The Additions of Acetic Acid to Limonene Catalyzed by Sulfuric Acid

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The additions of acetic acid (AcOH) to limonene (IV) catalyzed by H_2SO_4 ($(0.367—8.39)\times10^{-2}$ mol/l), without a solvent, were studied. The mole ratio of IV to AcOH was less than 1: 19, and the reaction temperature was 28.5—92.5 °C. The products were α- and β-terpinyl acetates (I and II), and a mixture of *p*-menthadienes (III) as isomers of IV. The selectivity for I and II against III was not affected by the amount of H_2SO_4. The rate constants for I, II, and III were proportional to the amount of H_2SO_4. The apparent activation energy was 10.9 kcal/mol for I and II, and 13.7 kcal/mol for III. Both the proton concentration and the acidity function (h_0) in the reaction medium were regarded as proportional to the H_2SO_4 concentration. It was concluded that the formations of I and II were related to the A-2-type solvolytic mechanism, while that of III was related to the A-1-type specific hydrogen-ion mechanism.

An acid-catalyzed addition of AcOH to an olefin is a convenient method for introducing a hydroxy group into the olefin. However, there have been only a few papers about this reaction.[1] In order to form α-terpinyl acetate (I), some investigators have studied the additions of AcOH or chlorinated acetic acids to limonene (IV) or pinene in the liquid phase, with homogeneous and heterogeneous proton-acid catalysts.[2] Their efforts were concentrated mainly on identifying the products and on improving the yield of I, because the olefinic terpenes are liable to shift double bonds and to resinify in the presence of a strong acid catalyst. So far as the AcOH addition to a terpene is concerned, though, there has been no systematic study of the reaction kinetics and the catalytic mechanism.

We obtained some kinetic data on the additions of AcOH to IV, and the simultaneous isomerizations of IV, under various concentrations of H_2SO_4. The effects of the acid property in the system on catalytic activities and selectivities were discussed. The kinetic study was simplified by using a large excess of AcOH over the stoichiometric requirement, without a solvent; these species are miscible homogeneously within the limited concentration used in this study.

Experimental

Materials. Limonene (IV), a fraction of orange terpenes, was purified by fractional distillation. The fraction used as the starting material consists of IV of 96.7 wt% and two unknown impurities (one: 2.5 wt% and the other: 0.5 wt%), as determined by gas chromatographic (glc) analysis. The AcOH and 98 wt% H_2SO_4 were of a guaranteed reagent grade and were used without further purification.

Procedure. 24.3 g of AcOH and the desired amount of H_2SO_4 were weighed into a 100-ml Erlenmeyer flask equipped with a condenser. An appropriate amount of naphthalene (of a guaranteed reagent grade) was added as an internal standard substance for the glc analysis prior to each reaction run. Then IV was weighed into the flask, and the mixture was promptly stirred with a magnetic stirrer in a water bath with a thermostat. At any reaction time, 2—3 ml of the reaction mixture was sampled, diluted with 70 ml of water saturated with NaCl to stop the reaction, and extracted with hexane. The extract was washed with NaCl-saturated water and, after concentration, used for the glc analysis. Sampling was repeated at arbitrary time intervals. 0.069—0.944 mol/l of IV, 3.67×10^{-3}—8.39×10^{-2} mol/l of H_2SO_4, and 17.5 mol/l (an amount corresponding to a large excess over the stoichiometric requirement) of AcOH were used. The reference volume of the reaction mixture used to express concentrations of species in it was taken at 28 °C.

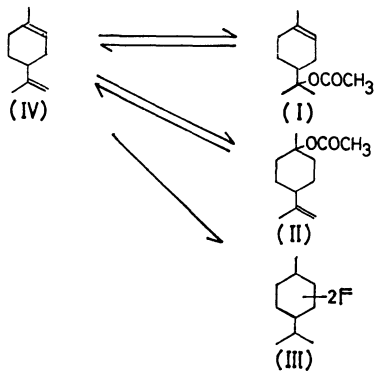
Analysis of the Products. Quantitative analysis was done by means of an internal-standard method, using a Shimadzu GC-3AH apparatus on a 3 m×3 mmφ column packed with 10 wt% of polyethylene glycol on Diasolin. At a column temperature of 172 °C, the IV, I, and II peaks all appeared in the chromatogram. Under those column conditions, the mixture of all the *p*-menthadienes except IV showed one peak. The difference between the initial content of IV and the sum of the contents of I, II, III, and IV in the reaction mixture was regarded as the resin content.

Identification of the Products. Gas chromatography-mass spectroscopy (Hitachi RMU-6MG) was used for the identifications. The addition products of AcOH to IV were identified as I and II. III was estimated to be a mixture of 1,3-*p*-menthadiene, 1,4-*p*-menthadiene, and 2,8-*p*-menthadiene.

Results

Conversion-Time Curves. Figure 1 shows that the conversions of I and II decrease after each maximum. On the contrary, the formation of isomers (III) shows no maximum in the curve. This suggests that the acetates (I and II) are formed reversibly or as intermediates to cause the irreversible formation of III by the elimination of AcOH. Consequently, the following scheme can be postulated.

In the reaction with 3.68×10^{-3} mol/l of H_2SO_4, 0.54 mol/l of IV, and 15.0 mol/l of AcOH, the maximum con-



Scheme 1.

versions were from 0.198 to 0.08 for I and from 0.05 to 0.02 for II at 35—92 °C.

Order of Reaction. The formation rates of I, II, and III were defined as $dC_i/d\theta$, where θ denotes the reaction time (hr) and where C denotes the concentration of a product, i; i=1, 2, and 3 indicates I, II, and III. Each rate at $\theta=0$ was plotted against the initial concentration of IV (C_0) in Fig. 2. The initial rate for each product is proportional to C_0 when C_0 is less than 0.66 mol/l. Consequently, the rates will be first-order with respect to the concentration of IV; $dC_i/d\theta=k_iC$. C denotes the concentration of IV, and k_i denotes a rate constant. The effect of the concentration of AcOH on the rates was regarded as constant, because the initial mole ratio of AcOH to IV was 28: 1 to 19: 1. The conversion-time curve for each product could be approximated to a straight line when the total conversion of IV was less than 10 mol%.

Effect of H_2SO_4. In Fig. 3, the log k_i values are plotted against log C', where C' is defined by the amount of H_2SO_4 used as a catalyst and not by the amount of the "H_2SO_4 molecule" in the reaction medium. From the linear correlation with a slope of 1.0 in Fig. 3, every k_i is proportional to C'.

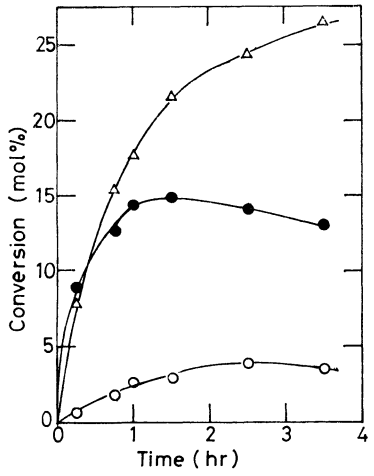


Fig. 1. Conversion-time curves of IV for I (●), II (○), and III (△) with H_2SO_4 3.68×10^{-3} mol/l and limonene 0.540 mol/l at 55 °C.

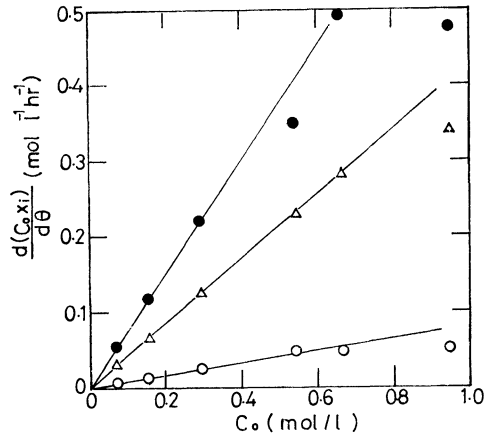


Fig. 2. Correlation between initial rate and initial concentration of limonene with H_2SO_4 2.27×10^{-2} mol/l and AcOH 15.0 mol/l at 35 °C. ●, I; ○, II; △, III.

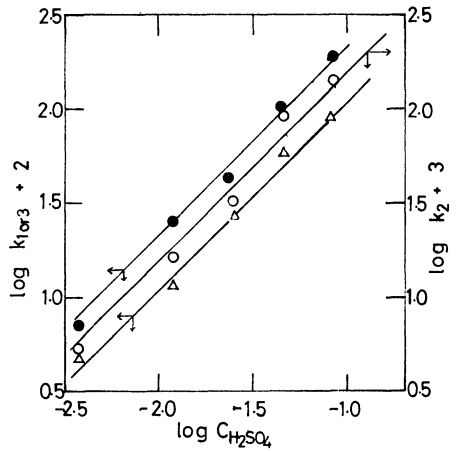


Fig. 3. Correlation between log $C_{H_2SO_4}$ and log k_i with limonene 0.606 mol/l and AcOH 15.0 mol/l at 28 °C. ●, I; ○, II; △, III.

TABLE 1. KINETIC DATA

Products	E_i (kcal/mol)	A_i[a] (hr^{-1})
α-terpinyl acetate	10.9	8.90×10^6
β-terpinyl acetate	10.9	6.91×10^5
isomers of limonene	13.7	5.24×10^8

a) The values are at $C'=3.68\times10^{-3}$ mol/l and AcOH: 15.01 mol/l.

Apparent Activation Energies and Pre-exponential Factors. The apparent activation energies (E_i) and the pre-exponential factors (A_i) shown in Table 1 were determined from the Arrhenius plots in Fig. 4. Here, the E_i values for I and II are the same, while the E_3 value for the III isomers is higher than they. This suggests that the mechanism of the formation of III may be different from that of the acetates (I and II), which have the same mechanism and rate-determining step.

The selectivity to form I against II depends entirely on the A_i's; $A_1/A_2\approx13$ from Table 1. This may be interpreted by considering the relative reactivity of the double bonds in the isopropenyl group and in the hexene

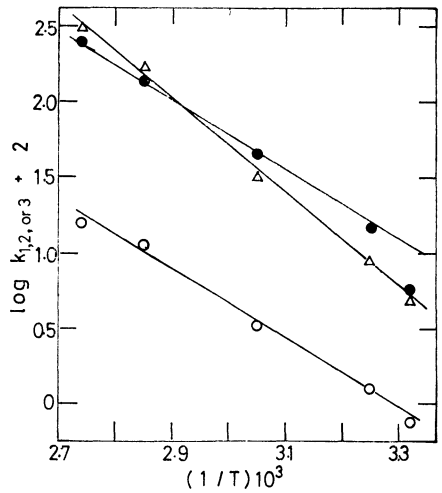


Fig. 4. Arrhenius plots for I (●), II (○), and III (△) with H_2SO_4 3.68×10^{-3} mol/l, limonene 0.540 mol/l and AcOH 15.0 mol/l.

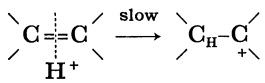
ring of IV. On the other hand, the $A_3/(A_1+A_2)\approx 55$ ratio may be interpreted in terms of the difference between the mechanisms.

Discussion

Isomerization of IV. Bates *et al.* and many other investigators have interpreted the acid-catalyzed isomerizations of *p*-menthadienes in terms of a carbonium-ion mechanism.[4] The isomerization of IV to form III, namely, 1,3-*p*-menthadiene, 2,8-*p*-menthadiene, and 1,4-*p*-menthadiene, will be interpreted to proceed *via* carbonium ions in a similar scheme.

Carbonium ions are also formed by the elimination of the AcO^- anion from the acetates (I and II), as well as by the protonation of IV, which sometimes become isomerized products (III) or resin. The elimination of the AcO^- anion is supported by the decrease in the concentration of I and II after the maxima are reached.

In the isomerization of IV, the rate-determining step is the step of forming carbonium ions from a protonated double bond:[4,5]

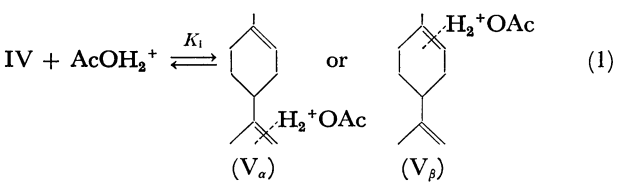


where H_2SO_4 acts as a specific hydrogen-ion catalyst. Therefore, the isomerization rate (also k_3) is proportional[5] to the acidity function, h_0[9], of the medium rather than to $C_{AcOH_2^+}$.

The acidity function, h_0, of H_2SO_4 in a water–AcOH solution has been related to C' by George *et al.*[6] The following relation was obtained from their data, where C' is less than 2.52 mol/l and where the water content is less than 0.99 wt%:[6] $h_0=(C')^{1.1}$. Here, h_0 indicates the ability of proton donation of an acid medium to weak, uncharged, indicator bases. This relation is applicable to estimating the h_0 in the present medium by assuming that h_0, the ability of proton donation to IV, is equal to, or at least proportional to, the h_0 to the indicator bases. Moreover, (1) the effect of IV and naphthalene on h_0 can be neglected, because their concentrations were less than 1 mol/l; (2) the trace of water contained with H_2SO_4 (98 wt%) and the other substances will make an amount not more than 1 wt% in the medium, and (3) C' is $(3.67—8.4)\times 10^{-2}$ mol/l. Consequently, the present h_0 value is nearly proportional to C', and the proportionality of k_3 to C' is observed.

Mechanism of the Acetates Formation. The addition of AcOH will proceed *via* $AcOH_2^+$ in the presence of a strong acid.[8] According to the facts that the formation rates of I and II are proportional to C' and have the same E_i, we propose the following mechanism, like the A-2-type solvolytic reaction defined by Hammett *et al*;[7]

$$HA + AcOH \rightleftharpoons (AcOH_2^+\ A^-) \rightleftharpoons AcOH_2^+ + A^-$$



(1)

$$\left.\begin{aligned} V_\alpha &\rightleftharpoons X_\alpha^* \longrightarrow I \\ V_\beta &\rightleftharpoons X_\beta^* \longrightarrow II \end{aligned}\right\} \text{rate-determining step} \qquad (2)$$

where HA denotes H_2SO_4. This mechanism corresponds to one of the hypothetical mechanisms derived by Corriu *et al.* for the addition of AcOH to cyclohexene.[1] They also supposed the slow formation of a carbonium ion by the elimination of AcOH from a coordination product like V_α and V_β, and the subsequent, rapid addition of AcOH to the carbonium ion; the rate-determining step is the same as the isomerization. The present case cannot be explained by this mechanism, which suggests that $E_1=E_2=E_3$.

The observed activation energies, E_1 and E_2, correspond, respectively, to the sum of the heat of the reaction in Step (1) and the activation energy in the rate-determining step (2). Because E_1 and E_2 are the same in value, the structural changes to the activated complexes, X_α^* and X_β^*, from IV and $AcOH_2^+$ are considered to affect the change of the potential energies in almost the same way. The difference between A_1 and A_2 depends entirely on the difference between the overall changes in entropy from IV and $AcOH_2^+$ to the activated complexes.

In the above scheme, the formation rates of I and II are proportional to the concentration of the solvated proton ($AcOH_2^+$). In such a solvolytic acid-catalyzed reaction of the A-2 types, $C_{AcOH_2^+}$ can be a better measure of the acidity than the acidity function.[9] In fact, the effect of C' on rates other than *via* $C_{AcOH_2^+}$ is not significant considering the small dielectric constant and ionic strength in the AcOH medium,[8] and assuming an analogy between the activated complex (X^*) and $AcOH_2^+$ with respect to the charged part.[7] Consequently, it can be deduced that $C_{AcOH_2^+}$ is proportional to C' in the present medium.

Aspects of the Selectivity of the Acetates. From the above discussion, it must be noted that the similar proportionality shown in Fig. 3 for the AcOH addition and the isomerization is effected *via* two different mechanisms: k_1 and $k_2\propto C_{AcOH_2^+}\approx\gamma C'$, and $k_3\propto h_0\approx\delta C'$. ($\gamma$ and δ are defined as constants in the present medium.) This conclusion suggests that it is impossible to improve the selectivity of the acetates (I and II) against the isomers (III) by changing C', for an increase in C' beyond the present concentration will cause a remarkable increase in δ, while γ probably decreases or, at most, remains constant with an increase in C', as a result of the low dielectric constant of AcOH.[7,8] In fact, we obtained plenty of resin from IV by using the higher C' value than in the present study.

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