Isomerization of 2-Pinene Catalyzed by Solid Acids

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The isomerization of 2-pinene (I) and 2(10)-pinene (II) in the liquid phase has been studied at 50 °C over solid acid catalysts such as silica–alumina, aluminum phosphate, nickel sulfate and zinc sulfide which have different acid strengths. The primary reaction products were camphene (III), 1,7,7-trimethyl-tricyclo[2.2.1.0^{2,6}]-heptane (IV) and *p*-mentha-1,8-diene (VI). The catalytic activities increased with increasing acid strength and acid amount of the catalysts. The selectivities for the formation of III+IV and VI from I were about 90 and 10% respectively over $NiSO_4$, but about 10 and 70% respectively over SiO_2–Al_2O_3 and $AlPO_4$. Those for the formation of I, III+IV and VI from II also depended on the acid strength. In the isomerization of VI, *p*-mentha-1,4(8)-diene (VII) was formed predominantly over $NiSO_4$ and *p*-cymene (IX) over SiO_2–Al_2O_3. From these results together with those of the isomerizations of III and IV, a reaction mechanism is proposed which consists of two parallel reactions proceeding *via* a common intermediate between I and II: one which gives monocyclic terpenes and the other bi- and tricyclic terpenes.

The isomerization of 2-pinene (I) over solid catalysts in the liquid phase was first reported by Gurvich in 1915.[1] Since then, a number of studies have been made on the isomerization and the following reaction products have been reported: bi- or tricyclic terpenes such as 2(10)-pinene (II), camphene (III), 1,7,7-trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (IV), bornene (V) *etc.*, monocyclic terpenes such as *p*-menthadienes (VI, VII, VIII *etc.*), *p*-cymene (IX) and polymers[2,3] (See Fig. 4 for structures of the compounds).

Catalysts used for the isomerization were mineral clay, active carbon, silica–alumina, titanium oxide, magnesium sulfate *etc.* which can be classified as solid acids. It was reported recently that alumina, a strong acid, showed a tendency to give monocyclic terpenes, while alkali poisoned aluminas, weak acids, form bi- or tricyclic terpenes in vapor phase reactions.[4] However, no systematic work has been done on the correlation between acidic property of solid acids and their catalytic activity or selectivity. In the present work, the correlation was examined by employing as catalysts nickel sulfate which has moderate acid strength and whose acidity can be easily changed by calcination,[5–7] silica–alumina and aluminum phosphate which have high acid strength and zinc sulfide which has weak acid strength[8] in liquid phase.

On the basis of the observed results, the reaction paths and intermediates of the isomerization are discussed.

Experimental

Reagents and Catalysts. 2-Pinene was purified from turpentine oil (Wako Pure Chemical Co.) by distillation over sodium, passage through a preparative gas chromatography (Perkin–Elmer F-21) with a 3 m×8 mm column containing 20% polyethylene glycol 1500 on Chromosorb W and distillation again over sodium under a stream of nitrogen. The purified material was stored in sealed ampoules. 2(10)-Pinene and camphene (Takasago Perfumery Co.) and 1,7,7-trimethyl-tricyclo[2.2.1.0^{2,6}]heptane, synthesized from camphor according to the method of Meerwein and Emster,[9] were purified similarly to 2-pinene.

Nickel sulfate catalysts were prepared by calcining the heptahydrate (guaranteed reagent, Kanto Chemical Co.) in the temperature range 150—550 °C in air, grinding after cooling and calcining again at the original temperature for 3 hr. Aluminum phosphate, prepared from H_3PO_4 and $AlCl_3 \cdot 6H_2O$,[10] was calcined in air at 450 °C for 3 hr. Silica–alumina (15 wt. % Al_2O_3, Nikki Chemical Co.) and zinc sulfide (guaranteed reagent, Nakarai Chemical Co.) were calcined in air at 600 and 450 °C respectively. All catalysts were stored in sealed ampoules.

Acidity and Kinetic Measurements The acid amounts at various acid strengths of the catalysts were measured by *n*-butylamine titration using various indicators,[5] or by the ultraviolet spectrophotometric method.[11] The indicators used for the titration method were phenylazonaphthylamine ($pK_a=+4.0$), *p*-dimethylaminoazobenzene (+3.3), dicinnamalacetone (−3.0) and anthraquinone (−8.2). 2,6-Dichloro-4-nitroaniline ($pK_a=-3.27$) was used for the spectrophotometric method.

The reaction was carried out under helium gas since it is sensitive to air. The reaction temperature was 50 °C unless otherwise stated. Reaction products were analyzed by a gas chromatograph with FID (Hitachi-Perkin-Elmer F-6D), using a 45 m capillary column of Ucon LB-500-X. The amount (mole %) of each product was obtained by measuring each peak area with an integrator (DISC Co.) and by multiplying by the respective correction coefficient.

Results

Acidity of Catalysts. The acid amounts at various strengths of the catalysts are shown in Table 1. Silica–alumina and aluminum phosphate have high acid strength ($pK_a=-8.2$), while zinc sulfide has a weak one ($pK_a=+4.0$). The acid strength of the nickel sulfates was moderate. The acid amount increased with the rise in calcination temperature, attaining a maximum value at 350 °C, and then decreased at higher temperatures.[5]

Isomerization of Camphene (III), 1,7,7-Trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (IV) and p*-Mentha-1,8-diene (VI).* Before the reaction of I, the isomerization of III, IV, and VI, main reaction products of I, was studied. The products of the isomerization of III (or IV) were IV (or III) and a small amount of V over nickel sulfates. Over silica–alumina and aluminum phosphate which

TABLE 1. ACID AMOUNTS AT VARIOUS ACID STRENGTHS OF CATALYSTS

Catalysts Calcination temp., °C	(pK_a)	$NiSO_4$ 150	$NiSO_4$ 200	$NiSO_4$ 250	$NiSO_4$ 350	$NiSO_4$ 450	$NiSO_4$ 550	SiO_2–Al_2O_3 600	$AlPO_4$ 450	ZnS 400
Acid amounts	+4.0	—	—	—	—	—	—	—	—	1.08
(mmol/g) at	+3.3	0.029	0.064	0.11	0.13	0.088	0.046	—	—	0
various acid	−3.0	0	—	0.016	0.046	0	0	—	—	—
strengths (pK's)	−3.27	—	0	0	0	—	—	—	—	—
	−8.2	—	—	—	—	—	—	0.25	0.42	—

TABLE 2. EQUILIBRIUM CONSTANTS BETWEEN CAMPHENE(III) AND 1,7,7-TRIMETHYL-TRICYCLO[2.2.1.$0^{2,6}$]HEPTANE (IV)

Catalysts Reaction temp., °C	$NiSO_4$ 50	$NiSO_4$ 70	$NiSO_4$ 80	$NiSO_4$ 90	$NiSO_4$ 100	$NiSO_4$ 110	$NiSO_4$ 140	$NiSO_4$ 150	$KHSO_4$ 200	Co/Al_2O_3 250	Al_2O_3 275
K=IV/III	0.20—0.23	0.23	0.20	0.20	0.19	0.21	0.20	0.20	0.25—0.28[a)]	0.33[b)]	0.33[c)]

a) Cited from Ref. 18, b) Ref. 19, c) Ref. 20

TABLE 3. SELECTIVITIES OF VAROPIS CATALYSTS FOR ISOMERIZATION OF p-MENTHA-1,8-DIENE (VI) AT 50 °C

Catalysts		$NiSO_4$ calcined at 400 °C	SiO_2–Al_2O_3	$AlPO_4$
Selectivity	VI→VII	0.84	—	0.21
	VI→IX	0.03	0.86	0.52

have high acid strength, considerable amounts of polymers were obtained in addition to the above products. The isomerization to I did not occur on any of the catalysts.

The equilibrium constants between III and IV, obtained from the mole % ratio of III to IV in equilibrium, are listed in Table 2. The values above 200 °C were cited from literature.

The main reaction products of VI were p-mentha-1,4(8)-diene (VII), p-mentha-1,3-diene (VIII) and p-cymene (IX). From initial slopes of the plots of VI, VII, and IX against reaction time the selectivity for the formation of VII and IX was obtained (Table 3). VII was formed predominantly over metal sulfates which have moderate acid strength, while IX was formed predominantly over strong solid acids, where polymers were also found.

Isomerization of 2-Pinene. The % conversion of 2-pinene (I) plotted against reaction time is shown in Fig. 1a. Since the isomerization did not obey the rate equation of a first- or second- order reaction, the initial rate per unit weight of catalyst was taken as the catalytic activity. The activities of various catalysts are given in Table 4. Because of high activity of silica–alumina, the reaction over the catalyst was carried out at ambient temperature. High activities were found for silica–alumina and aluminum phosphate and a low activity for zinc sulfide as expected from their acid strengths (Table 1). Calcined nickel sulfates showed intermediate activity, varying with changes in the calcination temperature. A correlation exists between the activity and the acid amount or strength.

It should be noted that the rate of isomerization is considerably affected by the presence of air. The reaction rate in the presence of air was too slow to measure at 50 °C but became measurable at 150 °C, at which temperature the reaction in the absence of air was too fast to follow. Thus, the unusual curve

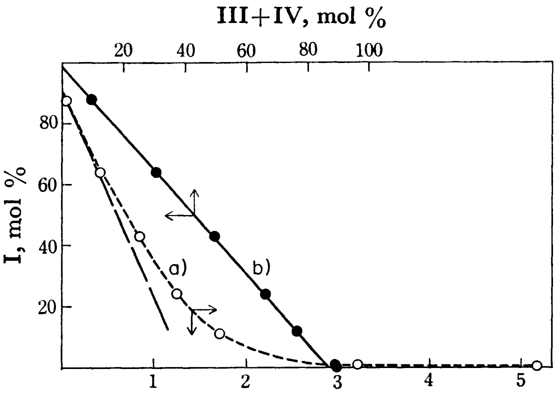

Fig. 1. a) Time dependence in mol % of 2-pinene (I). b) Mol % of 2-pinene (I) *vs.* mol % of camphene (III) + 1,7,7-trimethyl-tricyclo[2.2.1.$0^{2,6}$]heptane (IV). Reaction temp.: 50 °C, Catalyst: 0.877 g of nickel sulfate calcined at 350 °C.

TABLE 4. ACTIVITIES AND SELECTVIITIES OF VARIOUS CATALYSTS FOR ISOMERIZATION OF 2-PINENE (I) AT 50 °C

Catalysts Calcination temp., °C		$NiSO_4$ 150	$NiSO_4$ 200	$NiSO_4$ 250	$NiSO_4$ 300	$NiSO_4$ 350	$NiSO_4$ 400	$NiSO_4$ 450	$NiSO_4$ 600	SiO_2–Al_2O_3 600	$AlPO_4$ 450	ZnS 400
Selectivity	I→III+IV	0.93	0.77	0.83	0.84	0.89	0.78	0.79	0.87	0.14[a)]	0.12	0.61
	I→VI	—	0.14	0.11	0.10	0.09	0.10	0.15	0.08	0.67[a)]	0.68	0.33
Initital velocity $hr^{-1}g^{-1} \times 10^{-2}$		0.01	0.02	0.5	0.8	0.8	2.3	1.4	0.9	51[a)]	41	0.3

a) Values at room temperature.

of % conversion *vs.* reaction time in Fig. 1a is considered to be due to the poisoning effect of a very small amount of oxygen or moisture in the reaction system.

In order to see the selectivity of this reaction, % of I remaining at reaction time *t* was plotted against % of III+IV formed at time *t* in Fig. 1b.[12] The plots fell on a straight line. This indicates that there is no backward reaction to I and that III and IV are not converted into any other compounds under the reaction conditions, in accordance with the results of the reactions of III and IV. This indicates that III and/or IV are primary products of I. A linear relation was also found between I and VI, indicating that there is no backward reaction from VI to I.

The selectivities for the formation of III+IV and VI from I, calculated from the slopes of the straight lines over various catalysts, are shown in Table 4. The selectivity did not change much over nickel sulfates calcined at various temperatures, 80—90% of bicyclic terpenes (III+IV) and about 10% of monocyclic terpene (VI) being formed. On the other hand, a high selectivity (about 70%) for VI was found for silica–alumina and aluminum phosphate which have high acid strength. This is in agreement with the result which showed that monocyclic terpenes are formed more readily over alumina than over alkali poisoned alumina;[4] it also explains the result observed by Okada and Fushizaki where the yield of camphene was increased by the addition of magnesium oxide to mineral clay used as a solid acid,[13] since magnesium oxide, recently recognized to be a strong solid base,[14,15] is considered to weaken the acid strength of a mineral clay catalysts.

The relation between III and IV which were formed from I is shown in Fig. 2, where the catalyst used was nickel sulfate calcined at 300 °C. The slope of IV/III increased with the progress of reaction and finally reached the equilibrium value, the plots of I *vs.* III+IV falling on a straight line until the end of the reaction (Fig. 3a). The results suggest that the isomerization between III and IV takes place during a later stage of the reaction. It is shown in Fig. 3b that limonene (VI) is also converted into other compounds during a later stage of the reaction. Similar results observed by Rudakov *et al.* for titanium oxide[16] indicate that both III and IV are primary products.

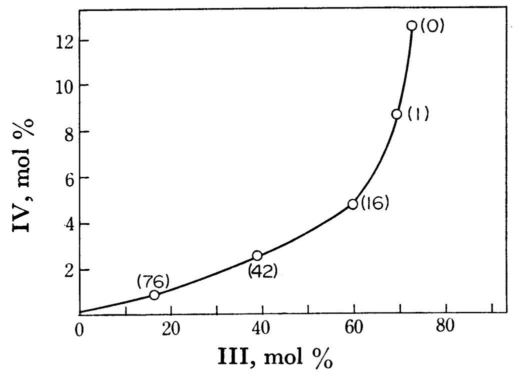

Fig. 2. Mol % of 1,7,7-trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (IV) *vs.* mol % of camphene (III). Catalyst: nickel sulfate calcined at 300 °C, Figures in parentheses show the mol % of 2-pinene (I).

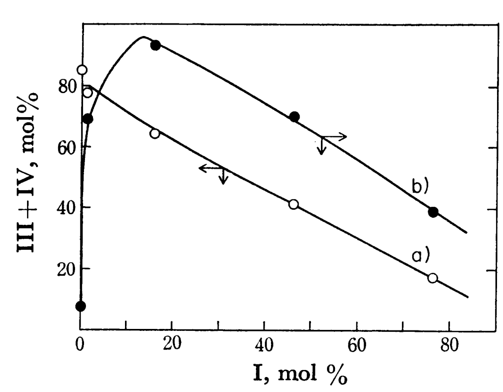

Fig. 3. Mol % of III+IV and *p*-mentha-1,8-diene (VI) *vs.* mole % of I. Catalyst: the same as in Fig. 2.

Isomerization of 2(10)-Pinene (II). The isomerization products of II were the same as those of I. The plots of III+IV *vs.* II, VI *vs.* II and I *vs.* II gave straight lines in the range 100—20 mol % of II as in Fig. 3. This indicates that III and/or IV, VI, and I are the primary products of II and that there is no backward reaction to II. This is in line with the result by Ivanova *et al.* which showed that I, III, and VI are not readsorbed on silica–alumina to react further until the concentration of II becomes less than 20—30%.[17] The selectivities for the formation of III+IV, VI and I from II, calculated from the slopes of the straight lines, are shown in Table 5, where the activity of various catalysts for the isomerization is also given. The values in parentheses, which show the selectivity recalculated by using the formula, selectivity of III+IV from II/(1−selectivity of I from II), can be compared with the selectivity values for the reactions from I given in Table 4, since II is not formed from I. The values are in fairly good accord with those in Table 5 except for silica–alumina, suggesting that III, IV, and VI are formed through a common intermediate from both.

TABLE 5. ACTIVITIES AND SELECTIVITIES OF VARIOUS CATALYSTS FOR ISOMERIZATION OF 2(10)-PINENE(II) AT 50 °C

Catalysts calcination temp., °C		$NiSO_4$		SiO_2–Al_2O_3	ZnS
		250	450	600	450
Selectivity	II→III+IV	0.52	0.66	0.31[a)]	0.55
		(0.76)	(0.84)	(0.41)[a)]	(0.62)
	II→VI	0.08	0.12	0.30[a)]	0.20
		(0.12)	(0.15)	(0.40)[a)]	(0.22)
	II→I	0.32	0.21	0.27[a)]	0.11
Initial velocity $hr^{-1}g^{-1} \times 10^{-2}$		0.6	2.4	4.4[a)]	0.1

a) Values at 15—20 °C.

Discussion

The maximum acidity of nickel sulfate was observed when the sulfate is calcined at 350 °C (Table 1). It is known that the acidity as measured by titrating with *n*-butylamine is the sum of Brönsted and Lewis acidity.

According to the infrared study on pyridine adsorbed on nickel sulfates, maximum Brönsted acidity appears at 250 °C and maximum Lewis acidity at 400 °C.[21] The fact that, in the isomerization of 2-pinene (I), maximum activity was observed when the sulfate was calcined at 400 °C seems to indicate that Lewis acid sites are active for the reaction. However, the isomerization of I is not catalyzed by Lewis acids such as BF_3, $AlCl_3$, $TiCl_4$ *etc.*, in the presence of an aprotic solvent such as benzene although polymers including dimer *etc.* were formed during the course of reaction.[22] The isomerization took place, however, in the presence of protic solvents such as alcohols which have proton donating ability.[23] Ozaki and Kimura reported that Lewis acid sites were converted into Brönsted acid sites by the adsorption of olefin and that the converted sites were active for olefin isomerization.[24] Thus, it can be said that the number of Lewis acid sites are correlated with the catalytic activity for the isomerization, but the actual active sites under the reaction conditions are all Brönsted acids.

Important results obtained are summarized as follows. 1) III, IV, and VI are formed through a common protonated intermediate from I and II. 2) There is no reverse reaction to I or II from III, IV, and VI. 3) VI is formed through a reaction path differing from that which III and IV are formed. 4) III, IV, and VI are not readsorbed on catalysts to react further in the presence of I or II, but turn to other compounds when the amount of I or II becomes small. 5) Over strong acid catalysts, VI is formed predominantly as compared with III and/or IV, polymers being formed from III and IV. 6) The reaction between III and IV is reversible, if I is absent. 7) The main products in the isomerization of VI are VII and IX, the latter being formed predominantly over strong solid acids.

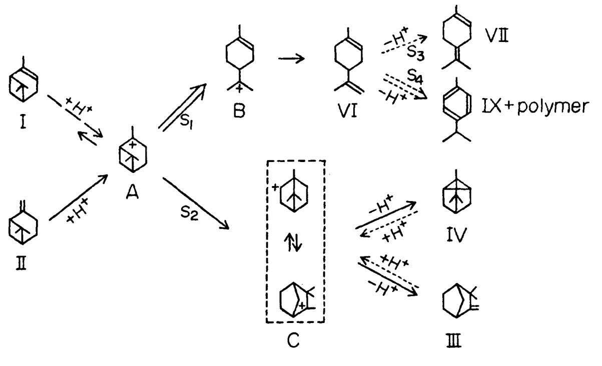

Fig. 4. Reaction scheme.

A, B, C: reaction intermediates.

——→ steps taking place independently of the amount of I.

—→ a step taking place when the amount of II becomes small.

-----→ steps taking place when the amounts of both I and II become small.

Steps S_1 and S_4 take place more predominantly than steps S_2 and S_3, respectively, as the acid strength of catalyst becomes higher.

These results lead us to the reaction scheme shown in Fig. 4, where the inferred structures of the reaction intermediates are also given. It is considered that the structures of intermediate A and an intermediate between VI and VII or IX change depending on the acid strength of catalyst.

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