on limonene yield from β-piene under argon.

Since myrcene seemed far from the end product of β-pinene in pressurized hot water, it was heated at 370 °C in pressurized hot water in separate batch reactions. It disappeared rapidly and limonene and β-pinene were detected in 6% and 2% yields, respectively, in 1 min, both of which decreased gradually. The C_{20} fractions were also detected. Their temporal variation is given in Table S3 and Figure 3. Interconversion among these hydrocarbons as depicted in Scheme 2 is concluded.

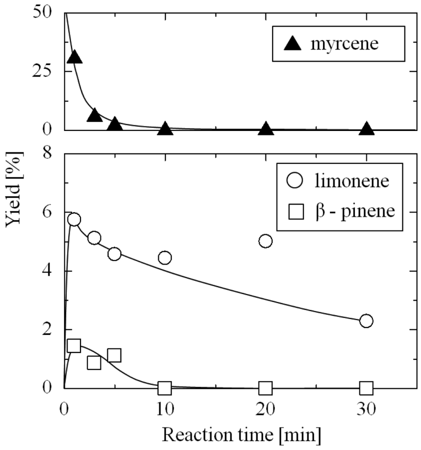
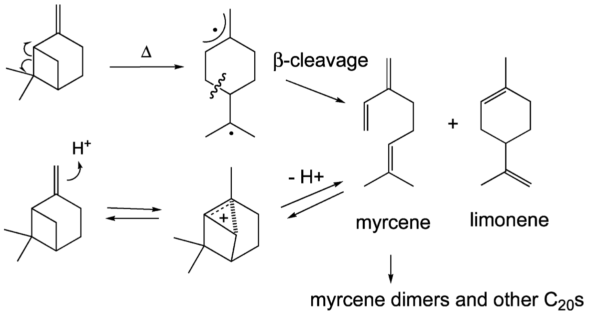


Figure 3. Effect of reaction time (1−30 min) on myrcene conversion and selectivity to limonene and β-pinene at 370 °C.

Scheme 2. Interconversion of Chemicals Related to β-Pinene in Pressurized Hot Water



Since myrcene and β-pinene have the standard molar enthalpy of formation of 98.8 and 38.7 kJ/mol at 298 K, respectively, the formation of myrcene from β-pinene is an endothermic reaction by ca. 60 kJ/mol and therefore should be favored thermodynamically as the temperature is increased. The diradical intermediate formed by the homolysis of the cyclobutane ring is considered to reside near the late transition state of the reaction path and undergo β-cleavage to give myrcene (Scheme 2).[5,6] The reverse reaction from myrcene to β-pinene has never been reported and provides novel product finding and postulated mechanism. There are at least two representative mechanisms possible for this reverse process. One is a microscopically reversible diradical mechanism in which the exothermic reaction product has to be quenched thermally by its collision with a second body for isolation at least in the gas phase. It might be possible that near-critical water molecules could have served as quenchers of the excess internal energy of the formed β-pinene molecules. Alternatively, the reverse reaction observed in this study could be ionic as are many terpenoid ring closure reactions under acid catalysis and take a route through a cyclobutylmethyl carbonium ion different from the pyrolytic forward reaction (Scheme 2).

II. Effect of the Amount of Water on the Reaction of α- and β-Pinenes in Supercritical Water under Argon. A series of experiments were performed for 1 min at 400 °C by changing the molar amount of water in the range 0−300 relative to one mole of α-pinene as starting materials. The results are given in Table S4 and Figure 4. Under these conditions the amount of the unconverted α-pinene was less than 1%. Limonene was obtained in 65% yield even in the

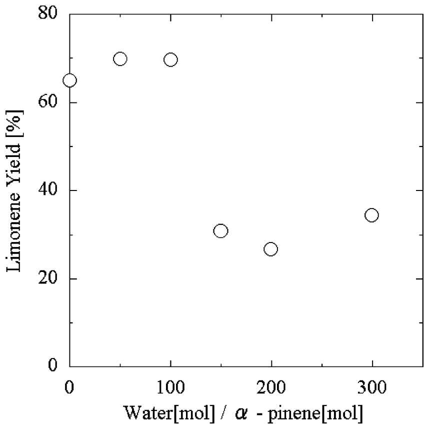


Figure 4. Effect of the amount (0−300 molar) of water relative to one mole of α-pinene on the yield of limonene for 1 min at 400 °C.

absence of water for a short contact time of 1 min. The yield of limonene increased slightly with increasing relative amount of water, reaching the highest yield of 70% at the water to substrate molar ratio of 50−100:1. However, it dropped to ca. 30% when the molar amount of water relative to α-pinene was increased to 150, 200, and 300:1. The decrease in the yield of limonene, namely, the decomposition of limonene in the presence of larger amount of water is somewhat puzzling. The reaction time of 1 min is slightly ambiguous for the batch reactions of immersing reaction vessels into a preheated salt bath in that the tube might have thermal gradients from the reaction vessel wall to the center of the tube and the temperature of the reactants might not be equilibrated at that temperature.

Therefore, a series of experiments on β-pinene were performed by changing the molar amount of water in the range of 0−400 relative to one mole of β-pinene as a starting material at longer reaction time, 7 min, at slightly lower temperature, 370 °C. The results are given in Table S5 and Figure 5. Just as in the α-isomer, limonene was obtained in the absence of water though in reduced 6.1% yield. The yield of limonene increased to 11.9% at the molar ratio 300:1 of water to β-pinene: an increase of almost twice as compared to the reaction in the absence of water.

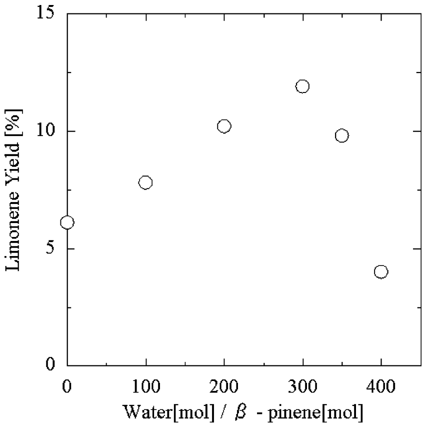


Figure 5. Relationship of molar ratio of water to β-pinene on the molar yield of limonene for 7 min at 370 °C and 21 MPa.

The trends observed for the effect of the amount of water on the two isomeric pinenes (Figures 4 and 5) are qualitatively similar in spite of the lower reaction temperature and longer reaction time for β-pinene. Contrary to the low reactivity of the pinenes in the absence of any catalyst expected from the literature references in the Introduction, they showed significant conversion to limonene and other products at water/pinene = 0. We recall that the reactor wall made of SS 316 contains Ni, Cr, and Mn components which may act as catalyst for such reactions as hydrogenation. However, seasoned reaction vessels have, to our knowledge, not shown accelerating effect for pyrolytic reactions. The reaction of α-pinene to limonene is estimated from their heats of formation to be exothermic by 38 kJ/mol, and therefore the diradical intermediate in Scheme 2 is considered to reside near the early transition state of the reaction path. The pinenes under our reaction conditions in the absence of water are in or near the supercritical conditions of their own: critical points are 356.70 °C, 2.93 MPa for α-pinene and 371.35 °C, 2.92 MPa for β-pinene. Further studies are necessary to see if they exhibit their unique reactivity under these conditions. Second, the observed increase in the yield of limonene with water could be interpreted in terms of the contribution of the added acid-catalyzed reaction pathway (Scheme 1) that is typical for the production of limonene from α-pinene in the presence of acid catalysts in the literature.[12,13,28,29] Further support may be found in a recent report by Anikeev showing that the formation of limonene from α-pinene in supercritical ethanol at 384 °C and 23.3 MPa proceeded *via* diradical mechanism and the yield increased gradually by addition of water. The latter effect was interpreted in terms of the growth of the hydronium ion (H_3O^+) concentration.[33] For a third, the observed decrease in the limonene yield as the relative amount of water was increased over 150 °C (Figure 4) and 350 °C (Figure 5) is still a problem that remains to be solved.

III. Reactions in the Presence of Oxygen. When α-pinene in pure water was not flushed with argon, the ca. 70% yield of limonene decreased to 41% in 1 min and continued to decrease with time. In 5 min, the product limonene was overtaken by p-cymene and its yield reached ca. 23% in 30 min at 400 °C (Table S6, Figure 6). Throughout the reaction, α-pinene was consumed.

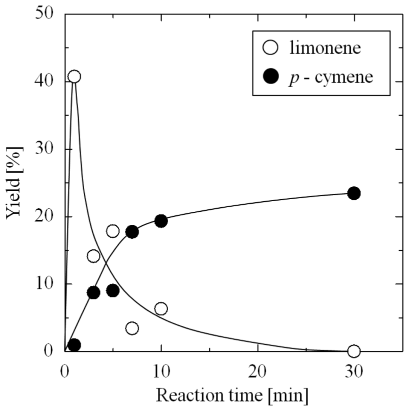
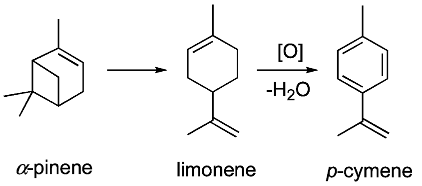


Figure 6. Effect of reaction time (1−30 min) on the yields of limonene and p-cymene from α-pinene at 400 °C and 30 MPa in the presence of oxygen.

p-Cymene is formed from α-pinene when heated with various catalysts.[9,10] Mesoporous silica-supported 12-tungstenophosphoric acid is also effective in these reactions.[34] Since the presence of air was suggested to be responsible for the present dehydrogenative aromatization reaction (Scheme 3), it was hoped that limonene and p-cymene might be selectively synthesized from the reaction of α-pinene in hot pressurized water by controlling the amount of oxygen. However, saturation of water with oxygen and filling the empty space of the reactor with oxygen gas did not improve the yield of p-cymene (yield 23 ± 2%) and the vessel was soot-blackened

Scheme 3. Dehydrogenative Aromatization of α-Pinene without Exclusion of Air



after 60 min. Addition of dilute aqueous hydrogen peroxide did not improve the yield of *p*-cymene.

Without exclusion of oxygen, the yield of limonene in ca. 11% from *β*-pinene also decreased rapidly with time and was overtaken by that of *p*-cymene in 10 min. Its yield reached ca. 24% in 30 min at 400 °C (Table S7) with neither *β*-pinene nor limonene remaining.

Since limonene was considered to be an intermediate from both isomeric pinenes to *p*-cymene, we treated limonene in hot pressurized water in the presence of oxygen. The results are given in Table S8 and Figure 7. Limonene was stable in the absence of water.

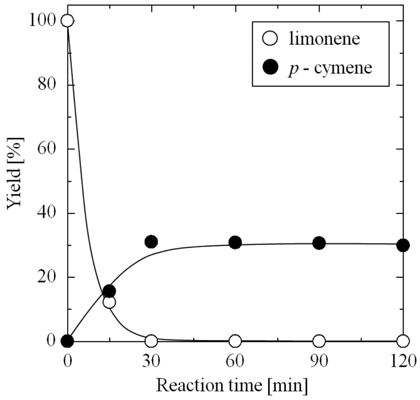


Figure 7. Effect of reaction time (1−120 min) on the yields of limonene conversion and *p*-cymene yield in the presence of oxygen at 400 °C and 30 MPa.

Recently, the formation of *p*-cymene was reported in the oxidation of *α*-pinene in moist air by the atmospheric oxidants OH, O_3, and NO_3. Sorbrerol,[35] a cyclic monoterpene diol was proposed as an intermediate for the formation of *p*-cymene.[36] Our results are not contradictory with this observation but would require some more mechanistic studies for confirmation.

■ CONCLUSION AND FUTURE DIRECTIONS

Our findings described in the previous sections are similar to but not the same as any of the reported cases in the references summarized in the Introduction. There are two most novel aspects. First, limonene had never been obtained in yields as high as 70% from *α*-pinene without using a catalyst. A series of reactions have been studied in supercritical lower alcohols where the ring-opening is mostly derived from pyrolytic diradical reactions[33] and the best result in terms of the formation of limonene is 40.0% yield for 300 s, at 300 °C, 10.1 MPa in 0.1 mol L^{-1} in propanol.[5] The lack of formation of significant amounts of dimers and polymeric materials from *α*-pinene seems to be unique to the pressurized hot water reaction presented here. Second, the formation of myrcene from *β*-pinene was found to be reversible. It is generally understood that terpenes undergo ionic cyclization under acid catalysis and biradical ring-opening.[7,19] It is not yet clear from the limited amount of our data if this rule applies to the partial ring-opening of the isomeric pinenes in pressurized hot water. Several possibilities remain to be explored. The difference in the chemical structure of *α*- and *β*-isomers lies in the position of the double bond. Mechanistically there are three possibilities for the initial intermediates: two different diradicals, two different carbocations, and two common cyclobutylcarbonium ion.[20] The last possibility is easily excluded.

Water under near-critical and supercritical conditions proved to be a novel media for ring-opening reactions of *α*- and *β*-pinenes. Lowering of its dielectric constant to those of organic solvents at ambient temperature and increase of the ion product almost by 3 orders of magnitude are considered to be responsible for the reactions. It goes without saying that thermal activation of the reaction by a factor ln*T* and provision for nonflammable media for combustible reactants are added merits of near-critical and supercritical water in addition to the above two factors.

Whereas the size of the reaction was limited by the reaction vessel used in these exploratory studies (Figure 8), it could readily be expanded by employing larger size reactors. One of the highest yields (70%) of limonene from *α*-pinene was obtained at 9 MPa and 300 °C in 20 min. Under these conditions, it must not be difficult to find a commercially available pressure bottle (an autoclave) of the inner volume of 500−1000 mL (e.g., a Parr 4605 high pressure 600−1200 mL vessel for maximum pressure: 34.5 MPa and temperature: 350 °C). Furthermore, it has been a definite improvement in the design of flow reactors of recent date using water under sub- and supercritical conditions in various laboratories since its prototype debuted in the early 1990s.[37,38] Our preliminary study using a homemade desktop flow reactor achieved the average limonene yield of 67% with each contact time of 20 s in 6 h for the feed speed 0.03 g/min of *α*-pinene. When extrapolated to the continuous operation for 24 h, it would allow us to obtain ca. 25 g of limonene.[31]

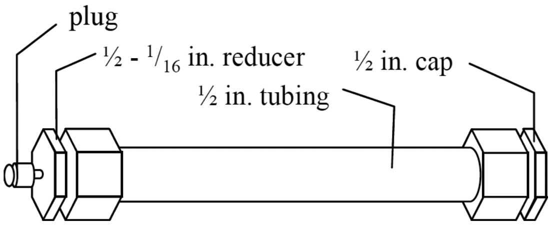


Figure 8. Batch reactor handmade from a SUS316 1/2-in. tube.

Our future efforts should be directed toward three aspects. Whereas linear dimers and Diels−Alder dimers due to myrcene are reported in the literature,[39] the reaction products including C_{20} fractions have to be identified. It is desirable to find effective radical scavengers usable for studying radical reactions in pressurized hot water. Lastly, optimization of the formation of *p*-cymene from both pinenes in pressurized hot water should be made using hydrogen acceptors other than silicates, copper chromite, iodine, or PCl_3.[21]

■ EXPERIMENTAL SECTION

Chemicals. *α*-Pinene ((1R)-(+), ≥80% e.e.) of chemical purity greater than 98% was purchased from Kanto Chemical Co., Inc. (ACROS Organics). *β*-Pinene ((1S)-(-), ≥95.6%), myrcene (≥77.6%), and alloocimene (mixture of isomers, ≥90.0%) were obtained from Tokyo Chemical Industries Co., Ltd., and used without further purification. Authentic samples of limonene (≥92%) and *p*-cymene (≥99%) were obtained from Kanto Chemical Co., Inc. (ACROS Organics).

Ultrapure water that had a specific resistivity greater than 18.2 MΩ and total organic carbon (TOC) smaller than 20 ppb was obtained by treating tap water through a Millipore Milli-RX75 ultrapure water production system. Other chemicals and solvents used were commercially available.

Experimental Apparatus and Procedures. Batch reactions were carried out in a handmade reactor of a SS316 1/2-in. tube (length: 170 mm, outside diameter: 12.7 mm, wall thickness: 2.1 mm (Mecc Technica Co.)). It was fitted with a SS316 1/2-in. cap (Swagelok Co., No. SS-810-C), a 1/16-in. to 1/2-in. reducing connector (Swagelok Co., No. SS-810-6-1), and a 1/16-in. plug (Swagelok Co., No. SS-100-P) to make an effective inner volume of ca. 10 cm^3 (Figure 8). Prior to its use in experiments, the reactor was rinsed with acetone and loaded with water and conditioned for 1 h at 300 °C to remove any residual lubricants/oils that may have been present due to the Swagelok manufacturing process. The reactor was cleaned with acetone and dried overnight at 60 °C prior to repeated use. Preliminary experiments showed that it took nearly one minute before the thermocouple placed at the center of the tube showed thermal equilibration with 3.57 g of water and at 400 °C.

Estimation of the Internal Pressure Due to Water at 250–400 °C and the Sufficient Volume Allowing for Expansion. In most cases, water is employed in large excess relative to organic substrates for the reactions in pressurized hot water. Therefore, the phase diagram of water itself may be used as an approximation of the reaction mixtures. The isobar curves in the temperature vs density diagram for water (Figure S1 written by K. Sue on the basis of the equations and data in the literature[40]) is instructive in determining the recommended amount of water for the batch reaction in steel reactors. Under supercritical conditions ($T_C \geq 374.15$ °C) in which there is only one phase of water, the amount of loaded water is directly reflected in the density, and therefore the inside pressure was estimated to become ca. 30 and 50 MPa at 400 °C when started with 3.5 and 5.8 g/10 mL of loaded water, respectively. The latter is about the limit of the allowed pressure of typical apparatus made of steel. Under subcritical conditions ($T_C <$ 374.15 °C), the isobaric curves in the temperature vs density diagram for water become bell-shaped corresponding to the separation of two phases due to saturated vapor and liquid. The saturated vapor pressure of 8.6 MPa at 300 °C is in principle independent of the amount of water. Since most acid-catalyzed reactions take place in the liquid phase, it would be preferable to load as much water as possible. However, once the amount of charged water reached 7.5 g/10 mL at 300 °C, for example, the pressure approaches that of one-phase water with density: 0.75 g/cm^3 and pressure of 30 MPa (see Figure S1). Furthermore, since the isobaric curves are densely populated in these density regions, the pressure inside the reactor could change drastically depending on the slight changes in the amount of loaded water. When the perturbation due to any added reactant is considered, it would be advisable to load 5–7 g water for the reactor of inner volume of 10 mL at 300 °C (see Figure S1 in Supporting Information for further detail).

Typical Runs. High-purity water was deaerated prior to use by a vacuum deaeration method to remove dissolved oxygen (O_2). Pure water (3.574 g, 199 mmol) and either α- or β-pinene (0.2705 g, 1.99 mmol) were charged in the reactor to make the starting materials of a 100:1 molar ratio. The mixture was further flushed with argon unless otherwise stated and heated to 250–400 °C in a salt bath (Thomas Kagaku Co. Ltd., Celsius 600H) which was preheated to the required temperature. Reaction times were 1–30 min, including ca. 1 min required to heat the reactor to the required temperature. Following a given heating period, the reactors were removed from the salt bath and submerged in room temperature water. A pair of heat-resistant gloves and security goggles were worn during these operations. The reaction mixture usually in the range 3–7 mL was flushed out of the reactor, collected, extracted with 3–4 portions of 30 mL of hexane, and analyzed as follows.

When the amount of water was changed relative to those of pinenes as described in subsection II of the Results and Discussion section, the amount of water was kept constant at 3.57 g and that of α-pinene was changed so that the inside pressure of a 10 mL reactor should be kept constant at 30 MPa at 400 °C.

Analytical Methods. Qualitative analyses were made on a Shimadzu Corporation GCMS-QP2010 gas chromatography–mass spectrometer. The mass spectral fragmentation of each GC peak was identified by comparison with that of the authentic samples or by means of similarity analyses using the provided MS data library in the case of 2,6-dimethyl-1,3,5-octatriene.[41]

Quantitative analyses were carried out on a Shimadzu Corporation GC-2010 gas chromatograph (GC-FID) with the inlet and detector temperatures of 250 and 280 °C, respectively. Calibration curves for determining the molar amounts of α-, β-pinenes, limonene, allo-ocimene, myrcene, and *p*-cymene from the corresponding GC peak areas were drawn in advance with internal standards 1-propanol and 1-pentanol for the analytes from the reactions of α- and β-pinene, respectively. A given amount of the internal standard was added to the hexane extract solutions of α- or β-pinene reactions, respectively. An aliquot of 1 μL was injected with a split ratio of 100. Chromatographic peaks were identified by comparing their retention times with those of authentic samples described under Chemicals.

For the α-pinene analyses, a highly polar capillary column HP-INNOWax (Agilent Technologies, Co., length: 30 m, inner diameter (i.d): 0.25 mm, and a film thickness of 0.25 μm) was used, in conjunction with helium carrier gas. The temperature program used for the oven of GC and GC-MS analyses started at 40 °C for 15 min, followed by a temperature ramp of 10 °C/min up to 70 °C, maintained for 5 min, another temperature ramp of 20 °C/min up to 250 °C, and then was held at the final temperature for 10 min.

For the β-pinene analyses, a medium polar capillary column DB-1701 (Agilent Technologies, Co., length: 30 m, inner diameter (i.d): 0.25 mm, and a film thickness of 0.25 μm) was used in conjunction with helium carrier gas. The temperature program used for the oven of GC and GC-MS analysis started at 40 °C for 5 min, followed by a couple of temperature ramps of 3 °C/min to 110 and 0 °C/min to 270 °C, and then was held there for 5 min.

Characterization of the Main Products: Limonene, Allo-Ocimene, Myrcene, and *p*-Cymene. A typical GC-FID chromatogram is shown in Figure 2S. Mass spectral analysis of the most abundant product peak in the gas chromatograph from α-pinene showed a molecular ion peak at $m/z = 136$, a base peak at $m/z = 68$, and other fragment peaks that were superimposed to those of an authentic sample of limonene. One of the peaks in the 25-min region was similarly found to be 2,6-dimethyl-1,3,5-octatriene having a molecular ion peak at $m/z = 136$, a base peak at $m/z = 93$, and other characteristic fragment peaks.

β-Pinene yielded other products as shown in a typical GC-FID chromatogram shown in Figure S3. In the C_{10} region, the formation of myrcene was confirmed by a GC-mass spectral analysis that showed a molecular ion peak at $m/z = 136$, a base peak at $m/z = 93$, and other fragment peaks that were superimposable on those of an authentic sample of myrcene. In addition there were several peaks in the diterpene C_{20} region of the GC/FID that remained to be identified.[39]

The main product from α- and β-pinenes in pressurized hot water without exclusion of air was similarly identified as p-cymene with a strong parent peak at $m/z = 134$ and other characteristic fragment peaks that matched with those of the authentic sample.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

i. Eight tables of numerical data on the reactions of α- and β-pinenes, limonene, and myrcene in hot pressurized water constituting Figures 1−7. ii. A temperature−pressure−density diagram for water with explanation. iii. Two GC chromatograms for the reaction mixture of α- and β-pinenes in hot pressurized water. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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