

## The Esterification of Carboxylic Acid with Alcohol over Hydrus Zirconium Oxide

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The esterification of carboxylic acids with alcohols proceeded efficiently with hydrus zirconium oxide to give the corresponding esters in the vapor phase, in the liquid phase, and in an autoclave. The steric hindrance of carboxylic acids and alcohols affected the esterification by lowering the reactivity. With a rise in the reaction temperature, the conversion of the carboxylic acid increased. The dehydration of alcohols was prevented by using hydrus zirconium oxide in spite of the high reaction temperature. The reaction rate is first-order with respect to the concentration of the catalyst and an alcohol and is inversely proportional to that of the carboxylic acid. Transesterification also proceeded efficiently.

In our previous papers,<sup>1–5</sup> we reported that hydrus zirconium oxide has the catalytic activity for the reduction of aldehydes and ketones with 2-propanol and the amidation of carboxylic acid with amine. Since the hydrus zirconium oxide was expected to have affinities for both carboxylic acids and alcohols, the esterification of carboxylic acids with alcohols was carried out by the catalysis of the oxide.

In the esterification of carboxylic acids with alcohols, homogeneous catalysts, such as sulfuric acid and hydrochloric acid, are usually used. These methods, however, need tedious work-up procedures in the isolation of the products. Recently, heterogeneous catalysts, such as Nafion-H,<sup>6</sup> the zirconium oxide-sulfate ion,<sup>7</sup> the titanium oxide-sulfate ion,<sup>8</sup> heteropoly acids supported on carbon,<sup>9</sup> silica-alumina, zeolite HY,<sup>10</sup> cation-exchange resin, and niobic acid,<sup>11</sup> have been reported to be effective catalysts for the esterification. These are all solid acid or solid superacid catalysts, however, there is a fear of unfavorable side reactions such as dehydration because of the strong acidity of the catalyst. As heterogeneous catalysts for the esterification, titanium alkoxide and zirconium alkoxide supported on silica, alumina, or silica-alumina have also been reported.<sup>12</sup> The preparation of these catalysts is, however, troublesome.

The hydrus zirconium oxide consists of hard and translucent granules. According to the X-ray diffraction analysis, the oxide was shown to be amorphous. Esterification over hydrus zirconium oxide has the following advantages: 1) the hydrus zirconium oxide is easily prepared by the neutralization of an aqueous zirconium dichloride oxide solution; 2) the products can easily be isolated by filtering-off the catalyst and subsequently evaporating the solvent, because the catalyst is insoluble in any solvent; 3) the oxide is stable at room temperature in air, and 4) the oxide is not sensitive to air or water, and the esterification does not require water-free conditions.

In this paper, we wish to report that the hydrus zirconium oxide catalyzes the esterification of carboxylic acid with alcohol efficiently and that it also catalyzes

the transesterification. These reactions were carried out in the vapor phase, in the liquid phase, and in an autoclave. The hydrus zirconium oxide does not have a strong acid strength on the surface, and such undesirable side reactions as dehydration can be avoided, unlike as in the cases of acid catalysts. The mechanism of esterification over hydrus zirconium oxide was also studied in vapor-phase reactions.

### Experimental

**Materials.** Commercial reagents were used for the reaction without any further purification.

**Hydrus Zirconium Oxide.** To a solution of zirconium dichloride oxide ( $ZrOCl_2 \cdot 8H_2O$ ) (200 g of a solid in 10 dm<sup>3</sup> of deionized water) we slowly added an aqueous solution of sodium hydroxide (1 mol dm<sup>-3</sup>) at room temperature. Constant, gentle stirring was maintained, and the addition was continued until the pH of the resulting solution reached 6.80. The resulting product was filtered and washed free from chloride ions. The gel was spread on a glass plate and dried in air at room temperature for 10 h and then at 80 °C for 2 h. Fifty-four grams of hydrus zirconium oxide were obtained in the form of granules, which were subsequently heated at 300 °C for 5 h.

**General Procedures for Vapor-Phase Reactions.** The catalytic esterification was carried out in a glass-flow reactor (6.5 mm in diameter) with a fixed-bed catalyst: flow rate of nitrogen gas=60 cm<sup>3</sup> min<sup>-1</sup>; catalyst=2.0 g, 24–60 mesh; reaction temperature=135–280 °C. A mixture of a carboxylic acid, an alcohol, and a hydrocarbon as an internal standard was fed into the reactor (5 or 10 cm<sup>3</sup> h<sup>-1</sup>) by means of a microfeeder. In some cases, benzene was also added to dilute the reaction mixture. The activity and selectivity of the reaction were determined after the steady states has been reached. The products were then analyzed by gas chromatography (a capillary column PEG 20M 30 m). The products were identified by a comparison of their retention times with those of authentic samples.

**General Procedures for Liquid-Phase Reaction.** In a 25 cm<sup>3</sup> round-bottomed flask equipped with a reflux condenser we placed the catalyst (2.0 g), a carboxylic acid, an alcohol, and a hydrocarbon as an internal standard. The contents were then heated under a gentle reflux. In some reactions, toluene was added to the solution in order to raise the reaction temperature. In some cases, the reaction

mixture was placed in an oil bath kept at  $77.0 \pm 0.1$  °C. The reaction mixture was collected after 5 hours, and the products were analyzed by means of gas chromatography.

**General Reaction Procedures in an Autoclave.** In a 100-cm<sup>3</sup> autoclave were placed the catalyst (2.0 g), a carboxylic acid, an alcohol, and a hydrocarbon as an internal standard. The autoclave was then heated to the reaction temperature (130–240 °C) and kept there for 2 h. The analysis of the products was performed in a manner similar to described above.

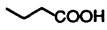
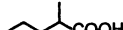
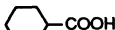




















**Surface Acidity.** The quantity of surface acidic sites was measured by the butylamine-titration method using various Hammett indicators.

## Results and Discussion

**Esterification in the Vapor Phase.** The results of vapor-phase esterification of carboxylic acids with alcohols over hydrous zirconium oxide are listed in Table 1. The esterification of carboxylic acids, except





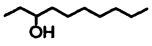


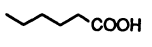
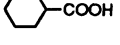
for adamantanecarboxylic acid, with primary alcohols gave the corresponding esters in high yields (Entries 1–7). In the case of the reaction with secondary alcohols, the conversion of the carboxylic acid increased in this order: tertiary < secondary < primary. These results can be explained by the steric hindrance of the carboxylic acid (Entries 9–14). The esterification with tertiary alcohol gave the ester in a low yield (Entry 16). The esterification of cyclohexanecarboxylic acid with primary alcohol gave the ester in a higher yield than that with secondary alcohol (Entries 3 and 11). As has been described above, the steric hindrance of alcohols also affected the esterification. The higher the reaction temperature, the more carboxylic acid was consumed. The selectivity for the ester, however, was lowered, and the reaction gave the alcohol as a by-product of the reduction of the carboxylic acid (Entries 4 and 5). The selectivity for the ester was 100% in the esterification with benzyl alcohol at 150 °C (Entry 8).

Table 1. Esterification in the Vapor Phase over Hydrous Zirconium Oxide<sup>a)</sup>

Entry	Reactant	Temperature/°C	Conversion/%	Selectivity/%
1		C <sub>2</sub> H <sub>5</sub> OH	200	100
2		C <sub>2</sub> H <sub>5</sub> OH	200	100
3		C <sub>2</sub> H <sub>5</sub> OH	215	100
4		C <sub>2</sub> H <sub>5</sub> OH	200	99
5		C <sub>2</sub> H <sub>5</sub> OH	250	100
6		C <sub>2</sub> H <sub>5</sub> OH	200	100
7			250	100
8 <sup>b)</sup>	CH <sub>3</sub> COOH		150	37
9			215	100
10			200	96
11			215	80
12			200	31
13 <sup>c)</sup>	CH <sub>3</sub> COOH		200	100
14 <sup>c)</sup>			200	34
15 <sup>c)</sup>			280	22
16	C <sub>2</sub> H <sub>5</sub> COOH		200	7

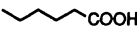



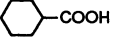

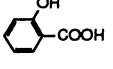



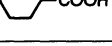

a) Catalyst: 2.0 g; carboxylic acid: 0.1 mol dm<sup>-3</sup> in alcohol; sample feed: 10 cm<sup>3</sup> h<sup>-1</sup>. b) Acetic acid: benzyl alcohol=2.5:1; sample feed: 5 cm<sup>3</sup> h<sup>-1</sup>. c) Carboxylic acid: 0.1 mol dm<sup>-3</sup>; alcohol: 0.5 mol dm<sup>-3</sup> in benzene.

Table 2. Transesterification of Ethyl Acetate in the Vapor Phase

Entry	Reactant	Temperature/°C	Conversion/%	Selectivity/%
1		200	100	100
2		200	99	99
3		200	98	98
4		190	97	96
5		200	93	99
6		200	43	100
7		200	14	—
8		200	27	84
9		200	1	95

Catalyst: 2.0 g; sample feed: 10 cm<sup>3</sup> h<sup>-1</sup>; carboxylic acid or alcohol: 0.10 mol dm<sup>-3</sup> in ethyl acetate.

Table 3. Esterification in the Liquid Phase over Hydrous Zirconium Oxide (1)<sup>a)</sup>

Entry	Reactant(mmol)		Catalyst/g	Conv./%	Select./%
1	 (2)	C <sub>2</sub> H <sub>5</sub> OH (100)	2	100	100
2 <sup>b)</sup>	CH <sub>3</sub> COOH (2)	C <sub>2</sub> H <sub>5</sub> OH (20)	2	98	100
3	C <sub>2</sub> H <sub>5</sub> COOH (25)	 (63)	2	91	100
4 <sup>c)</sup>	CH <sub>3</sub> COOH (2)	 (32)	4	100	100
5 <sup>d)</sup>	CH <sub>3</sub> COOH (1)	 (10)	1	100	100
6	 (2)	C <sub>2</sub> H <sub>5</sub> OH (100)	2	87	100
7	 (2)	C <sub>2</sub> H <sub>5</sub> OH (100)	2	50	100
8	 (2)	CH <sub>3</sub> OH (100)	2	13 <sup>e)</sup>	—
9	CH <sub>3</sub> COOH (31)	 (13)	1	65	100
10	CH <sub>3</sub> COOH (31)	 (13)	1	10	100
11 <sup>b)</sup>	CH <sub>3</sub> COOH (31)	 (13)	1	42	100
12	 (31)	 (13)	1	28	100

a) Reflux for 5 h. b) Toluene (4 cm<sup>3</sup>) was added. c) Reflux for 2 h. d) Toluene (2 cm<sup>3</sup>) was added and reflux for 1 h. e) Yield of methyl salicylate.

Since the reaction with benzyl alcohol at 150 °C over Nafion H caused undesirable polymerization,<sup>6)</sup> the hydrous zirconium oxide is superior to the superacid catalyst. Moreover, the hydrous zirconium oxide caused scarcely any dehydration of alcohols.




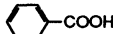


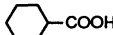
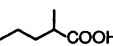
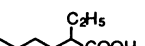

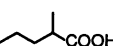



**Transesterification in the Vapor Phase.** The reactions of alcohols or carboxylic acids with ethyl acetate—that is, transesterification—were investigated by means of the catalysis of the hydrous zirconium oxide in the vapor phase. The transesterification, an useful method for the preparation of esters, needs water-free conditions; and it is used for the preparation of polyesters. The results of the reaction catalyzed by the hydrous zirconium oxide are listed in Table 2.

Generally, most of the alcohols were converted to the corresponding acetates in the transesterification with ethyl acetate; the selectivity of the reaction was very high in each case. Primary alcohols were more reactive than secondary ones, while tertiary ones were not efficiently reacted. In the case of menthol, the reactivity was lowered by its steric hindrance. The transesterification of carboxylic acids gave the esters in low yields.

**Esterification in the Liquid Phase.** The esterifications of carboxylic acids with alcohols over the

hydrous zirconium oxide were investigated in the liquid phase; the results are listed in Table 3. The reactions were carried out at the reflux temperature of the solution. Most of the carboxylic acids were converted to the corresponding esters in high yields. In the esterification with primary alcohol, the reactivities increased in this order: tertiary carboxylic acid < secondary one < primary one, the same as in the vapor-phase reactions (Entries 1–7). The yields of the ester in the reactions with primary alcohols were higher than in those with secondary alcohol. The esterification of acetic acid with menthol gave the ester in a lower yield than that with cyclohexanol (Entries 9 and 10). The yield was, however, increased by adding toluene to the reaction mixture. This suggests that raising the reaction temperature enhanced the reactivity, even in the reaction of menthol (Entry 11). In the case of the reaction of salicylic acid with methanol, the corresponding methyl ester was obtained in a 13% yield (Entry 8). The low conversion of salicylic acid was explained by its strong adsorption, since the  $pK_a$  value of salicylic acid (2.98) was lower than that of the other carboxylic acid (ca. 4.8) shown in Table 3. This suggests that the reactivity was inhibited by the adsorption of carboxylic acid. In order to clarify the

Table 4. Esterification in the Liquid Phase over Hydrous Zirconium Oxide (2)<sup>a)</sup>

Entry	Reactant		Temp./°C	Conv./%	Select./%
1		C <sub>2</sub> H <sub>5</sub> OH	77	94	100
2		C <sub>2</sub> H <sub>5</sub> OH	77	84	100
3 <sup>b)</sup>		C <sub>2</sub> H <sub>5</sub> OH	77	30	100
4		C <sub>2</sub> H <sub>5</sub> OH	77	29	100
5			77	59	100
6		C <sub>2</sub> H <sub>5</sub> OH	77	72	100
7		C <sub>2</sub> H <sub>5</sub> OH	77	46	100
8		C <sub>2</sub> H <sub>5</sub> OH	77	5	100
9		C <sub>2</sub> H <sub>5</sub> OH	77	16	100
10 <sup>b)</sup>		C <sub>2</sub> H <sub>5</sub> OH	77	35	100
11			77	15	100
12	CH <sub>3</sub> COOH		77	Trace	—

a) Catalyst: 1.0 g; carboxylic acid: 5 mmol; alcohol: 50 mmol; reaction for 5 h. b) Catalyst: 0.5 g; carboxylic acid: 2.5 mmol; alcohol: 50 mmol; reaction for 5 h.

difference in reactivity between carboxylic acids and between alcohols, the esterification was carried out at the same temperature (77 °C) in the liquid phase. The results are shown in Table 4. In the reaction of primary carboxylic acid with primary alcohol, the reactivity of the esterification was lowered according to the length of the carbon chain (Entries 1—3, and 5). In the reaction of secondary carboxylic acid with primary alcohol, the reaction of the carboxylic acid which possessed a methyl group at a  $\alpha$ -position was lower than that of cyclohexane carboxylic acid. Further, the carboxylic acid which possessed an ethyl group in the  $\alpha$ -position gave the ester in a lower yield. These results suggest that the steric hindrance of carboxylic acid affects the reaction. The esterification of tertiary carboxylic acid with primary alcohol gave the ester in a low yield because of the steric hindrance. In the case of benzoic acid, the reactivity was relatively low. This result was caused by the relatively low  $pK_a$  value (4.20) of benzoic acid, much as in the case of salicylic acid. The reactivities of alcohol increased in this order: tertiary alcohol < secondary one < primary one. The esterification in the liquid phase over hydrous zirconium oxide was affected by the steric hindrance of carboxylic acids and alcohols. Though the conversion in the liquid-phase esterification was lower than the vapor-phase reaction because of the lower reaction

temperature, the selectivity was always 100%.






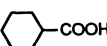
**Transesterification in the Liquid Phase.** The results of the transesterification of alcohols and carboxylic acids with ethyl acetate in the liquid phase are shown in Table 5. The tendency of the reactivities of several alcohols was similar to that in the vapor phase. The yield of the ester in the transesterification of primary alcohol was higher than that of the secondary one, and the reaction of carboxylic acid did not proceed. The selectivities of the esters were usually 100%.

**Dependence on the Molar Ratio of Carboxylic Acid to Alcohol in Liquid-Phase Esterification.** Table 6 shows the dependence on the molar ratio of acetic acid to ethyl alcohol in liquid-phase esterification. When either carboxylic acid or alcohol was used in excess, the ester was given efficiently. The reaction in even an equimolecular quantity of acetic acid and ethyl alcohol gave the ester in a 77% yield. The selectivity of the ester was always 100%.

**Esterification in an Autoclave.** It has been described that the reaction temperature affects the esterification over hydrous zirconium oxide. In order to obtain the ester in a higher yield, the esterification was carried out in an autoclave at a high temperature. The results are shown in Tables 7 and 8. The esterification in an autoclave gave the ester in a higher yield than that in a vapor-phase or liquid-phase reaction. The decarboxylation of salicylic acid and the dehydration of secondary and tertiary alcohol occurred slightly. It was learned that *t*-butyl alcohol could easily be dehydrated by using an acid catalyst at a high temperature. However, it was interesting that the esterification proceeded preferentially over hydrous zirconium oxide. The reaction of acetic acid with ethylene glycol and glycerol gave, selectively, the diacetate and triacetin respectively. Although the reaction of terephthalic acid gave both diacetate and monoacetate, the reactions of other dibasic acids and acid anhydrides gave the diesters selectively. By using an autoclave, the esterification of the polyhydric alcohol or dibasic acid over hydrous zirconium oxide proceeded effectively.

**Transesterification in an Autoclave.** Table 9 shows the results of the transesterification over hydrous zirconium oxide in an autoclave. The yields were higher than those in a vapor-phase or liquid-phase reaction. The conversion of carboxylic acid increased,

Table 5. Transesterification of Ethyl Acetate in the Liquid Phase over Hydrous Zirconium Oxide<sup>a)</sup>

Entry	Reactant	Conversion /%	Selectivity /%
1		32	100
2		44	100
3		22	100
4		12	100
5		—	0
6		—	0

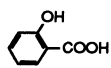
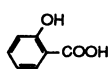
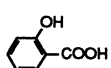
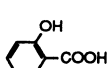





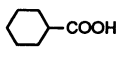



a) Catalyst: 2.0 g; carboxylic acid or alcohol: 2 mmol; ethyl acetate: 60 mmol; reaction for 5 h.

Table 6. Dependence on the Molar Ratio of Acid to Ethyl Alcohol in the Liquid Phase over Hydrous Zirconium Oxide<sup>a)</sup>

Entry	Acetic acid/mmol	Ethyl alcohol/mmol	Conversion <sup>b)</sup> /%	Selectivity /%
1	25	125	96	100
2	25	62.5	86	100
3	25	25	77	100
4	62.5	25	94 <sup>c)</sup>	100

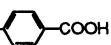


a) Catalyst: 2.0 g; reflux for 5 h. b) Based on acetic acid. c) Based on ethyl alcohol.

Table 7. Esterification in an Autoclave over Hydrous Zirconium Oxide (1)<sup>a)</sup>

Entry	Reactant (mmol)	Temp./°C	Conv./%	Select./%
1	 (10)    CH <sub>3</sub> OH (740)	180	69	99.6 <sup>c)</sup>
2	 (10)    CH <sub>3</sub> OH (740)	210	100	95 <sup>c)</sup>
3	 (10)    CH <sub>3</sub> OH (740)	240	100	91 <sup>c)</sup>
4 <sup>b)</sup>	 (30)    CH <sub>3</sub> OH (740)	210	100	91 <sup>c)</sup>
5 <sup>b)</sup>	CH <sub>3</sub> COOH (520)  (10)	210	99	99
6	CH <sub>3</sub> COOH (520)  (30)	180	98	95
7	CH <sub>3</sub> COOH (520)  (30)	210	81	70
8	CH <sub>3</sub> COOH (30)  (315)	180	25	100
9	CH <sub>3</sub> COOH (30)  (315)	210	50	100
10	 (10)  (288)	210	100	100
11	 (10)  (390)	210	54	100





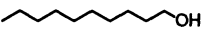

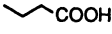

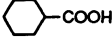
a) Catalyst: 2.0 g; reaction for 2 h. b) Reaction for 1.5 h. c) Product was methyl salicylate.

Table 8. Esterification in an Autoclave over Hydrous Zirconium Oxide (2)<sup>a)</sup>

Entry	Reactant (mmol)	Temp./°C	Conv./%	Select./%
1	CH <sub>3</sub> COOH (350)    HO-CH <sub>2</sub> -CH <sub>2</sub> -OH (10)	180	100	100
2	CH <sub>3</sub> COOH (350)    HO-CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -OH (20)	180	80	99 <sup>b)</sup>
3	CH <sub>3</sub> COOH (350)    HO-CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -OH (10)	200	96	100 <sup>b)</sup>
4	HOOC-  -COOH (10)    HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH (220)	180	86	48 <sup>c)</sup>
5	 (10)    HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH (220)	180	69	100
6	 (10)    HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH (127)	200	99	100
7	HOOC-CH <sub>2</sub> -CH <sub>2</sub> -COOH (10)    HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH (220)	180	98	100

a) Catalyst: 2.0 g; reaction for 2 h; product was diester. b) Product was triacetin. c) The other product was a monoester.

Table 9. Transesterification in an Autoclave over Hydrous Zirconium Oxide

Entry	Reactant	Temperature/°C	Conversion/%	Selectivity/%
1		150	100	66
2		130	96	98
3		150	68	68
4		130	18	100
5		150	98	100
6		160	4	62
7		180	84	85
8		200	33	100
9		200	75	100

a) Catalyst: 2.0 g; carboxylic acid or alcohol: 10 mmol; ethyl acetate: 20 cm<sup>3</sup>; reaction for 2 h.

Table 10. Acid Amounts on The Hydrous Zirconium Oxide

Acidity Amount/mol g <sup>-1</sup>	$H_0 \leq -8.2$ 0	$H_0 \leq -5.6$ $8 \times 10^{-6}$	$H_0 \leq -3.0$ $5 \times 10^{-4}$	$H_0 \leq 1.5$ $1.4 \times 10^{-3}$
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and the selectivity decreased, with the rise in the reaction temperature. The reaction with menthol gave the ester in a low yield because of its steric hindrance. Although the transesterification with carboxylic acid gave the ester in neither a vapor nor a liquid phase, it could proceed efficiently in an autoclave.

**Durability of Hydrous Zirconium Oxide in Vapor-Phase Esterification.** In order to estimate the durability of the hydrous zirconium oxide, the esterification of acetic acid with ethyl alcohol was carried out at 250 °C in the vapor phase. As a result, the catalytic activity of the hydrous zirconium oxide was kept for at least 170 h. This showed that the hydrous zirconium oxide is a durable heat-stable catalyst.

**Surface Acidity.** The findings on the surface acidity of the hydrous zirconium oxide are shown in Table 10. The acid amounts at  $H_0 \leq -8.2$  and  $H_0 \leq -5.6$  are 0 and  $8 \times 10^{-3}$  mmol · g<sup>-1</sup> respectively. This shows that the hydrous zirconium oxide does not have as strong acid sites as the other solid acid catalysts. From the point of view of avoiding such side reactions as the dehydration of alcohols, low acidity is an advantage in an esterification catalyst. The hydrous zirconium oxide has the same activity for esterification as a superacid catalyst such as Nafion H. This suggests that the hydrous zirconium oxide is different from an acid

catalyst. Most solid acids decrease in acidity upon the adsorption of water; however, it has been reported<sup>19</sup> that the niobic acid is not deactivated by the adsorption of water. Judging from the result of keeping its activity under an atmosphere of water vapor, the hydrous zirconium oxide might have a character similar to that of the niobic acid. However, the surface acidity of the hydrous zirconium oxide is lower than that of niobic acid.<sup>19</sup>

**Dependence on the Catalyst Amount in a Vapor-Phase Reaction.** For determining the order of catalyst amounts, the esterification rates of acetic acids with ethyl alcohol were measured over the range from 1.0 to 6.0 g of the catalyst. As a result, the esterification rates,  $r$ , were directly proportional to the amounts of the catalysts. Hence the rate,  $r$ , should be introduced as:

$$r = k \cdot [\text{cat.}], \quad (1)$$

where [cat.] and  $k$  are the concentration of the catalyst and the first-order rate constant respectively. Therefore, the specific rate,  $r_0$ , is:

$$r_0 = r/[\text{cat.}], \quad (2)$$

**Dependence on the Reaction Temperature in a Vapor-Phase Reaction.** In order to investigate the

dependence on the reaction temperature, the esterifications of acetic acid with ethyl alcohol were carried out under the following two kinds of conditions: 1) the concentration of acetic acid, that of ethyl alcohol, the sample feed, and the temperature range were  $2.77 \text{ mmol}\cdot\text{cm}^{-3}$ ,  $13.9 \text{ mmol}\cdot\text{cm}^{-3}$ ,  $10 \text{ cm}^3\cdot\text{h}^{-1}$ , and  $120\text{--}220^\circ\text{C}$  respectively; 2) they were  $6.66 \text{ mmol}\cdot\text{cm}^{-3}$ ,  $9.88 \text{ mmol}\cdot\text{cm}^{-3}$ ,  $5 \text{ cm}^3\cdot\text{h}^{-1}$ , and  $135\text{--}250^\circ\text{C}$  respectively. Linear relationships between the natural logarithm of the specific rate vs. the reciprocal the absolute temperature, that is, the Arrhenius plot, were obtained in both cases. From the inclination of the lines, the activation energies were estimated to be, on the average,  $12.4 \text{ kcal}\cdot\text{mol}^{-1}$ .

**Dependence on the Alcohol Concentration in a Vapor-Phase Reaction.** For determining the order of alcohol concentrations, the esterification rates of acetic acid with ethyl alcohol were measured under the following conditions: the concentration of acetic acid was constant at  $1.53 \text{ mmol}\cdot\text{cm}^{-3}$ , the concentration of ethyl alcohol was changed in the range from  $1.53$  to  $15.3 \text{ mmol}\cdot\text{cm}^{-3}$ , and benzene was added as a diluent to keep the volume of the reaction mixture constant. The correlation between the natural logarithm of the concentration of ethyl alcohol and that of the specific rate indicated that the order in alcohol concentrations was estimated to be first-order.

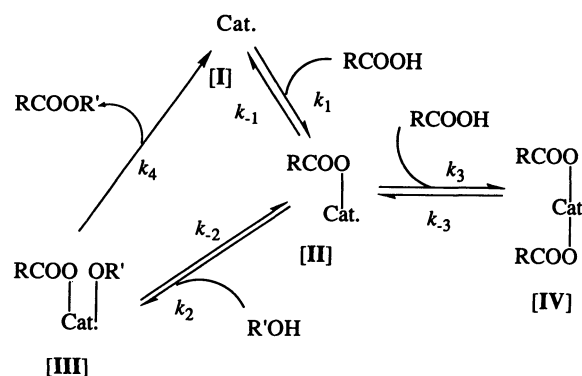
**Dependence on the Carboxylic Acid Concentration in a Vapor-Phase Reaction.** In order to investigate the dependence on the carboxylic acid concentration, the esterification of acetic acid with ethyl alcohol was carried out under the following conditions: the concentration of ethyl alcohol was constant at  $7.65 \text{ mmol}\cdot\text{cm}^{-3}$ , the concentration of acetic acid was changed in the range from  $0.918$  to  $2.55 \text{ mmol}\cdot\text{cm}^{-3}$ , and benzene was used as a diluent. The correlation between the natural logarithm of the concentration of acetic acid and that of the specific rate indicated that the reaction rate could be estimated to be of a minus first-order dependence on the concentration of acetic acid.

**Kinetic Discussion in a Vapor-Phase Reaction.** As has been described above, the reaction rate of the esterification over hydrous zirconium oxide in the vapor phase,  $r$ , is:

$$r = k' \cdot [\text{cat.}]^1 \cdot [\text{A}]^1 \cdot [\text{C}]^{-1}, \quad (3)$$

where  $k'$ ,  $[\text{cat.}]$ ,  $[\text{A}]$ , and  $[\text{C}]$  are the rate constant, the concentration of the catalyst, that of ethanol, and that of acetic acid respectively. These results suggest that the rate-determining step is the step subsequent to the adsorption of the carboxylic acid and alcohol on the catalyst.

The result of the minus first-order dependence on the concentration of acetic acid suggests that acetic acid inhibits the reaction by adsorption on the surface of the hydrous zirconium oxide. We assume that the



Scheme 1.

mechanism of the esterification of carboxylic acid with alcohol over the hydrous zirconium oxide in the vapor phase is as is shown in the Scheme 1.

Based on the proposed scheme, the following equation was obtained by the use of the stationary-state method, while the esterification rate is expressed by:

$$r = \frac{k_1 \cdot k_2 \cdot k_4 \cdot [\text{A}] \cdot [\text{C}] \cdot [\text{cat.}]}{k_{-1} \cdot k_{-2} + k_1 \cdot k_2 \cdot [\text{C}] + k_1 \cdot k_2 \cdot [\text{A}] \cdot [\text{C}] + k_{-1} \cdot k_{-2} \cdot K_3 \cdot [\text{C}]^2 + k_4 \cdot B}$$

$$= \frac{k \cdot K_1 \cdot K_2 \cdot [\text{A}] \cdot [\text{C}] \cdot [\text{cat.}]}{1 + K_1 \cdot [\text{C}] + K_1 \cdot K_2 \cdot [\text{A}] \cdot [\text{C}] + K_1 \cdot K_3 \cdot [\text{C}]^2 + k \cdot B / (k_{-1} \cdot k_{-2})}, \quad (4)$$

$$(B = k_{-1} + k_2 \cdot [\text{A}] + k_1 \cdot [\text{C}] + k_{-1} \cdot k \cdot K_3 \cdot [\text{C}]^2)$$

where  $K_1$ ,  $K_2$ , and  $k$  are  $k_1/k_{-1}$ ,  $k_2/k_{-2}$ , and  $k_4$  respectively. The kinetic results show that the last step constitutes the rate-determining step. Therefore,  $k$  is far less than  $k_n$ , and the rate equation can be rewritten as:

$$r \approx \frac{k \cdot K_1 \cdot K_2 \cdot [\text{A}] \cdot [\text{C}] \cdot [\text{cat.}]}{1 + K_1 \cdot [\text{C}] + K_1 \cdot K_2 \cdot [\text{A}] \cdot [\text{C}] + K_1 \cdot K_3 \cdot [\text{C}]^2}. \quad (5)$$

Furthermore, the inhibition of the carboxylic acid suggests that  $k_3$  is larger than  $k_{-3}$ —that is,  $K_3 > K_n$ ; hence, the rate equation becomes:

$$r \approx \frac{k \cdot K_1 \cdot K_2 \cdot [\text{A}] \cdot [\text{C}] \cdot [\text{cat.}]}{K_1 \cdot K_3 \cdot [\text{C}]^2} = \frac{k \cdot K_2 \cdot [\text{A}] \cdot [\text{cat.}]}{K_3 \cdot [\text{C}]}. \quad (6)$$

This equation apparently corresponds to Eq. 3, and the proposed scheme may be concluded to be reasonable.

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