Kinetic Studies in the Selective Formation of Thymol from *m*-Cresol and Propylene in the Liquid Phase over "$FeSO_4$-Al_2O_3" Catalysts

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The kinetics in a liquid-phase isopropylation of *m*-cresol (I) with 9—25 kg/cm^2 of propylene (VI) was studied at 240—280 °C over catalysts prepared from $FeSO_4$ and γ-Al_2O_3. The rates of the formation of thymol (II) and 4-isopropyl-5-methylphenol (III) and the subsequent isopropylations of II and III were fitted to an irreversible, firstorder rate equation with respect to each starting material. All of the rate constants were roughly proportional to the 1.5th power of the surface acidity of $1 \leq H_0 \leq 3$ of catalysts and the 2.2nd power of the pressure of VI. The apparent activation energies were 22 kcal/mol for Steps I→II, II→2,4-diisopropyl-5-methylphenol (V), and III→V and 6.5 kcal/mol for Steps I→III and II→2,6-diisopropyl-5-methylphenol (IV).

For several years,$^{1)}$ we have been studying the development of solid catalysts for the isopropylation of *m*-cresol (I) with propylene (VI) in the liquid phase, trying to prepare thymol (II), which is an important starting material for menthol. γ-$Al_2O_3$$^{2,3)}$ and some metal sulfates$^{1,3)}$ impregnated on γ-Al_2O_3 have been reported as catalysts of a high selectivity for thymol formation in the vapor$^{3)}$ and liquid phases.$^{1,2)}$ However, the isopropylations over these catalysts are accompanied by multiple reaction steps; the Reaction Scheme below shows an example. So far as the isopropylation of I is concerned, there has been no systematic study of the reaction kinetics. In order to design a reactor, it is necessary to describe quantitatively the distribution of products under various reaction conditions.

"$FeSO_4$–Al_2O_3"$^{1a)}$ is an excellent catalyst which has a selectivity as high as γ-Al_2O_3 and a catalytic activity 100 times as high as γ-Al_2O_3. In this paper, the rates of the formation of II and the by-products over "$FeSO_4$–Al_2O_3" catalysts will be determined, and then the apparent rate constants will be correlated to the surface acidity of the catalysts and the reaction conditions.

Experimental

Catalysts. A 47.3-g portion of $FeSO_4 \cdot 7H_2O$ of a guaranteed reagent grade was dissolved in 150 ml of distilled water at 40—60 °C, and then a 75-g portion of γ-Al_2O_3 (Nikki Chemicals Co., Ltd.) of 100—200 mesh was stirred into the solution. After standing for 15—16 h, the solid was filtered and washed 3 times with 200 ml of distilled water. The resultant solid was dried on a water bath, calcined in a stream of dry air or dry nitrogen at 500 or 450 °C, and used as a catalyst. No particular caution was taken to exclude traces of moisture. The BET surface area of the γ-Al_2O_3 was 205 m^2/g. In a series of preparetive runs, the resultant catalysts varied in their impregnated amounts of $FeSO_4$; these amounts were 8.7 wt% (Catalyst No. 2), 4.3 wt% (No. 3), 5.0 wt% (No. 4), 5.9 wt% (No. 5), 4.3 wt% (No. 9), 4.1 wt% (No. 10).

Surface Acidity of Catalysts. The acid-base strength distribution of catalysts were measured by a titration method.$^{4)}$

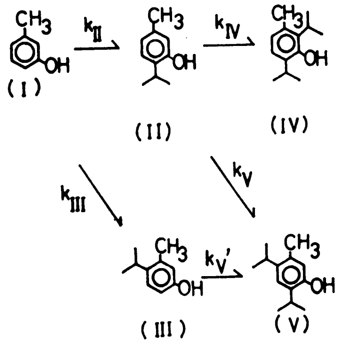
Isopropylation and the Analysis of the Products. Desired amounts of I (of guaranteed reagent grade) and of a catalyst were weighed into a reactor, which consisted of an autoclave with a capacity of 100 ml equipped with a magnetic stirrer and with gas inlet-outlet pipes. The pressure of VI (P) was kept constant at 9—25 kg/cm^2 by the incremental addition of VI. The reaction temperature was 240—280 °C and was kept constant within ±2 °C. The amount of catalyst (W) was 2.5—25 wt% of the initial amount of I. After an appropriate reaction period, the reactor was cooled rapidly in a cold-water stream, and the unreacted VI was released. The reaction mixture was dissolved with ether, washed with water, dried over Na_2SO_4, and concentrated.

The reaction mixture was analyzed by gas chromatography, using a Kotaki Model GU-21A on a 2 m×5 mm ϕ column packed with 20 wt% of silicone oil (D. C. 200) on Celite-545 (60—80 mesh), at 165 °C and with 1.2 kg/cm^2 of He as the carrier. Isopropyl benzoate was used as the internal standard. Some of the reaction mixture was fractionated into components by modified fractional gas chromatography, and each of the fractions was identified by IR absorption spectroscopy in a Nujol mull.

Isopropylations of II or III were carried out in the same way as above.

Results and Discussion

Rate Equations. The isopropylation of I was assumed to proceed *via* the following scheme. Ethers of I and of the products were also formed, but the contents of isopropyl *m*-tolyl ether and of the total ethers in the reaction mixture were not more than 0.04 and 0.1 in mole fraction respectively. Therefore, their formation was excluded from the scheme. Figure 1 illustrates the composition-time plots of a reaction mixture. At 240—280 °C, the I content in the reaction mixture decreased monotonously with the time.



The overall reaction was well expressed by a set of irreversible rate equations:

$$dC_I/d\theta = -kC_I = -(k_{II} + k_{III})\,C_I \qquad (1)$$

$$dC_{II}/d\theta = k_{II}C_I - (k_{IV} + k_V)\,C_{II} \qquad (2)$$

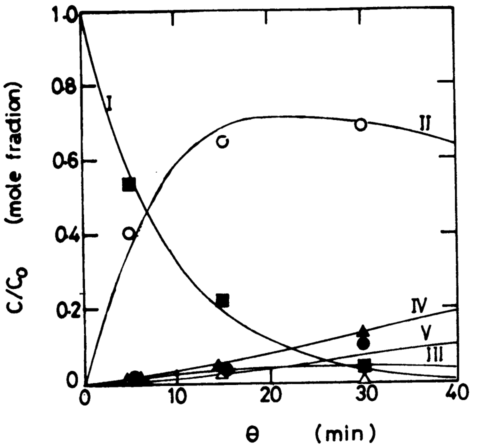


Fig. 1. Change in the composition of a reaction mixture with the reaction time at 260 °C, with 15 kg/cm^2 of propylene. *W* of the catalyst (No. 3) was 15 wt%. ○, II; △, III; ▲, IV; ●, V; □, I; ——, calculated value.

$$dC_{III}/d\theta = k_{III}C_I - k_V' C_{III} \tag{3}$$

$$dC_{IV}/d\theta = k_{IV} C_{II} \tag{4}$$

$$dC_V/d\theta = k_V C_{II} + k_V' C_{III} \tag{5}$$

where θ, C, and k represent the time, the concentration of the species defined by the suffix, and the apparent rate constant shown in the Reaction Scheme.

In each experimental run of the isopropylation using I, II, or III as the starting material, a linear correlation was found between $\{-\log(1-\text{conversion})\}$ and θ.

Rate Constants. The apparent rate constants were determined as follows. 1) k_{II} and k_{III} were determined from the slopes of the curves of C_{II}/C_0 and C_{III}/C_0 against θ, at $\theta=0$; C_0 denotes C_I at $\theta=0$. 2) Replacing the left-hand sides of Eqs. 2—5 with the slopes of the concentration-time curves of II, III, IV, and V at any time, θ, and applying the corresponding concentrations, the rate constants were obtained. Their values are presented in Figs. 2 and 4.

Most of the compositions of the reaction mixtures which were calculated by integrating Eqs. 1 to 5 and by applying the rate constants at any time, θ, agreed within a deviation of less than 0.05 in mole fraction with the observed values over a full range of isopropylations, where the total conversion of I was from 0.17 to 0.95 in mole fraction. The composition-time curves in Fig. 1 are the calculated ones.

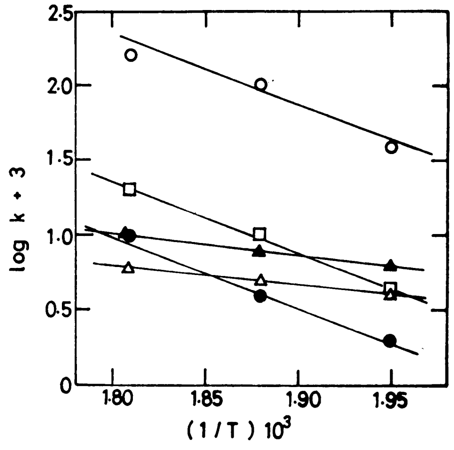


Fig. 2. Arrhenius plots of k_{II} (○), k_{III} (△), k_{IV} (▲), k_V (●), and k'_V (□). *W* of the catalyst (No. 3) was 15 wt% and propylene of 15 kg/cm^2 was used.

Each k value was proportional to the amount of catalyst (W).

From the Arrhenius plots of the rate constants in Fig. 2, the apparent activation energies in each step were determined to be 22 kcal/mol for Steps I→II, II→V, and III→V and 6.5 kcal/mol for Steps I→III and II→IV. Probably, the rate-determining step was different between these two groups of reactions. From Fig. 2, the apparent pre-exponential factors are in the order of I→II>III→V>II→V>II→IV>I→III.

Effect of the Pressure of Propylene. All of the rate constants were apparently proportional to the 2.2nd power of the pressure of VI (P).

Effect of the Surface Acidity. The acid-strength distributions of the catalysts used in this study are shown

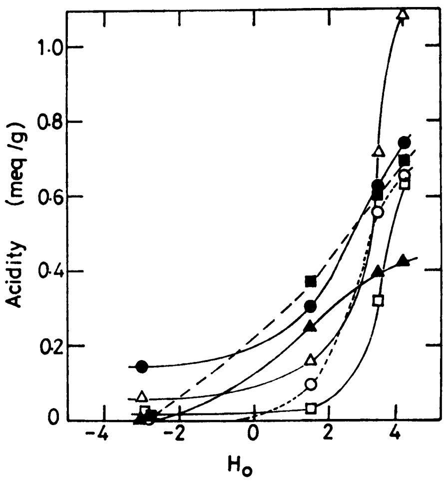


Fig. 3. Acid strength distributions of catalysts, No. 2 (▲), No. 3 (△), No. 4 (■), No. 5 (○), No. 9 (●), and No. 10 (□).

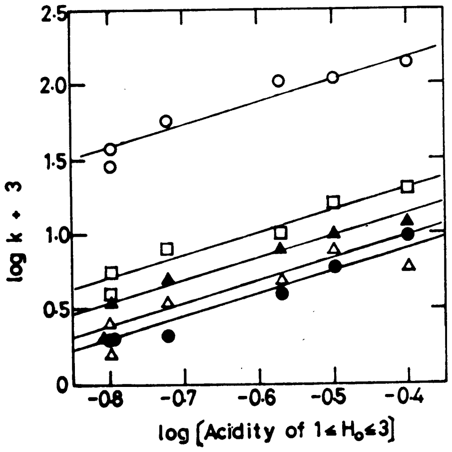


Fig. 4. Effect of the surface acidity of $1 \leq H_0 \leq 3$, α, of catalysts on k_{II} (○), k_{III} (△), k_{IV} (▲), k_V (●), and k'_V (□), at 260 °C, with 15 kg/cm^2 of propylene. *W* was 15 wt%.

in Fig. 3. The acidity at any H_0 value shows the amount of acidic sites whose acid strength is equal to or less than the H_0 value. Over most of the catalyst surfaces, the amount of acidic sites was at a maximum at $H_0=$ 1—4.

The rate constants were not correlated with the total amount of acidic sites of $H_0 \leq 4$, or with the amount of acidic sites of any H_0 range other than $1 \leq H_0 \leq 3$. As is shown in Fig. 4, the rate constant in each step is similarly roughly proportional to the 1.5th power of the acidity of $1 \leq H_0 \leq 3$. It should be noticed that the efficient acidic sites seem not to be of $H_0 < 1$ but to be of $1 \leq H_0 \leq 3$, this will be interpreted in the following section.

Catalytic Actions. The isopropylation of I with VI has been reported to be catalyzed by solid acid catalysts *via* the formation of an isopropyl cation (HP^+).[3,5] The acidic sites of $1 \leq H_0 \leq 3$ will be Brönsted acidic sites and will protonate propylene. On the other hand, phenols were regarded as being adsorbed on the basic site of catalysts with the OH group.[3,6,7] On γ-Al_2O_3 used as the carrier, basic sites whose conjugate acids had H_0 values of less than 7 were observed.[4] These basic sites are probably exposed on the present catalysts' surface.[1a] The π-electron densities at C_2- and C_4-positions of the adsorbed *m*-cresol are greater than those of *m*-cresol in the liquid phase.[8] Hence, the isopropylation of I must take place between the adsorbed *m*-cresol and HP^+:

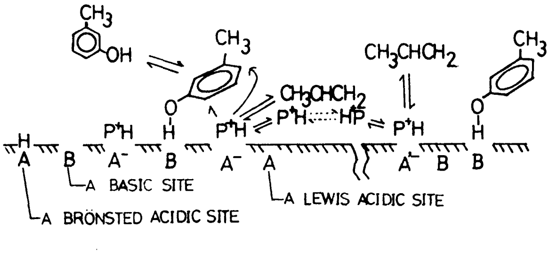
$$\mathrm{HA} + \mathrm{VI} \longrightarrow [\mathrm{HP}^+ \cdots\cdots \mathrm{A}^-]\ (\mathrm{VII}) \tag{6}$$

$$\mathrm{B} + \mathrm{I} \overset{K_\mathrm{I}}{\rightleftharpoons} [\mathrm{I} \cdots\cdots \mathrm{B}]\ (\mathrm{VIII}) \tag{7}$$

$$\mathrm{VII} + \mathrm{VIII} \xrightarrow{k'_\mathrm{II}} \mathrm{II} + \mathrm{HA} + \mathrm{B} \tag{8}$$

$$\mathrm{VII} + \mathrm{VIII} \xrightarrow{k'_\mathrm{III}} \mathrm{III} + \mathrm{HA} + \mathrm{B} \tag{9}$$

where HA and B denote an acidic site of $1 \leq H_0 \leq 3$ and a basic site which are adjacent to each other. A^-, K, and k' denote the conjugate base of HA, an equilibrium constant, and a rate constant in the corresponding step respectively. A^- will facilitate the isopropylation by accepting a proton from the C_2- or C_4-position subsequently to the attack of HP^+.



Because the C_4-position of VII is more remote from the surface than C_2,[3,5] the migration of HP^+ to C_4 from the surface is less frequent than the direct attack of HP^+ on C_2. This is supported by the difference between the apparent pre-exponential factors of k_II and k_III. The diffusion of HP^+ has a lower activation energy than the surface reaction between HP^+ and the C_2-position of VIII. This is supported by the difference between the apparent activation energies in Steps I→II and I→III, which shows that the energy barrier in Step (9) is *ca.* 16 kcal/mol lower than that in Step (8).

Provided that the structures of the surface in the vicinity of B are almost the same, the amount of B will be proportional to the amount of HA.

The reason why acidic sites of $H_0 < 1$ seemed to have no effect on the rate constants is either that they were Brönsted acidic sites which were not adjacent to B or that they were Lewis acidic sites. These Brönsted acidic sites protonate propylene as well as those of $1 \leq H_0 \leq 3$. If HP^+ migrates rapidly and freely enough over the surface, HP^+, which are formed at the Brönsted acidic sites of $H_0 \leq 3$, contribute to the activity of HP^+ as a whole. On the other hand, if HP^+ does not migrate, only the HA in the vicinity of B contributes to the activity of HP^+, which affects the rate constants. Therefore, the activity of HP^+ will be independent of the amount of HA over all the surface. In this case, the rate constants will be proportional to the amount of HA, which represents the amount of the reaction loci where the isopropylation is catalyzed by a set of HA and B. The dependency of the rate constants on the acidity of $1 \leq H_0 \leq 3$ by the 1.5th power suggests a restricted mobility of HP^+. For clarifying the behavior of HP^+ consistently with the behavior of propylene in gas- and liquid-phase, however, further investigations will be required interpreting the 2.2nd-power dependency of k on the P value.

Because the acid strengths of I, II, and III are estimated to be nearly equal,[9] the differences among their heats of adsorption will not be substantial. As Steps II→V and III→V had apparent activation energies equal to that of Step I→II, those steps must proceed *via* an activated state similar to that of VIII at the C_4-position of II and the C_2-position of III. The observed differences of the pre-exponential factors from that of Step I→II suggest a disadvantage in the steric factors of Steps II→V and III→V, *e.g.*, a disadvantageous entropy change in the adsorption of II because of the *ortho*-isopropyl group.

Between the competitive steps, II→V and II→IV, the relatively low activation energy and pre-exponential factor in Step II→IV indicate that the C_6-position of II is sterically unfavored, like the C_4-position of I.

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