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# Catalytic Conversion of $\alpha$ -Pinene to High-Density Fuel Candidates Over Stannic Chloride Molten Salt Hydrates

Seong-Min Cho <sup>1</sup>, June-Ho Choi <sup>1</sup>, Jong-Hwa Kim <sup>1</sup>, Bonwook Koo <sup>2</sup> and In-Gyu Choi <sup>3,4,\*</sup>

<sup>1</sup> Department of Forest Sciences, Seoul National University, Seoul 08826, Korea; csmin93@snu.ac.kr (S.-M.C.); jhchoi1990@snu.ac.kr (J.-H.C.); wmfty@snu.ac.kr (J.-H.K.)

<sup>2</sup> Green and Sustainable Materials R & D Department, Korea Institute of Industrial Technology, Cheonan 31056, Korea; bkoo@kitech.re.kr

<sup>3</sup> Department of Agriculture, Forestry and Bioresources, Seoul National University, Seoul 08826, Korea

<sup>4</sup> Research Institute of Agriculture and Life Sciences, Seoul National University, Seoul 08826, Korea

\* Correspondence: cingyu@snu.ac.kr; Tel.: +82-2-880-4785

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**Abstract:** The synthesis of dimeric products from monoterpene hydrocarbons has been studied for the development of renewable high-density fuel. In this regard, the conversion of  $\alpha$ -pinene in turpentine over stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) as a catalyst was investigated, and the reaction products were analyzed with gas chromatography/flame ionization detector/mass spectrometer (GC/FID/MS). Overall, the content of  $\alpha$ -pinene in a reaction mixture decreased precipitously with an increasing reaction temperature. Almost 100% of the conversion was shown after 1 h of reaction above 90 °C. From  $\alpha$ -pinene, dimeric products (hydrocarbons and alcohols/ethers) were mostly formed and their yield showed a steady increase of up to 61 wt% based on the reaction mixture along with the reaction temperature. This conversion was thought to be promoted by Brønsted acid activity of the catalyst, which resulted from a Lewis acid-base interaction between the stannic ( $\text{Sn}^{\text{IV}}$ ) center and the coordinated water ligands. As for the unexpected heteroatom-containing products, oxygen and chlorine atoms were originated from the coordinated water and chloride ligands of the catalyst. Based on the results, we constructed not only a plausible catalytic cycle of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  but also the mechanism of catalyst decomposition.

**Keywords:** renewable fuel; high-density fuel;  $\alpha$ -pinene dimerization; turpentine; stannic chloride molten salt hydrates

## 1. Introduction

Aspirations for alternative biofuel have emerged vigorously worldwide, amid increasing concern about fossil fuel sustainability and environmental pollution. In this respect, cellulosic biomass-derived chemicals such as furfural, 5-hydroxymethylfurfural, 2-methylfuran, levulinic esters, and angelica lactone have attracted considerable attention as renewable resources for the sustainable production of biofuels [1–3]. Another promising renewable chemical in order to produce synthetic fuel is turpentine. Turpentine can be obtained by either the distillation of oleoresins or the kraft pulping process as a side-product and it is mainly composed of  $\alpha$ -pinene and lesser amounts of isomers ( $\beta$ -pinene, camphene, and limonene), which all belong to monoterpene hydrocarbons [4]. Because fuel properties depend on what consists of the fuel, the fact that hydrocarbons make up the majority of turpentine is an advantage of itself as the resource of biofuels [5]. It has been reported that the blends of monoterpenes and petroleum-based fuel could be utilized as drop-in fuels [6,7].

When it comes to the application of fuel to an aerospace field and ramjet engines, however, drop-in fuels are required for much higher energy density than neat turpentine. To synthesize high-energy density fuel from turpentine ( $\alpha$ -pinene), dimerization over acid catalysts has been devised to increase density, thereby increasing energy density [5]. With the advantage of facile separation, various heterogeneous Brønsted acid catalysts have been studied to carry out the dimerization [8,9]. Because the four-membered ring of  $\alpha$ -pinene is labile to acidic conditions, the ring is easily opened or extended to five-membered ring. This furnishes isomers including both monocyclic monoterpene hydrocarbons such as limonene and bicyclic monoterpene hydrocarbons such as camphene. Thus, the acid-catalyzed dimerization of  $\alpha$ -pinene always accompanies the isomerization, which is followed by inevitable cross-dimerization and makes the reaction mixture consist of not only the isomers of  $\alpha$ -pinene but also the various dimers [8]. It has been found that a dimer fraction has too high viscosity to apply it to a field where the fuel is exposed to extremely low temperatures [10]. To come up with this problem, blending the dimer fraction with monoterpene hydrocarbons or the partial dimerization of  $\alpha$ -pinene has been devised [5].

Inorganic molten salts hydrates, such as  $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ , are the hydrated form of inorganic salts that easily melted like butter at an elevated temperature. A chemical reaction system exploiting the inorganic molten salts hydrates as a reaction medium has been applied to several processes, particularly biopolymer conversion. It has been reported that an acidic LiBr salt hydrates can hydrolyze both the  $\beta$ -1,4 glycosidic bond of cellulose [11] and the aryl ether bond of lignin [12] and co-produce boromomethylfurfural and furfural directly from lignocellulosic biomass within the biphasic system [13]. In addition to LiBr salt hydrates,  $\text{ZnCl}_2$  and  $\text{SnCl}_4$  salts hydrates have been used for the synthesis of isosorbide from cellulose [14] and 5-hydroxymethylfurfural from fructose, inulin, glucose, and chitosan [15–18].

Herein, we focused on the acidic nature of stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ).  $[\text{SnCl}_4\text{L}_2]$  complexes in anhydrous conditions have been reported as Lewis acid-assisted Brønsted acid catalysts when the  $\text{L}_2$  are 2'-methoxy-[1,1'-binaphthalen]-2-ol (BINOL-Me), 2'-isopropoxy-[1,1'-binaphthalen]-2-ol (BINOL-*i*Pr), 2-methoxyphenol (guaiacol), or 2,6-dimethoxyphenol (syringol), because they can coordinate to the stannic ( $\text{Sn}^{\text{IV}}$ ) center via the vicinal hydroxy and alkoxy groups in a bidentate manner [19–22]. Therefore, we have expected that the coordinated water ligands of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  can also act as Lewis acid-assisted Brønsted acids for the catalytic conversion of  $\alpha$ -pinene. It has been remarkable that  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  can furnish the dimerized products (up to 61 wt% based on the reaction mixture) from turpentine in a solvent-less condition. However, the decomposition of the catalyst results in oxygen-containing or chloride-containing products. To overcome this limitation and ponder the improvement of the reaction system, we have discussed the mechanism of the catalytic conversion of  $\alpha$ -pinene over  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ .

## 2. Materials and Methods

### 2.1. Materials

All purchased chemicals were used without further purification. Turpentine ( $\alpha$ -pinene  $\geq 92\%$  by GC) was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). Stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 98%) and n-hexane (95%) were obtained via Samchun Pure Chemicals Co., Ltd. (Seoul, Korea).

### 2.2. General Procedure for Catalytic Conversion of $\alpha$ -pinene by Stannic Chloride Molten Salt Hydrates

We set reaction time as 1 h and considered the effect of the reaction temperature (60, 70, 80, 90, 100, and 110 °C) or set reaction temperature as 70 °C and considered the effect of reaction time (1, 3, and 5 h) because, upon the reaction temperature crossed, the melting point of stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ),  $\alpha$ -pinene, quickly disappeared from the reaction mixture. In a typical experiment, 10 g of turpentine and 1 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was added to 50-mL double-neck

round flask equipped with a magnetic Teflon coated stirrer, a thermometer, and a reflux condenser. After being purged with nitrogen gas, the reactor was then loaded on a preheated aluminum heating block and stirred smoothly for 1 h. The temperature of a reaction mixture was reached at the desired temperature ( $\pm 3$  °C) in less than 5 min. Upon completion of the reaction, the reactor was then removed from the heating block and immediately cooled to room temperature with a water bath. After cooling, the crude reaction mixture was diluted in 100 mL of n-hexane and filtered over a celite pad to remove metal compounds. The solvent was removed under reduced pressure. The purified product was analyzed by Agilent Technologies 7890B gas chromatograph equipped with a DB-5ms column (30 m  $\times$  250  $\mu$ m, 0.25  $\mu$ m thickness), a 5977A mass spectrometer detector, and a flame ionization detector (Agilent-Technologies, Seoul, Korea). The yield of products was calculated based on the below equation on the basis of the internal standard method (tridecane).

$$\text{Yield of product } i \text{ (\%)} = \frac{\text{Weight of product } i \text{ after reaction}}{\text{Initial weight of } \alpha\text{-pinene}} \times 100 \quad (1)$$

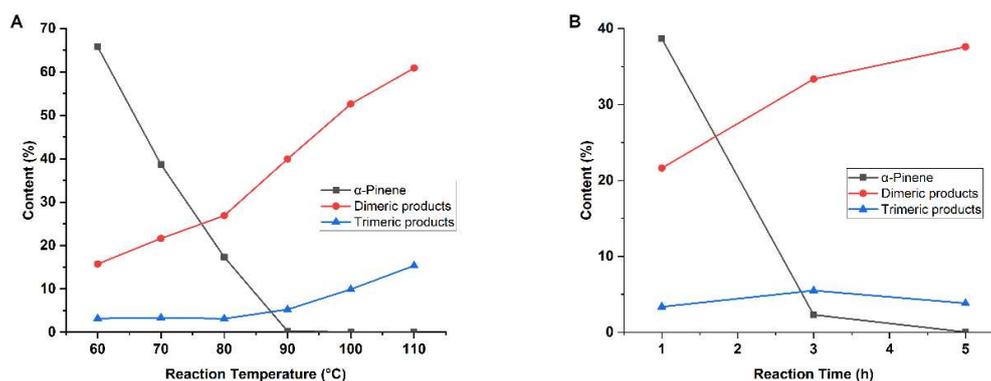
### 3. Results and Discussion

#### 3.1. Catalytic Conversion of $\alpha$ -Pinene over Stannic Chloride Molten Salt Hydrates

As previously mentioned in the introduction, what we have expected was that the Lewis acid-assisted Brønsted acidic nature of stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) would work as a catalyst. In accordance with this expectation, the catalytic amount of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was active for the conversion of  $\alpha$ -pinene in a solvent-less condition. As shown in Figure S1, the reaction products could be divided into four main groups (monomeric hydrocarbon, heteroatom-containing monomeric, dimeric, and trimeric product regions) on the basis of retention time in gas chromatography/flame ionization detector (GC/FID) chromatogram and molecular ion peaks in mass spectra. Figure S2A,B show the representative mass spectra of dimeric and trimeric hydrocarbons including molecular ion peaks at  $m/z$  272 [ $\text{C}_{20}\text{H}_{32}$ ]<sup>+</sup> and  $m/z$  408 [ $\text{C}_{30}\text{H}_{48}$ ]<sup>+</sup>, respectively.

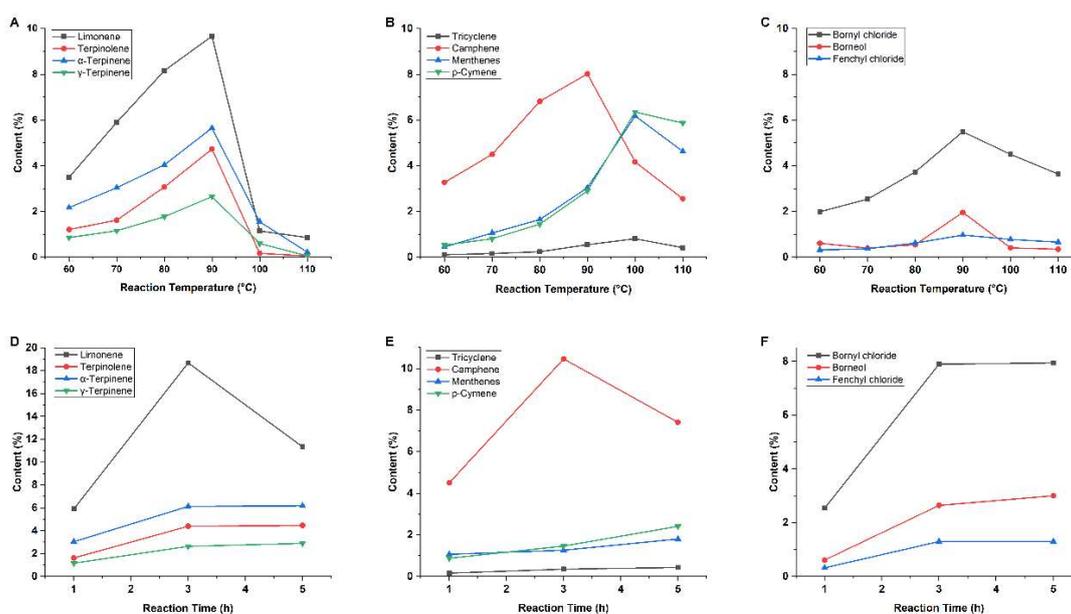
Figure 1A shows that  $\alpha$ -pinene, which is the main constituent of turpentine, was consumed precipitously with increasing reaction temperature and the content thereof eventually stands at 0% in the reaction mixture heated above 90 °C. For the cases of dimeric and trimeric products, the contents increased approximately four-fold and eight-fold when the reaction temperature increased from 60 to 110 °C, standing at 60.9% and 15.4%, respectively, at 110 °C. There was a large discrepancy in the conversion of  $\alpha$ -pinene and yields of dimeric and trimeric products, which denotes the presence of other monomeric products formed from  $\alpha$ -pinene. Remarkably, our results differ from those of Nie et al. who suggested that, when phosphotungstic acid supported on MCM-41 was applied, the isomerization of  $\alpha$ -pinene is the main reaction pathway at 100 °C and the dimeric products are formed mainly from the isomers at 160 °C [23]. As shown in Figure 1B, even at 70 °C of reaction temperature, 100% conversion of  $\alpha$ -pinene can be achieved by increasing the reaction time. Given that the dimeric products were produced without  $\alpha$ -pinene after 3 h of reaction, it can be thought that the monomeric products from  $\alpha$ -pinene also participated in the dimerization [8].

Unfortunately, several mass spectra involving an unexpected molecular ion peak at  $m/z = 290$  (Figure S2C) were extracted from the dimeric product region in Figure 1B. Given the difference between the  $m/z$  of molecular ions, the molecular ion having  $m/z = 290$  could be described as [ $\text{C}_{20}\text{H}_{34}\text{O}$ ]<sup>+</sup>, which means that oxygen-containing dimeric products, possibly dimeric alcohols or ethers, were also produced during the reaction. In the dimerization of monoterpenes over acidic catalysts, dimeric products having  $m/z = 290$  as a molecular ion have often been reported. Nie et al. suggested a dimeric alcohol product in the dimerization of crude turpentine [23]. Moreover, heteropoly acid-catalyzed conversion of camphene furnished diisobornyl ether in a moderate yield and good selectivity [24].



**Figure 1.** Effect of reaction temperature and reaction time on the conversion of  $\alpha$ -pinene and yields of dimeric and trimeric products. The reaction was carried out (A) for 1 h and (B) at 70 °C.

Figure 2A,B show the main hydrocarbon product distribution in the monomeric hydrocarbon region in Figure S1B as a function of the reaction temperature. These monomeric hydrocarbons could be divided into two groups based on the tendency in the content thereof, according to the reaction temperature. Limonene, terpinolene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, and camphene except for tricyclene presented a sudden decrease in their yield above 90 °C, meaning their participation in dimerization. On the other hand, the contents of menthenes and *p*-cymene increased with increasing reaction temperature until 100 °C. These have been reported to form by the disproportionation of *p*-menthadienes [25]. In our results, the similar contents of menthenes and *p*-cymene also support the disproportionation mechanism. Meanwhile, as the same as the case of dimeric products, heteroatom-containing monomeric products were also furnished (Figure 2C). Non-negligible amounts of borneol, bornyl chloride, and fenchyl chloride were only produced as bicyclic compounds during the reaction. Figure 2D–F show the distribution of monomeric products with increasing reaction time at 70 °C of the reaction temperature. The considerable amounts of limonene (18.9%) and camphene (10.5%) were produced when  $\alpha$ -pinene still remained in the reaction system whereas their yields decreased after the conversion of  $\alpha$ -pinene was complete, which denotes their participation in dimerization.

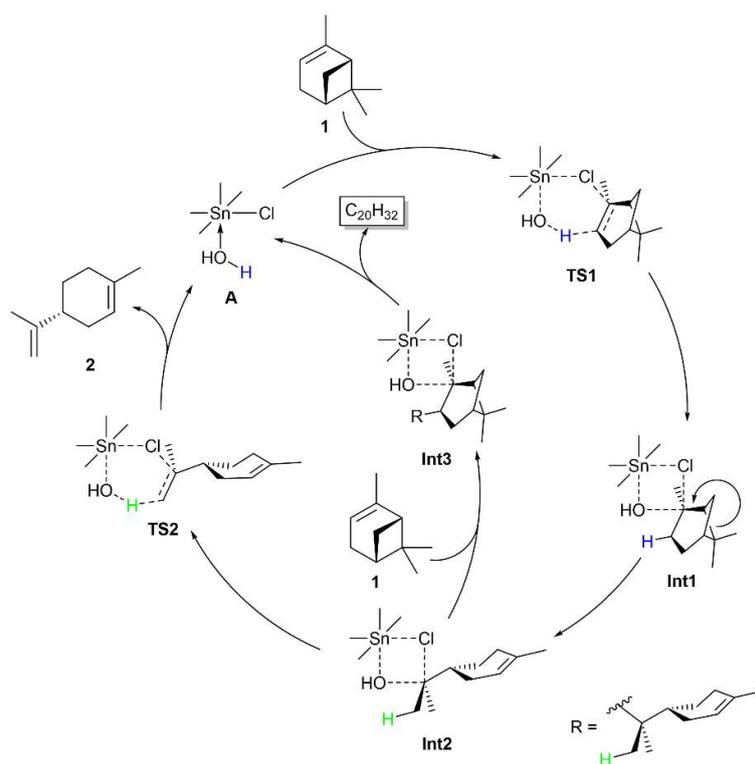


**Figure 2.** Effect of reaction temperature and reaction time on the yields of (A,D) *p*-menthadiene isomers, (B,E) other monomeric hydrocarbons, and (C,F) heteroatom-containing monomeric products. The reaction was carried out (A–C) for 1 h and (D–F) at 70 °C.

### 3.2. Rationalization of the Formation of Monoterpene Isomers and Dimeric Hydrocarbons

There have been a few papers on the  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ -catalyzed organic reactions. Based on the crystal structure of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  that consists of  $[\text{SnCl}_4(\text{H}_2\text{O})_2]$  linked by hydrogen bonding with additional water molecules [26], the mechanism of those reactions has been explained in the manner of both Lewis and Brønsted acid-base interaction. When Lewis basic heteroatom-containing reactants are used, their coordination to stannic ( $\text{Sn}^{\text{IV}}$ ) center is considered to be an important step of the reaction. Such examples involve  $\beta$ -amino alcohol synthesis by epoxide ring-opening [27] and  $\beta$ -amino carbonyl compound synthesis by the Mannich-type reaction [28]. On the other hand, in the absence of heteroatom in reactants, the Brønsted acidity of the coordinated water ligands is considered to be important. For example, the hydration of alkyne has been explained by the initial protonation of reactants by water, which is activated by the coordination to the stannic center [29]. Such Lewis acid-assisted Brønsted acids were also developed for enantioselective polyene cyclization [19,20] and enantioselective protonation of silyl enol [21,22]. Given  $\alpha$ -pinene has no heteroatom that can directly interact with the stannic center in a Lewis acid-base manner, the catalytic conversion of  $\alpha$ -pinene by  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  should follow the second explanation above.

The possible mechanisms for the conversion of  $\alpha$ -pinene to isomerized products (tricyclene, camphene, limonene, terpinolene,  $\alpha$ -terpinene, and  $\gamma$ -terpinene), disproportionated products (menthenes and *p*-cymene), and dimerized products by various acid catalysts have been proposed in the previous papers [8,23]. In this work, we focused on a plausible mechanism involving interaction between  $\alpha$ -pinene and the catalyst, which is shown in Scheme 1.



**Scheme 1.** A plausible catalytic cycle of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (A) proposed for the synthesis of limonene (2) and dimeric hydrocarbons ( $\text{C}_{20}\text{H}_{32}$ ) from  $\alpha$ -pinene (1).

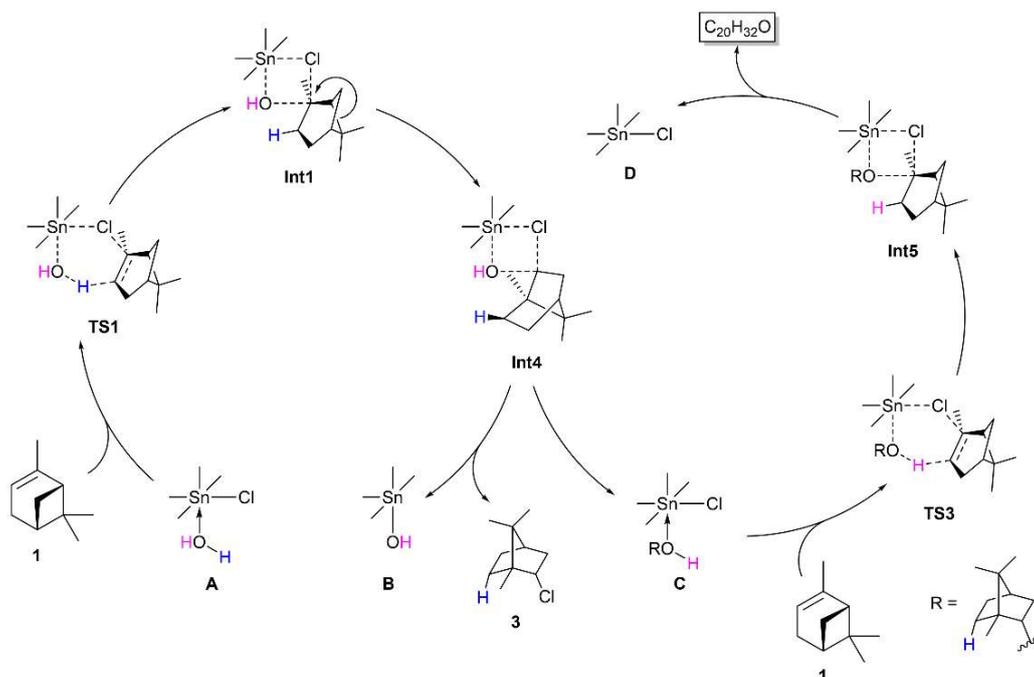
First, the protonation of  $\alpha$ -pinene (1) is thought to be promoted by the Lewis acid-assisted Brønsted acid activity of the coordinated water ligands in the  $\text{Sn}^{\text{IV}}$  complex (A) via TS1 (Scheme 1). Since there is no polar solvent that can solvate the generated ions, an intimate ion-pair between carbocation and  $\text{Sn}^{\text{IV}}$  ate complex should be a reaction intermediate (Int1) [19,30]. To form limonene (2), the main isomerized product from compound 1, the pinanyl moiety in the intimate ion-pair Int1 should suffer

from a ring-opening rearrangement, which generates a carbocation/ $\text{Sn}^{\text{IV}}$  ate complex ion-pair (Int2). In this intimate ion-pair Int2, the abstraction of a proton from the carbocation moiety by the hydroxo ligand via TS2 regenerates stannic complex A and furnishes compound 2 as the product of a catalytic cycle. If the insertion of another compound 1 into the intimate ion-pair Int2 is prior to the proton abstraction step, a carbocation/ $\text{Sn}^{\text{IV}}$  ate complex ion-pair (Int3) appears for dimeric hydrocarbons ( $\text{C}_{20}\text{H}_{32}$ ) as the product of the catalytic cycle. Along with the case of compound 2, we can construct distinct routes to complete the catalytic cycle involving the possible combination of carbocation/ $\text{Sn}^{\text{IV}}$  ate complex ion-pairs, which are able to explain the various isomers and dimeric hydrocarbons from compound 1.

### 3.3. Rationalization of the Formation of Heteroatom-Containing Dimeric Products

As previously mentioned, from  $\alpha$ -pinene, stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) can produce dimerized products that are high-density fuel candidates. There is one limitation of this reaction system, however, which involves forming not only the dimeric hydrocarbons that show molecular ion peaks at  $m/z = 272$  [ $\text{C}_{20}\text{H}_{32}$ ] $^+$  but also the oxygen-containing dimeric products, such as possibly dimeric alcohols or dimeric ethers, that show molecular ion peaks at  $m/z = 290$  [ $\text{C}_{20}\text{H}_{34}\text{O}$ ] $^+$ . Although the inclusion of oxygen-containing species increases the overall density of the fuel mixture [5], which matches the purpose of augmenting the energy density of renewable fuel, this is not suitable considering the synthesis of hydrocarbons for drop-in fuel. Therefore, to exclude the production of oxygen-containing species from the reaction system catalyzed by  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , we have started the rationalization of how such species are formed.

From the fact that the formation of bornyl chloride (3), one particular chlorine-containing side-product, the decomposition of  $\text{Sn}^{\text{IV}}$  complex (A) during the reaction can be postulated (Scheme 2, left circle). In other words, to form compound 3, the protonation of  $\alpha$ -pinene (1) by stannic complex A and successive ring enlargement by Wagner-Meerwein rearrangement occur first, furnishing a carbocation/ $\text{Sn}^{\text{IV}}$  ate complex ion-pair (Int4). This intimate ion-pair Int4 then suffers from the dissociation of chloride ligand, producing both compound 3 and decomposed  $\text{Sn}^{\text{IV}}$  complex (B).



**Scheme 2.** A plausible mechanism of catalyst (A) decomposition suggested based on the production of bornyl chloride (3, left circle) and oxygen-containing dimeric products ( $\text{C}_{12}\text{H}_{32}\text{O}$ , right circle).

As previously mentioned, for the conversion of  $\alpha$ -pinene (1) to occur, carbocation/ $\text{Sn}^{\text{IV}}$  ate complex ion-pairs (Int1-4) should be reaction intermediates (Schemes 1 and 2). We considered that these intermediates are essential clues for the explanation of how the oxygen-containing species are formed. While bornyl chloride (3) is formed when the dissociation of chloride ligand (Sn-Cl bond) occurs in the intimate ion-pair Int4, monoterpene alcohols can be formed by the dissociation of hydroxo ligand (Sn-O bond). At this point, the monoterpene alcohols can occupy an empty coordinate site of the stannic center as an alcohol ligand, which generates ligand exchanged  $\text{Sn}^{\text{IV}}$  complex (C) (Scheme 2, right circle). Since the same Lewis acid-assisted Brønsted acidic water ligands work as both catalysts and reactants, this alcohol ligand can also protonate another compound 1, furnishing a carbocation/ $\text{Sn}^{\text{IV}}$  ate complex ion-pair (Int5) via TS3. From this intimate ion-pair Int5, the dissociation of the remained alkoxy ligand can cause the formation of dimeric ethers ( $\text{C}_{20}\text{H}_{32}\text{O}$ ) and decomposed  $\text{Sn}^{\text{IV}}$  complex (D).

Based on the above rationalization, we have concluded that, although the reaction system catalyzed by the Lewis acid-assisted Brønsted acid activity of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  can produce high-density fuel candidates from  $\alpha$ -pinene, to synthesize dimeric products as only hydrocarbons, the water ligands must be switched. Instead of them, monodentate alcohols or phenol ligands, which will form alkoxy or aryloxy ligand after the protonation of  $\alpha$ -pinene, respectively, also should be avoided since these ligands can furnish undesirable ether products. Therefore, we have considered bidentate 2-alkoxyphenol ligands such as 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol), given they can be tightly bonded to the metallic center with their methoxy group even after the protonation of  $\alpha$ -pinene [19–22]. To prove this hypothesis, further study should be followed.

#### 4. Conclusions

To synthesize renewable high-density fuel from monoterpenes, we investigated whether the catalytic amount of stannic chloride molten salt hydrates ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) can furnish dimeric products from  $\alpha$ -pinene in a solvent-less condition.  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  would work as a catalyst for the dimerization of  $\alpha$ -pinene under milder conditions than previously reported ones. This conversion was thought to be promoted by a Lewis acid-assisted Brønsted acidic nature of the coordinated water ligands on the stannic ( $\text{Sn}^{\text{IV}}$ ) center. However, we can also observe the unexpected heteroatom-containing products of which oxygen and chlorine atoms resulted from the decomposition of the catalyst. Considering the proposed catalytic cycle and the mechanism of the catalyst decomposition, we suggested bidentate ligands to minimize the above problem.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2076-3417/10/21/7517/s1>. Figure S1: GC/FID chromatograms of (A) the neat turpentine used in this study and (B) the reaction mixture after 1 h of reaction at 100 °C. Figure S2: Representative mass spectra of (A) dimeric hydrocarbons, (B) trimeric hydrocarbons, and (C) oxygen-containing dimeric products.

**Author Contributions:** Conceptualization, S.-M.C. Methodology, S.-M.C. and J.-H.C. Formal analysis, S.-M.C. and J.-H.K. Investigation, S.-M.C. and J.-H.C. Resources, S.-M.C. Data curation, J.-H.C. and J.-H.K. Writing—original draft preparation, S.-M.C. and J.-H.C. Writing—review and editing, S.-M.C. and B.K. Supervision, I.-G.C. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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