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The Additions of Acetic Acid to Limonene over Solid Acid Catalysts

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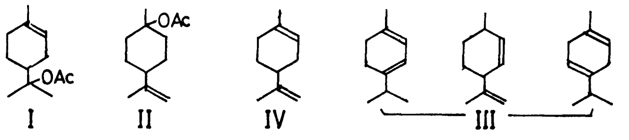
The addition of acetic acid (AcOH) to limonene (IV) over 111—333 g/l of solid acid catalysts, at 28—92 °C and in an excess of AcOH (19—100 times of IV in molarity), were studied in terms of the kinetic data, at a total conversion of IV less than 10 mol%, and in terms of acid strength distributions of the catalysts. In the reaction medium, a leveling of the acid strength on solids was observed. For the formation of α- and β-terpinyl acetates (I and II) and a mixture of the isomeric *p*-menthadienes (III) as by-products, (1) the rates are proportional to the square root of the initial concentrations of IV; (2) the apparent activation energies are 18.3 kcal/mol for all the catalysts, and (3) the pre-exponential factors are roughly proportional to the square root of the highest acidity ($h_{0,\max}$) of the catalyst surface in the medium. The effects of the acid properties of the catalyst on the catalytic activity and the selectivity are different from those in a homogeneous liquid acid-catalyst system.

Recently,¹⁾ we studied the addition of AcOH to limonene (IV), with H_2SO_4 as a catalyst, in a homogeneous system with a large excess of AcOH and without solvent. Considerable amounts of *p*-menthadienes (III) and β-terpinyl acetate (II) were formed besides the desired product, α-terpinyl acetate (I). It was regarded as very difficult to suppress the formation of III by the variation in the H_2SO_4 concentration.



Scheme 1.

In the present study, the kinetic data of the same additions over solid acids, such as metal sulfates and silica-alumina, in an AcOH solution were obtained and related to the acid properties of the solids in order to compare them with the previous results.¹⁾ Those catalytic mechanisms were also discussed in connection with the catalytic activities and selectivities. In general, in the liquid phase, the extrapolations of the catalytic properties of homogeneous acids to heterogeneous solid acids are still uncertain,²⁾ although such extrapolations are desirable for both practical and theoretical reasons. Comparing the two catalytic systems experimentally will be helpful in establishing such extrapolations. The same reaction conditions as in the previous paper¹⁾ were taken, except that solid catalysts were used instead of H_2SO_4.

Experimental

Solid Catalysts. $MgSO_4$, $Al_2(SO_4)_3$, $NiSO_4$, and $Fe_2(SO_4)_3$ of a guaranteed reagent grade and silica-alumina (Silica-alumina-L; Nikki Chemicals Co., Ltd.; termed Si-Al-L in this study) were ground and sieved to prepare powder of a 100—200 mesh. Some of them were calcined before grinding. $NiSO_4$ was calcined at 520 °C for 3 hr; $Fe_2(SO_4)_3$, at 100 °C for 3 hr, and $MgSO_4$, at 520 °C for 2 hr, all in a dry nitrogen stream. $Al_2(SO_4)_3$ and Si-Al-L were used without calcination.

Materials. Limonene (IV) was purified in the same way as before.¹⁾ The content of IV was 96.7 wt%. AcOH was a guaranteed reagent and was not purified further.

Analysis. The composition of the products was determined by quantitative gas-chromatographic (glc) analysis with an internal standard, using a Shimadzu GC-3AH under the same conditions as before.¹⁾

Procedure. The reaction was the same as before,¹⁾ except that a solid catalyst was suspended instead of H_2SO_4. A 24.3-g portion (which corresponds to a large excess over the stoichiometric requirement) of AcOH, 0.5—3.0 g of IV, and 3.0—9.0 g of the catalyst were used. At any reaction time, a 2—3 ml sample of the suspended solution of catalyst was taken out, diluted with 70 ml of NaCl-saturated water to stop the reaction, and extracted with *n*-hexane. The extract was then concentrated and used for the glc analysis.

During the reaction, sampling was repeated at arbitrary time intervals. The reaction temperature was 28—92 °C. The reference volume of the reaction mixture used to express the concentration of components or solids was taken at 28 °C. The concentration of IV was 0.151—0.782 mol/l, while that of the catalyst was 110.8—333 g/l.

Measurement of the Acid-base Strength Distribution. During the reaction, a drop of a basic indicator in benzene (0.1 wt%) was added to a portion of the suspended reaction medium in order to examine the existence of acid sites on the solid by means of the color change. The indicators used were Neutral red (+6.8), 1-phenylazo-4-naphthylamine (+4.0), Butter yellow (+3.3), *p*-(phenylazo)diphenylamine (+1.5), and dicinnamylideneacetone (−3.0); the values in parentheses are the pK_a values of the conjugate acids. On the other hand, a modified Johnson method³⁾ using a set of the same indicators was used to determine the acid-base strength distributions of fresh solids.

Results

Acidities of Catalysts. The acid-base strength distributions of the fresh catalysts are shown in Table 1, together with the qualitative data in the reaction medium, where H_0 denotes the acid strength on a solid defined by Benesi⁵⁾ employing the acidity function as defined by Hammett and Deyrup⁴⁾ in the liquid phase. The acidity and basicity in the reaction medium could not be titrated because of the existence of AcOH. Therefore, in Fig. 1, the extent of the color change to an acid one in the medium is indicated to decrease in this order: ++, +, −. As may be seen in Table 1, the stronger acid sites of most catalysts disappeared upon the addition of AcOH or IV. The range of the highest H_0 value of the remaining acid sites was estimated qualitatively from

TABLE 1. ACID-BASE STRENGTH DISTRIBUTIONS OF CATALYSTS

	Range of highest-H_0[a]	Acid amount (meq/g) at different H_0				
		+6.8	+4.0	+3.3	+1.5	−3.0
$Fe_2(SO_4)_3$		0.969	0.848	0.751	0.175	0.071
	<−3.0	++	++	++	++	++
$NiSO_4$		9.502	0.393	0.278	0.127	0.070
	−3.0—+1.5	++	++	++	+	−
$Al_2(SO_4)_3$		0.097	0.083	0.075	0.037	B
	+1.5—+3.3	++	++	+	−	−
$MgSO_4$		0.191	0.101	0.0	B (0.035)[b]	B
	+3.3—+4.0	++	+	−	−	−
Si-Al-L		1.67	1.47	0.570	0.169	0.089
	+1.5—+3.3	++	++	+	−	−

a) Remained range of highest-H_0 during reaction. b) Basic color of an indicator and the value in parenthesis shows the base amount.

the color change. Except for $Fe_2(SO_4)_3$, each catalyst lowered the highest H_0 value in the medium. In every reaction medium, the color in the liquid phase did not change, and the color change of a catalyst was not affected by the reaction time or by the amount of the catalyst.

Reaction Order. The components of the products were the same as in the homogeneous system —*i.e.*, I, II, and III. The concentration-time curve for each product, the acetates (I and II), and isomers (III) could be taken as a straight line when the total conversion of IV was less than 10 mol%. The formation rate (r_i) of I, II, and III was defined as $dC/d\theta$, where θ denotes the reaction time (hr). The C and i terms denote the concentration; the components I, II, and III, correspond to i=1, 2, and 3 respectively. Figure 1 shows the logarithmic plots of the initial rates (at $\theta=0$) *vs.* C_0 over Si-Al-L, where C_0 denotes the initial concentration of IV. The straight lines of the slope=0.5 indicate that every rate (r_i) at $\theta=0$ is proportional to the square root of C_0: $r_{i,\theta=0}=k_iC_0^{0.5}$. k_i was defined as a rate constant for each product.

Dependency on the Catalyst Amount. In Fig. 2, the log k_i values are plotted against the log W of Si-Al-L. The linear correlation of the slope=1.0 for each product means that every k_i is proportional to W. It may be reasonable to consider that the catalytic action is restricted in the neighborhood of a solid surface in the heterogeneous catalyst system.

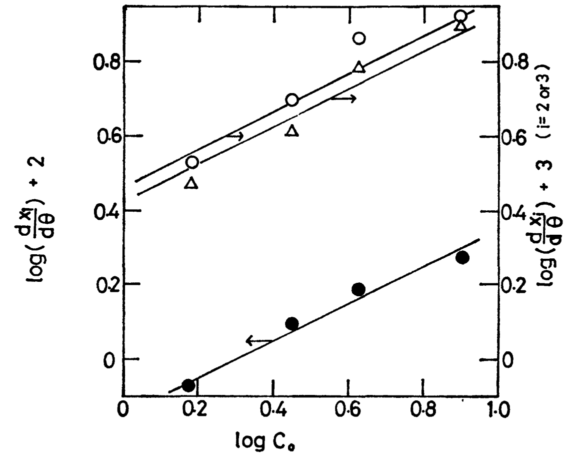


Fig. 1. Dependency of initial rates on initial concentrations of IV over Si-Al-L (166.5 g/l) at 78.5 °C. ●, I; ○, II; △, III.

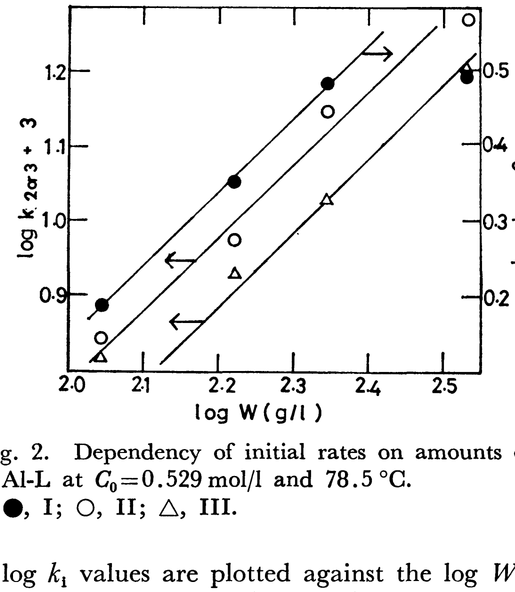


Fig. 2. Dependency of initial rates on amounts of Si-Al-L at C_0=0.529 mol/l and 78.5 °C. ●, I; ○, II; △, III.

Temperature Dependency of k_i. In Fig. 3, the Arrhenius plots for k_i over every catalyst are shown. All the apparent activation energies (E_i) are the same in all cases, *i.e.*, 18,300 cal/mol. Therefore, the relative catalytic activity of the solids must be entirely due to the pre-exponential factors (A_i) of k_i in the equation: $k_i=A_i\exp(-E_i/RT)$. The constant activation energy in Fig. 3 suggests that all the reactions to form I, II, and III over each catalyst have equivalent rate-determinig steps and activated complexes with identical structures at the double bonds. A_i in every case was calculated to be as is shown in Table 2. In each catalyst, the A_i's are in almost the same order.

Effects of the Catalyst Acidity on the Activity and Selectivity. In Fig. 4, each log A_i is plotted against the highest H_0 value in the reaction medium. The correlations between log A_i and the highest H_0 seem to follow straight lines with a slope of ≈0.5. Therefore, the catalytic activities are roughly proportional

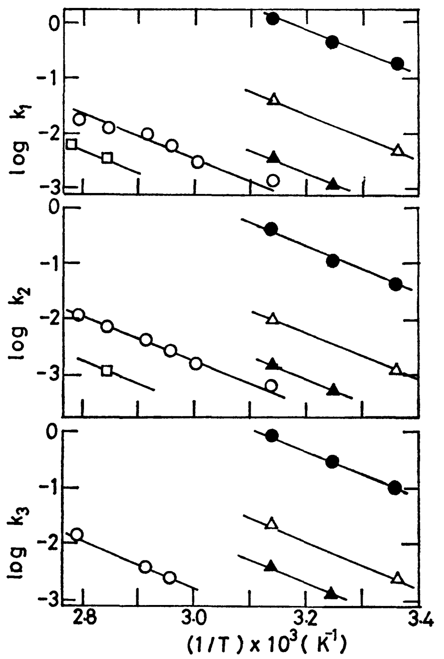


Fig. 3. Dependency of rate constants on reaction temperature over various solid acids ($W=166.5$ g/l). ●, $Fe_2(SO_4)_3$; △, $NiSO_4$; ▲, $Al_2(SO_4)_3$; ○, Si-Al-L; □, $MgSO_4$.

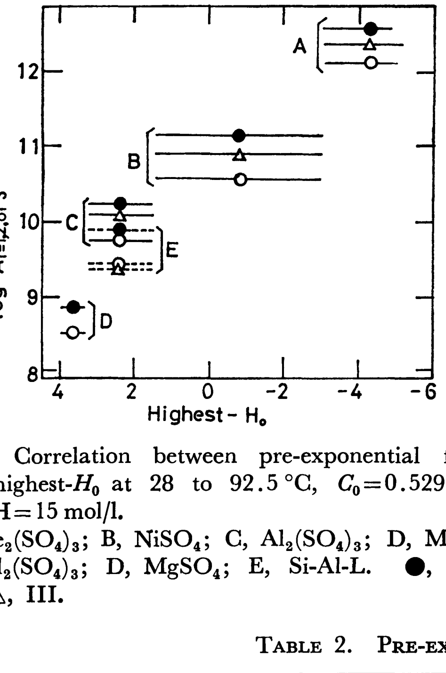


Fig. 4. Correlation between pre-exponential factors and highest-H_0 at 28 to 92.5 °C, $C_0=0.529$ mol/l, AcOH=15 mol/l.
A, $Fe_2(SO_4)_3$; B, $NiSO_4$; C, $Al_2(SO_4)_3$; D, $MgSO_4$; C, $Al_2(SO_4)_3$; D, $MgSO_4$; E, Si-Al-L. ●, I; ○, II; △, III.

to the square root of the maximum h_0 (termed by $h_{0,\mathrm{max}}$; highest $H_0=-\log(h_{0,\mathrm{max}})$; $H_0=-\log h_0$) in the medium. When are compared A_i with the acid properties of catalyst (Tables 1 and 2), it must be noted that no significant correlation can be found between the highest H_0 or the acidity at a definite H_0 on the fresh catalyst and A_i.

The selectivities of the products depend entirely on the pre-exponential factors. They are presented in Table 2. The selectivity of I against II (A_1/A_2) lies in the range from 2.09 to 3.68. These values are different from those in the homogeneous system.[1] On the other hand, the selectivities of the isomers against the two acetates $A_3/(A_1+A_2)$ fall into two groups; one consists of $Fe_2(SO_4)_3$, $NiSO_4$, and $Al_2(SO_4)_3$ with 0.44—0.55, while the other consists of Si-Al-L and $MgSO_4$ with ≤ 0.27.

Discussion

Acid Sites in the Reaction Medium. In the medium, a positive shift of the highest H_0 from the original value was observed (Table 1). This must be due to a leveling effect[7] of the medium caused by a neutralization of the acid sites with AcO^-. Although IV may also neutralize acid sites, it has little effect because of its weak basicity. Therefore, the leveling effect must consist of the following steps:

$$2AcOH \rightleftharpoons AcOH_2^+ + AcO^- \qquad (1)$$

$$AcO^- + HA_s \rightleftharpoons AcOH\cdot A_s^- \qquad (2)$$

$$AcO^- + A_{sL} \rightleftharpoons AcO^-\cdot A_{sL} \qquad (3)$$

where HA_s and A_{sL} denote a proton-acid site and a Lewis-acid site respectively. Steps (2) and (3) are possible with an acid site having $H_0\leq 4.76$ ($=pK_a$ of AcOH). A decrease in the AcO^- in Steps (2) and (3) will result in an increase of $AcOH_2^+$ *via* the autoprotolysis of Step (1). $AcOH_2^+$ also orients to sites where AcO^- has been adsorbed, there to supply the unbalanced negative charge of the surface by AcO^-. However, because of the low dielectric constant of the medium, the concentration of $AcOH_2^+$ can not be increased to finish the neutralization of acid sites, and the above steps will be settled into an equilibrium before the neutralization of the acid sites is complete. The case of $Fe_2(SO_4)_3$ seems to be the most obvious. After all, the leveling effect by Eqs. (1) to (3) will enrich the surface with AcOH. The observed highest H_0 value in the reaction

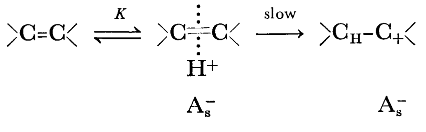
Table 2. Pre-exponential factors and selectivities

	Pre-exponential factors A_i ((mol/l)$^{0.5}$·hr^{-1})			Selectivities	
	A_1	A_2	A_3	A_1/A_2	A_3/A_1+A_2
$Fe_2(SO_4)_3$	3.78×10^{12}	1.24×10^{12}	2.69×10^{12}	3.06	0.545
$NiSO_4$	1.27×10^{11}	3.44×10^{10}	7.13×10^{10}	3.68	0.443
$Al_2(SO_4)_3$	1.59×10^{10}	$5.27\times10^{9)}$	1.16×10^{10}	3.01	0.550
$MgSO_4$	6.62×10^{8}	3.16×10^{8}	—	2.09	—
Si-Al-L	6.33×10^{9}	2.60×10^{9}	2.38×10^{9}	2.44	0.266
H_2SO_4[a]	8.90×10^{6}	6.91×10^{5}	5.24×10^{8}	12.9	0.6—1.7[b]

[a] Taken from the previous paper at $C_{H_2SO_4}$ 3.68×10^{-3} mol/l, and C_0 0.529 mol/l. In this case, A_i's are represented by hr^{-1}. [b] The values in the range of 28 to 92 °C.

medium is considered to be the highest acid strength, among the remaining acid sites or some of the neutralized acid sites, capable of exchanging AcO^- with a weak base such as the indicators.

Catalytic Activity. It is clear that IV acts as a weak base to acid sites. Therefore, the following scheme can be postulated for the double bonds of IV with the remaining acid sites and AcOH on the surface:



(IV) (V) (VI)

$$\text{VI} \xrightarrow[(\text{AcOH})_s]{k\alpha} \text{I},\quad \text{VI} \xrightarrow[(\text{AcOH})_s]{k\beta} \text{II},\quad \text{and}\quad \text{VI} \xrightarrow{k_{\text{III}}} \text{III}$$

In the above scheme, Step V→VI is considered to be the rate-determining step, because the diffusion of IV and the products (I, II, and III) in AcOH will be rapid enough; the activation energy is estimated to be 2—3 kcal/mol. Steps VI→I, VI→II, and VI→III can not be rate-determining steps because the same activation energies were observed.

The reaction rates are proportional to the concentration of the chemisorbed π-complex (C_{V}). C_{V} will be represented by $K\ C_{\text{IV}}{}^{1/n}$, where K denotes the apparent equilibrium constant in the chemisorption step (IV→V) and where n denotes a constant; $n=1$ in a chemisorption of the Langmuir type and $n>1$ in a chemisorption of the Freundlich type.[6] From the fact that each reaction rate (r_i) is proportional to $C_0^{0.5}$, within the low conversion range (Fig. 1), n can be estimated to be 2.0. This suggests a Freundlich-type adsorption and seems consistent with the concept of "surface heterogeneity,"[6] because a solid surface is considered heterogeneous in having sites of various acid strengths, or the surface, at least, behaves as a heterogeneous one the overall acid-strength, h_0, of which varies with the coverage of the sites. On the other hand, the fact that each pre-exponential factor (A_i) is proportional to $(h_{0,\max})^{0.5}$ suggests that K is proportional to $(h_{0,\max})^{0.5}$.

The apparent activation energy of overall reactions is the difference between the activation energy in Step V→VI and the apparent heat of the chemisorption. The equivalent activation energy over solids of various $h_{0,\max}$ values suggests that the variation in the heats of chemisorption on different solid surfaces is negligibly small. Considering that the variation depends entirely on the variation in the energy of interaction between a protonated double bond and a conjugated anion ($A_s{}^-$), the interaction must be weak enough to result in a nearly constant heat of chemisorption.

The $K \propto (h_{0,\max})^{0.5}$ relation explains the efficiency or the nature of the h_0 function on a solid surface. An h_0 is considered to be a parameter which indicates the overall ability of proton donation on the surface and its neighbor, supplied by various acid sites. Limonene (IV) will enter the vicinity of acid sites with the strength of h_0 and will be protonated at a double bond. The facility of the proton addititon will depend on h_0. The protonated IV will be immediately adsorbed to the anion ($A_s{}^-$), which itself came from an acid site upon the release of the proton. The adsorbed state, V, will be kept by an electrostatic interaction; the energy of the interaction seems neither to vary very much with the strength of the original acid site nor to be affected directly by h_0.

It must be noted that the catalytic mechanism in this study is quite different from that of the homogeneous catalyst system.[1]

Selectivity. According to the above scheme, the selectivities are represented:

$$A_1/A_2 = zK_\alpha/((1-z)k_\beta)$$

$$A_3/(A_1+A_2) = k_{\text{III}}/(C_{\text{VII}}[zK_\alpha+(1-z)k_\beta])$$

where z represents a fraction of C_8-position ion in C_{VI}; k_α, k_β, and k_{III} denote the rate constants in Step VI→I, VI→II, and VI→III respectively, of the above scheme; C_{VII} denotes the concentration of the AcOH adsorbed on the surface, $(\text{AcOH})_s$.

The selectivity (A_1/A_2) will be determined by steric effects. The chemisorption (IV→V) at the double bond in the isopropenyl group is sterically more favored; $z>(1-z)$. On the contrary, in an adsorbed state, the carbonium ion at the β-position (C_1) might be less hindered from an attack of AcOH. Consequently, such a steric effect will settle the selectivity in a narrow range, compared with the case of the homogeneous system, where the α-position (C_8) is entirely predominant.[1]

The selectivity of III ($A_3/(A_1+A_2)$) will be due to the C_{VII} on the surface. The low selectivity of III over Si-Al-L may be interpreted in terms of the fact that a large number of acid sites are consumed, resulting in a large C_{VII} on the surface; the consumed acidity may be 0.169 meq/g, while it is 0.1 meq/g, at most, on the other solids. It must also be noted that, in a solid system, the formation of the isomeric *p*-menthadienes (III) can be suppressed by the selection and design of the catalyst, and that the effects of the steric factors and the catalyst acidity on the selectivity in a heterogeneous system are different from those in a homogeneous system.

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