The Preparation of Heavy Metal Hydride and Its Catalytic Activity. VII. The Hydrogenation of Various Olefins with a Ferric Chloride-Lithium Aluminum Hydride or a Cobaltous Chloride-Lithium Aluminum Hydride Catalyst*

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In preceding publications[1,2] we reported our observation that certain heavy metal halides react readily with a solution of lithium aluminum hydride in tetrahydrofuran to give a new catalyst system for the hydrogenation of styrene and cyclohexene. A typical catalyst is composed of ferric chloride plus lithium aluminum hydride (the iron catalyst) in an $LiAlH_4/FeCl_3$ ratio of 1:1. In the course of investigating this catalyst system, we were led to the conclusion that iron hydride, present in appreciable concentrations in the catalyst system, might be responsible for the hydrogenation reaction.

We will now report on an extension of the scope of this iron catalyst. The hydrogenations of various compounds containing olefinic linkages have been studied. In addition, a cobaltous chloride plus lithium aluminum hydride (the cobalt catalyst) system has been included in this study in order to compare the two catalysts.

Experimental

Materials.—Lithium aluminum hydride was obtained from Metal Hydride, Inc. A lithium aluminum hydride solution in tetrahydrofuran was prepared and used as a clear solution. The concentration of the stock solution (0.2−0.3 mol./l.) was determined by analysis using active hydrogen prior to use (by hydrolysis). The anhydrous heavy metal halides and olefins used were the purest among the available commercial materials. Tetrahydrofuran was dried over sodium and freshly distilled just before use.

Procedure.—Since in all cases the catalysts were sensitive to air and moisture, all operations were carried out in a nitrogen or a hydrogen atmosphere. The apparatus for the preparation of catalysts and the hydrogenation of olefins consisted of a four-necked flask equipped with a stirrer, a dropping funnel (60 ml.), and a thermometer, and was jointed to a gas burrete through a silica gel tube. Before the reaction, the apparatus was flushed with hydrogen. A solution of 70 ml. of tetrahydrofuran containing about 0.005 mol. of the heavy metal halide was stirred at 0°C for 40 min. To this solution a desired amount of a lithium aluminum hydride solution was then added through the dropping funnel. The time of addition varied from 2 to 10 min. The color of the solution immediately changed black or brown-black, and there was an accompanying hydrogen evolution. The mixture was stirred for an additional several hours until the hydrogen evolution ceased.

The hydrogenation of the olefin was carried out by introducing 5 ml. of the olefin into the catalyst solution described above. The speed of stirring was kept at 900 r.p.m. during the hydrogenation reaction. After the hydrogenation, the catalyst was destroyed

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1) Y. Takegami and T. Ueno, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 67, 246 (1964).

2) Y. Takegami, T. Ueno and T. Fujii, ibid., 67, 1009 (1964).

by the addition of 20 ml. of 15% aqueous hydrochloric acid; the amount of hydrogen thus evolved was measured. The hydrogenation product was extracted with diethyl ether, washed with water, concentrated by the evaporation of ether, and analyzed by gas chromatography.

The amounts of hydrogen evolved on the hydrolysis of the catalysts at several $LiAlH_4/FeCl_3$ ratios are given in Table I. For purposes of comparison, the amounts of hydrogen evolved during the preparation of the catalysts, reported in a preceding paper,[2] are also included in Table I.

TABLE I. THE AMOUNTS OF HYDROGEN EVOLVED

Catalyst	$LiAlH_4/MX_n$ ratio	On hydrolysis	During the preparation
		mol./mol. MX_n	
Iron	0.8	1.22	1.46
	1.0	1.58	1.79
	1.2	2.04	2.22
	1.5	2.88	2.41
Cobalt	0.8	1.28	1.78
	1.0	1.76	1.92

Results

Hydrogenation with Iron Catalysts. — The hydrogenation reaction was carried out under hydrogen at an atmospheric pressure and at 0°C. Among the solvents tested, diethyl ether, pyridine and tetrahydrofuran, the last was the best for this catalyst system. For most of the experiments, 5 ml. of olefin was used, the ratio of olefin to the iron catalyst being about 10 : 1. In order to establish a general relationship between the activity and the composition (the $LiAlH_4/FeCl_3$ ratio) of the iron catalyst, the amounts of absorbed hydrogen are plotted in Fig. 1 against the reaction times for the hydrogenation reaction of cyclohexene with the iron catalyst at various $LiAlH_4/FeCl_3$ ratios. No attempt has been made to estimate the rate constants of the hydrogenation reaction. The first reaction was carried out with the iron catalyst at an $LiAlH_4/FeCl_3$ ratio of 0.71 : 1. No hydrogen absorption was observed with this catalyst. Then several aliquots of a lithium aluminum hydride solution were added to the system at intervals. An appreciable activity appeared when the $LiAlH_4/FeCl_3$ ratio reached 0.89 : 1. Then the catalytic activity of the iron catalyst was found to rise steadily as the $LiAlH_4/FeCl_3$ ratio rose from 0.89 : 1 to 1.00 : 1, but thereafter to decrease as the ratio increased further. These successive procedures, in which the $LiAlH_4/FeCl_3$ ratio is raised step by step, will be described as "the step-by-step procedures" in a further discussion. In addition to the step-by-step procedures, the hydrogenation was also carried out with an iron catalyst freshly prepared in the $LiAlH_4/FeCl_3$ ratio of 1.00 : 1, the most active of the step-by-step procedures. The rate of this single hydrogenation, shown by a dotted line in Fig. 1, nearly corresponds to that observed in the hydrogenation at an $LiAlH_4/FeCl_3$ ratio of 1.00 : 1 in the step-by-step procedures.

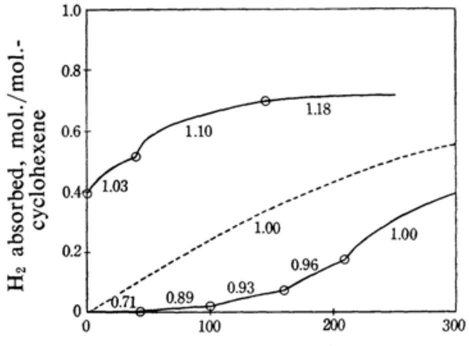

Fig. 1. Hydrogenation of cyclohexene with the iron catalyst.

Conditions; $FeCl_3$: 4.92 mmol., THF: 100 ml., cyclohexene: 5 ml. (49.6 mmol.), reaction temp.: 0°C

The thick or dotted line represents the step-by-step or single hydrogenation, respectively. Figures represent the $LiAlH_4/FeCl_3$ ratios.

○ represents the point where lithium aluminum hydride solution was added.

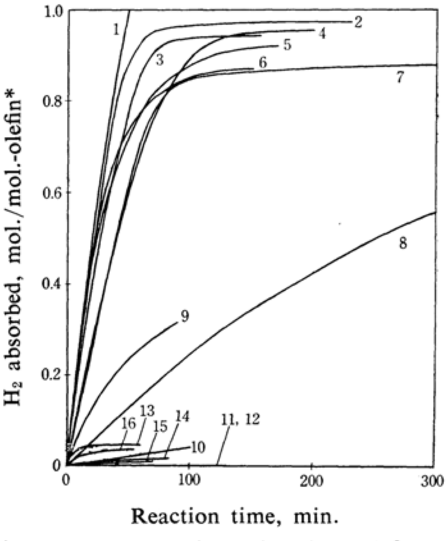

Fig. 2. Hydrogenation of various olefins with the iron catalyst.

Names of the compounds, the $LiAlH_4/FeCl_3$ ratio for the catalyst used and the amounts of hydrogen evolved during the hydrolysis subsequent to the hydrogenation are given in Table II.

* It changes to 1/2 (mol./mol.-olefin), in the cases of isoprene(7) and *d*-limonene(9).

TABLE II. HYDROGENATION WITH THE IRON CATALYST[*1]

Curve No. in Fig. 2	Olefin	$LiAlH_4/FeCl_3$ ratio	Ratio of hydrogen evolution[*2]
1	Styrene	1.00	—
2	α-Methylstylene	1.02	0.88
3	Safrole	1.02	0.76
4	Indene	1.01	0.74
5	Isosafrole	1.12	0.59
6	Anethole	1.21	0.59
7	Isoprene	1.00	0.89
8	Cyclohexene	1.00	—
9	*d*-Limonene[*3]	1.08	0.78
10	α-Pinene	0.80—1.20	0.83
11	Furan	0.82—1.54	0.80
12	Squalene	0.79—1.19	0.74
13	Ethyl acrylate	0.88—1.20	0.08
14	Vinyl acetate	0.80—1.70	0.09
15	Acrylonitrile	1.00—1.36	0.04
16	Allyl chloride	0.79—1.43	0.18

[*1] $FeCl_3$: 0.005 mol., THF : ca. 100 ml., olefin : 5 ml., reaction temp. : 0°C. Hydrogen absorption curves are given in Fig. 2.

[*2] The amounts of hydrogen evolved are represented by the ratio R/R_0, where R is the amount of hydrogen evolved during hydrolysis subsequent to the hydrogenation (mol./mol. $FeCl_3$) and R_0 is the amount of hydrogen evolved during the hydrolysis of the catalyst with same $LiAlH_4/FeCl_3$ ratio without hydrogenation.

[*3] A mixture of cis- and trans-isomers.

In order to determine how the olefin structure influences the rate of hydrogenation, the iron catalyst was tested with various olefinic compounds. The bulk of the experiments were performed according to the step-by-step procedures, and the value of the $LiAlH_4/FeCl_3$ ratio of the most active catalyst was determined in each case. The hydrogen absorption curves obtained with the most active catalysts are shown in Fig. 2. The values of the $LiAlH_4/FeCl_3$ ratios of the catalysts employed and the amounts of hydrogen evolved on the hydrolysis subsequent to the hydrogenation are given in Table II.

On the basis of the information given in Fig. 2, the olefins and unsaturated compounds employed in this work can be divided into three groups according to the ease of hydrogenation: (I) styrene, α-methylstyrene, safrole, isosafrole, indene, anethole and isoprene; (II) cyclohexene and *d*-limonene, and (III) α-pinene, squalene, furan, vinyl acetate, ethyl acrylate, allyl chloride and acrylonitrile.

The Hydrogenation of the Olefins in the First Group.—When compared at the most active composition of the catalysts, the rates of the hydrogenation of the olefins of this group were almost the same, as Fig. 2 shows. However, the ranges of the $LiAlH_4/FeCl_3$ ratios of the active catalysts and the values of the ratios of the most active catalysts varied to some extent; the ranges of the $LiAlH_4/FeCl_3$ ratios of the active catalysts for the hydrogenation of styrene, isosafrole, anethole and isoprene, for instance, were 0.78–1.45 : 1, 0.99–1.43 : 1, 1.21–1.41 : 1 and 0.78–1.23 : 1 respectively.

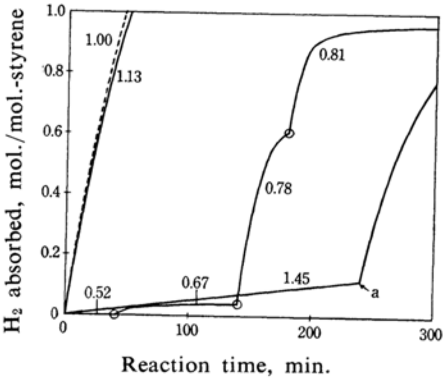

Fig. 3. Hydrogenation of styrene with the iron catalyst.

$FeCl_3$: 4.94 mmol., THF: 100 ml., styrene: 5 ml. (43.5 mol.), reaction temp.: 0°C
5 mmol. of water was added at "a."
Others are same to in Fig. 1.

The results of a representative run for styrene are shown in Fig. 3. At low $LiAlH_4/FeCl_3$ ratios, the initial rates were high, but either instantaneously or gradually the rates decreased, as may be seen from the curves corresponding to the (0.67) and (0.78) ratios in Fig. 3. For the run carried out with the optimum ratio, the plots of the amounts of hydrogen absorbed vs. the reaction time were linear up to almost 100% conversion. The slope, however, became gentle with a further increase in the $LiAlH_4/FeCl_3$ ratio, as may be seen from the curve representing the (1.45) ratio in Fig. 3. Similar trends were observed in the runs carried out with the other olefins.

If a small amount (0.005 mol.) of water was added to the less active catalyst with a larger $LiAlH_4/FeCl_3$ ratio, the catalyst became highly active, as may be seen in Fig. 3. A similar phenomenon was observed for the hydrogenation of indene with the iron catalyst with the $LiAlH_4/FeCl_3$ ratio of 1.69 : 1. We previously reported[1)] that the iron catalyst has catalytic activity when its hydrogen content is limited in a certain region and that the hydrogen content rises with an increase in the $LiAlH_4/FeCl_3$ ratio. From these facts, it is evident that the iron catalyst with a high $LiAlH_4/FeCl_3$ ratio is less active because of its large hydrogen content. Therefore, the activation of the catalyst when a small amount of water is added is conceivably due to the diminution of the hydrogen content of the catalyst.

On the other hand, in the hydrogenation of anethole with the iron catalyst with the $LiAlH_4/FeCl_3$ ratio of 1.61 : 1, which had no activity at the initial stage of the hydrogenation, an appreciable activity gradually appeared after a long induction period (about 12 hr.) with no addition of water.

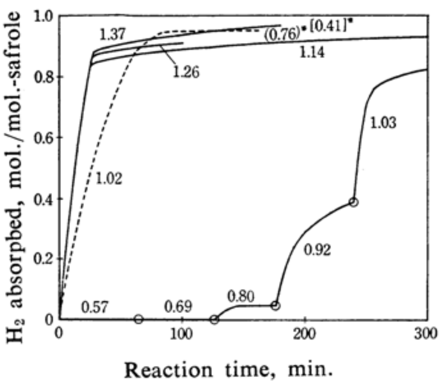

Fig. 4. Hydrogenation of safrole with the iron catalyst.

$FeCl_3$: 4.60 mmol., THF: 100 ml., safrole: 5 ml. (33.9 mmol.), reaction temp.: 0°C

* Amount of hydrogen evolved during the hydrolysis subsequent to the hydrogenation (see footnote of Table II). The amount of hydrogen evolved during the single hydrogenation is given in parenthesis and that subsequent to the stepwise hydrogenation is given in brackets. Others are same to in Fig. 1.

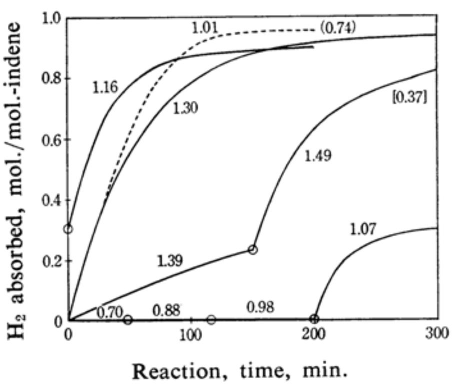

Fig. 5. Hydrogenation of indene with the iron catalyst.

$FeCl_3$: 4.26 mmol., THF: 100 ml., indene: 5 ml. (42.7 mmol.), reaction temp.: 0°C
Others are same to in Figs. 1 and 4.

The ranges of the $LiAlH_4/FeCl_3$ ratios of the active catalysts for the hydrogenation of safrole, indene and ethyl vinyl ether were somewhat different from those of styrene. The results of the hydrogenation of safrole and indene are shown in Figs. 4 and 5 respectively. As may be seen in Fig. 4, the iron catalysts with the $LiAlH_4/FeCl_3$ ratios of 1.26 : 1, 1.37 : 1 and 1.41 : 1 had almost the same activities in the hydrogenation of safrole. If the catalyst was hydrolyzed after the step-by-step hydrogenation, the amount of hydrogen evolved* was relatively small (0.41), whereas it was relatively large (0.76) after the single hydrogenation. As may be seen in Fig. 5, the range of the $LiAlH_4/FeCl_3$ ratio of the active catalyst for the hydrogenation of indene was also different from that for styrene, and the amount of hydrogen evolved on hydrolysis subsequent to the step-by-step hydrogenation was again relatively small.

On the other hand, as may be seen in Fig. 5, the iron catalyst freshly prepared in the $LiAlH_4/FeCl_3$ ratio of 1.01 : 1 was more active than the catalyst with the $LiAlH_4/FeCl_3$ ratio of 1.07 : 1 in the step-by-step procedures. A similar phenomenon was observed in the hydrogenation of isoprene; the iron catalyst freshly prepared in the $LiAlH_4/FeCl_3$ ratio of 1.04 : 1 was more active than the catalyst with the ratio of 1.01 : 1 in the step-by-step procedures, as may be seen in Fig. 6. Thus, the catalytic activity of the catalyst with the same $LiAlH_4/FeCl_3$ ratio can be greatly altered by the method of preparation chosen (that is, it depends on whether the step-by-step or the single procedure is used).

The relationship between the $LiAlH_4/FeCl_3$

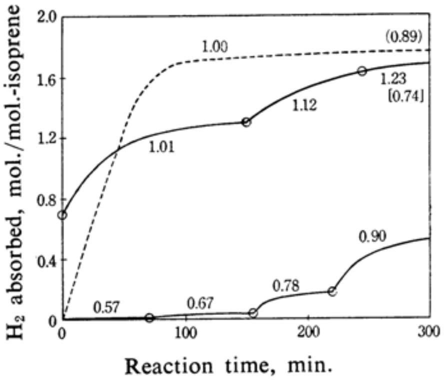

Fig. 6. Hydrogenation of isoprene with the iron catalyst.

$FeCl_3$: 4.71 mmol., THF: 80 ml., isoprene: 5 ml. (50.0 mmol.), reaction temp.: 0°C
Others are same to in Figs. 1 and 4.

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* See footnote of Table II.

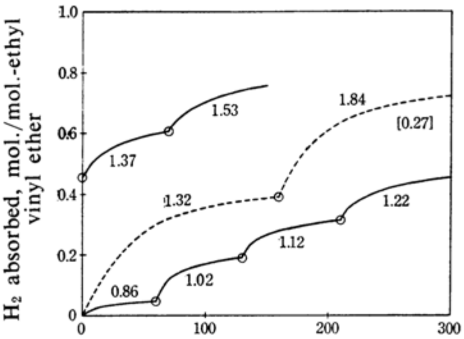

Fig. 7. Hydrogenation of ethyl vinyl ether with the iron catalyst.
$FeCl_3$: 4.68 mmol., THF: 110 ml., ether: 5 ml. (52.9 mmol.), reaction temp.: 0°C
Others are same to in Figs. 1 and 4.

ratio and the catalytic activity was much more complicated in the hydrogenation of ethyl vinyl ether; as may be seen in Fig. 7, when the $LiAlH_4/FeCl_3$ ratio was raised step-by-step, $0.86 \rightarrow 1.02 \rightarrow 1.12 \rightarrow \cdots$, the rate of hydrogen absorption decreased after about 0.15 (mol./mol.-ether) of hydrogen had been absorbed at each ratio. With the iron catalyst prepared in the $LiAlH_4/FeCl_3$ ratio of 1.32 : 1, the rate decreased after about 0.4 (mol./mol.-ether) of hydrogen had been absorbed, as the dotted line in Fig. 7 shows. A similar phenomenon was observed when the ratio was raised from 1.32 : 1 to 1.84 : 1. That is, the amount of hydrogen absorbed seems to correspond to the amount of lithium aluminum hydride added to raise the $LiAlH_4/FeCl_3$ ratio. The amount of hydrogen evolved on the hydrolysis subsequent to the hydrogenation was quite small.

The Hydrogenation of d-Limonene (Olefins in the Second Group).—The range of the $LiAlH_4/FeCl_3$ ratio for the active catalyst for the hydrogenation of *d*-limonene was almost the same as that for the hydrogenation of cyclohexene described above, whereas the value of the $LiAlH_4/FeCl_3$ ratio for the most active catalyst was somewhat different—1.00 : 1 and 1.08 : 1 for the hydrogenation of cyclohexene and *d*-limonene respectively. *d*-Limonene did not absorb more than 1.0 (mol./mol.-limonene) of hydrogen.

The Hydrogenation of Unsaturated Compounds in the Third Group.—Squalene, α-pinene, furan, vinyl acetate, ethyl acrylate, allyl chloride and acrylonitrile did not appreciably absorb hydrogen in the presence of the iron catalyst at any $LiAlH_4/FeCl_3$ ratio. The amounts of hydrogen evolved on the hydrolysis subsequent to the hydrogenation seem to indicate that these compounds can be divided into two groups. In the cases of squalene, α-pinene and furan, the amounts of hydrogen evolved were relatively large, whereas they were quite small or practically zero in the cases of vinyl acetate, ethyl acrylate, allyl chloride and acrylonitrile. For the latter compounds, the color of the reaction mixture changed during the course of the hydrogenation, from black to blackish brown for ethyl acrylate and acrylonitrile, and to ocher for allyl chloride.

Hydrogenation with Cobalt Catalysts.—Since the iron catalyst was less active in the hydrogenation of cyclohexene, *d*-limonene, squalene, α-pinene, ethyl vinyl ether, vinyl acetate, ethyl acrylate, allyl chloride and acrylonitrile, the hydrogenation of these compounds was performed with the cobalt catalyst with a view to exploring the more active catalyst. The results obtained with the cobalt catalyst are shown in Fig. 8 and Table III. As may be seen in Fig. 8, cyclohexene and *d*-limonene were rapidly hydrogenated with this catalyst. *d*-Limonene probably did not absorb more than 1.0 (mol./mol.-limonene) of hydrogen in spite of the very rapid hydrogenation because only the terminal bouble bond of *d*-limonene was hydrogenated. The hydrogenation of ethyl vinyl ether, which was achieved with only a limited success with the iron catalyst (Fig. 7),

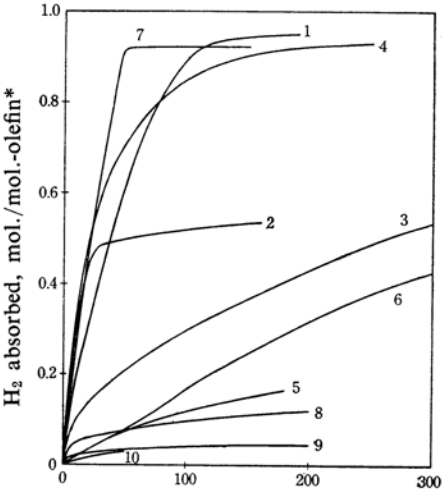

Fig. 8. Hydrogenation of various olefins with the cobalt catalyst.
Names of the compounds, the $LiAlH_4/CoCl_2$ ratio for the catalyst used and the amounts of hydrogen evolved during the hydrolysis subsequent to the hydrogenation are given in Table III.
* It changes to 1/2 (mol./mol.-olefin) in the cases of *d*-limonene(2) and furan(5), and to 1/6 (mol./mol.-olefin) in the case of squalene(6).

TABLE III. HYDROGENATION WITH THE COBALT CATALYST*1

Curve No. in Fig. 8	Olefin	$LiAlH_4/CoCl_2$ ratio	Ratio of hydrogen evolution*2
1	Cyclohexene	0.82	—
2	*d*-Limonene*3	0.98*4	0.58
3	α-Pinene	1.00*4	0.63
4	Ethyl vinyl ether	0.81	0.71
5	Furan	0.79	0.62
6	Squalene	0.98*4	0.60
7	Ethyl acrylate	0.80	0.66
8	Vinyl acetate	0.80	0.36
9	Acrylonitrile	0.82	0.00
10	Allyl chloride	0.81	0.06

*1 $CoCl_2$: ca. 0.005 mol., THF: ca. 100 ml., olefin: 5 ml., reaction temp.: 0°C. Hydrogen absorption curves are given in Fig. 8.

*2 See footnote of Table II.

*3 A mixture of cis- and trans-isomers.

*4 When the $LiAlH_4/CoCl_2$ ratio was 0.78—0.80, no appreciable hydrogen absorption was observed.

was performed successfully with the cobalt catalyst. It is noteworthy that a very large variation in catalytic activity for the hydrogenation of ethyl acrylate exists among the iron and cobalt catalysts. Furthermore, squalene and α-pinene were found to undergo a relatively fast hydrogenation, while furan was found to undergo a slow hydrogenation with the cobalt catalyst, although these compounds did not undergo any hydrogenation at all with the iron catalyst. Only a small amount of hydrogen was evolved on the hydrolysis subsequent to the hydrogenation of vinyl acetate, acrylonitrile and allyl chloride. However, a relatively large amount of hydrogen was evolved on the hydrolysis subsequent to the hydrogenation of ethyl acrylate. This hydrogen evolution seems to be related to the fast hydrogenation of ethyl acrylate with the cobalt catalyst.

Discussion

The effect of the nature of the olefin on the hydrogenation rate with the iron catalyst is illustrated in Fig. 2. The relative order of the hydrogenation rate expressed by the half-periods is: styrene $>\alpha$-methylstyrene $\simeq$ safrole $\simeq$ isosafrole $\simeq$ anethole $>$ isoprene $\simeq$ indene $>$ cyclohexene $\simeq$ *d*-limonene $\gg$ squalene $\simeq \alpha$-pinene. Evidently, terminal olefins are hydrogenated more rapidly than internal olefins.

d-Limonene absorbed only 1.0 (mol./mol.-limonene) of hydrogen, and α-pinene did not absorb any appreciable amount of hydrogen at all. These facts suggest that only the terminal double bond of *d*-limonene was hydrogenated. Comparisons of the rate for α-methylstyrene with that of *d*-limonene and of indene with cyclohexene show that the conjugated olefins were hydrogenated more rapidly than the nonconjugated ones.

The $LiAlH_4/FeCl_3$ ratios corresponding to the active catalysts vary with the nature of the olefins, such as styrene, safrole, indene and ethyl vinyl ether. We shall discuss this variation in the $LiAlH_4/FeCl_3$ ratios below.

We have previously studied[2,3] the amount of ethylbenzene produced during the reaction of the iron catalyst with styrene under a nitrogen atmosphere; the results may be summarized thus: (a) the hydrogen which migrates from the catalyst (iron hydride) to the styrene amounts to 1.0 g. atom/mol. $FeCl_3$ when the $LiAlH_4/FeCl_3$ ratio is 1 : 1; (b) after the hydrogen migration, a part of the iron hydride is regenerated rapidly when the reaction atmosphere is changed from nitrogen to hydrogen, but the remaining part is regenerated very slowly; (c) this rapidly-regenerated hydride is considered to be responsible for the catalytic activity, and (d) the rapidly-regenerated hydride amounts to 0.3—0.4 g. atom/mol. $FeCl_3$ when the $LiAlH_4/FeCl_3$ ratio is 1 : 1 and decreases with the increase in the ratio, although the total hydrogen content of the catalyst increases steadily with the increase in the ratio. The variation in the ranges of the $LiAlH_4/FeCl_3$ ratio for the active catalysts and the values of the ratios for the most active catalyst may be explained in terms of the diminution of the hydrogen content of the catalyst through the hydrogen migration from the catalyst to olefins, followed by a very slow hydrogen absorption. The fact that the iron catalysts with the relatively high $LiAlH_4/FeCl_3$ ratios of 1.3—1.4 : 1 were active in the hydrogenation of safrole and indene in the step-by-step procedures, whereas the iron catalyst with the $LiAlH_4/FeCl_3$ ratio of 1.41 : 1 was less active in the hydrogenation of styrene, is due to the diminution in the hydrogen content of the catalyst through the hydrogen migration from the catalyst to the safrole or indene. This hydrogen migration may occur more rapidly in the hydrogenation of ethyl vinyl ether, in which the successive addition of a lithium aluminum hydride solution is necessary to continue the hydrogen absorption (Fig. 7). The facts that the amounts of hydrogen evolved during the hydrolysis subsequent to the step-by-step procedure were smaller than those subsequent to the single hydrogenation, and that a long induction period appeared in the

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3) Y. Takegami, T. Ueno and T. Fujii, *Catalyst* (*Shokubai*), **6**, 339 (1964).

hydrogenation of anethole with the iron catalyst with the relatively high $LiAlH_4/FeCl_3$ ratio of 1.61 : 1, can be taken as further support of the diminution of hydrogen content through the hydrogen migration from the catalyst to the olefins.

In the hydrogenation of vinyl acetate, ethyl acrylate, acrylonitrile and allyl chloride, no hydrogen absorption was observed, and the amounts of hydrogen evolved during the hydrolysis subsequent to the hydrogenation were quite small. In these cases, not hydrogenation but, rather, the reaction of these compounds with the iron catalyst occurred.* When vinyl acetate was added to the active catalyst with the $LiAlH_4/FeCl_3$ ratio of 1 : 1, the catalyst was " killed " and became quite inactive in the hydrogenation of styrene.

As has been mentioned above, the iron catalyst is selective in its hydrogenating ability. On the other hand, it can be seen from a comparison of Figs. 2 and 8 that the cobalt catalyst is highly active in its hydrogenating ability; internal olefins can be hydrogenated successfully with the cobalt catalyst.

For practical purposes, perhaps only the slow addition of a lithium aluminum hydride solution to a mixture of olefin and heavy metal salt, before the occurrence of hydrogen absorption, can provide a simple and convenient procedure for the hydrogenation of various olefins.

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* For example, 3-pentanol and ethyl acetate were obtained by the reaction of the iron catalyst with diethyl ketone and vinyl acetate respectively.