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A Novel Synthesis of Cyclohexanol Derivatives by the Catalytic Hydrogenation of Benzene with Acid Additives

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The hydrogenation of benzene over a platinum group metal in the presence of various strong acids was carried out. Cyclohexanol derivatives ($C_6H_{11}X$, X=OH, OAc, Cl, Br) were found to be produced by the catalytic hydrogenation of benzene with acid additives. The following two sequences of adsorption strength were observed between platinum metals (adsorbent) and additive reagents (adsorbate):

$$\mathrm{Ru} \gg \mathrm{Rh} > \mathrm{Pd} > \mathrm{Ir} > \mathrm{Pt} \qquad \text{(I)}$$

and

$$\mathrm{HI},\ \mathrm{HCOOH} \gg \mathrm{HBr} > \mathrm{HCl} \gg \mathrm{AcOH},\ \mathrm{H_2O}. \qquad \text{(II)}$$

When a weak adsorbate, such as acetic acid or water, was used as an additive reagent, ruthenium, the strongest adsorbent, exhibited the best selectivity. When hydrogen chloride, a strong adsorbate in the sequence (II), was used an additive reagent, palladium or rhodium, moderately strong adsorbent, exhibited excellent selectivity. By the reaction of 2 ml of benzene, 5 ml of 35% HCl and 0.2 g of 5% Pd/SiO$_2$, under 10 atm-G (P atm-G$=1.013(P+1)\times10^5$ Pa) hydrogen at 100 °C for 20 h, 8.4% of the yield of chlorocyclohexane was obtained at 64.2% of the selectivity (13.1% of the conversion of benzene).

Catalytic hydrogenation of benzene by a platinum group metal usually gives cyclohexane (CHA) as the sole product. However, it has been reported that an intermediate cyclohexene (CHE) is produced in moderate yield under specific conditions.[1—3] It is also known that cyclohexylbenzene is obtained from benzene, by using a platinum group metal catalyst supported on a solid acid.[4—6]

We speculated that if the intermediate CHE reacts smoothly with water (or a similar reagent) on a catalyst surface, cyclohexanol (CHOH, or its derivatives) will be obtained by a one-step reaction that may be called a "hydroaddition".

In this paper we report that this novel reaction proceeds. The selectivity is fairly high, at least in the case of chlorocyclohexane (CHCl) preparation. The reaction mechanism is also discussed.

Experimental

Materials. Most of the materials that were commercially available in high purity were used without further purification. As an authentic sample, cyclohexyl formate was prepared by a method described in the literature.[7]

Catalyst Preparation. Catalysts were usually prepared from an aqueous solution of following metal compounds: $RuCl_3\cdot H_2O$, $RhCl_3\cdot 3H_2O$, $PdCl_2$, $IrCl_4$, and $H_2PtCl_6\cdot 6H_2O$. Typical examples are as follows.

Method (A): A mixture of 6.6 g of silica hydrosol "Snowtex 30" (provided from Nissan Chemical Industries) and 2.6 ml of 10% aqueous rhodium chloride was placed in a flask, and heated at 80—90 °C to dry in vacuo (10—20 Torr, 1 Torr=133.3 Pa). The mixture thus solidified was ground to a powder and passed through a 100-mesh sieve. The powder was treated with gaseous ammonia at room temperature overnight and reduced in an atmospheric hydrogen stream at 150 °C for 5 h. The powder was washed with water thoroughly and dried in a hydrogen stream at 150 °C for 5 h again. The thus obtained catalyst is designated 5% Rh/SiO$_2$.

Method (B): Lanthanum substituted Y-faujasite was prepared according to the literature.[8] To a slurry comprising of 440 ml of water and 40 g of lanthanum substituted Y-faujasite, 180 ml of 0.1% aqueous ruthenium chloride was added drop by drop for 4 h. After standing overnight, the mixture was filtered and dried at 110 °C for 5 h in vacuo (5—10 Torr). The thus obtained catalyst is designated 0.2% Ru/La-Y.

Method (C): A mixture of 5.0 g of phosphotungstic acid (PWA, $H_3[PW_{12}O_{40}]\cdot 14H_2O$) and 10.5 ml of 2% aqueous ruthenium chloride was dried in a 1 atm nitrogen stream at 110 °C for 4 h. Then, the residue was reduced in 1 atm hydrogen at 150 °C for 5 h. The catalyst thus produced is designated 2% Ru/PWA.

Procedure. A glass autoclave with a capacity of 25 ml was used as a reaction vessel for low-pressure (3—10 atm-G) experiments. In the autoclave, raw materials (for example, 2 ml of benzene, 5 ml of acid solution and 0.2 g of catalyst) were placed with a Teflon®-covered magnetic stirring bar. The autoclave was connected to a hydrogenation unit, and put under the prescribed reaction conditions. After toluene was added in the autoclave as the internal standard, the autoclave was filled with saturated aqueous sodium chloride. The upper organic layer was analyzed quantitatively by the GC method. In high-pressure (15—100 atm-G) experiments, the glass autoclave was set into a special stainless steel autoclave that had a connecting pipe to equalize the pressure both inside and outside of the glass autoclave.

In the experimental results, the conversion of benzene is the sum of all the benzene converted to reaction products

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as a percentage. Also, the selectivity (%) of the product is the ratio of moles of the product to total moles of benzene converted.

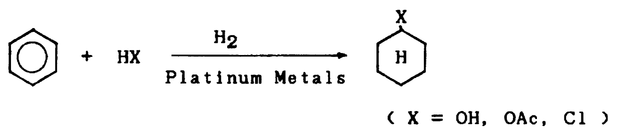
Identification of Products. The product was identified by GC-MS with parallel experiments of an authentic sample. Furthermore, CHCl was isolated from the reaction mixture by distillation, and confirmed by an IR measurement.

Results and Discussion

Preliminary Experiments. The results of preliminary experiments are listed in Table 1. As expected, the following reaction was confirmed (Scheme 1):

The presence of a strong acid, such as boron trifluoride or sulfuric acid (SA), is essential in this reaction. The results of Exper. No. 17 show the possibility of three hydroaddition products: CHOH, cyclohexyl acetate (CHOAc), and CHCl in the ratio 1 : 12 : 549.

Preparation of Cyclohexanol. It was observed that the Ru catalyst exhibited the best catalytic performance among several platinum metals, even though the selectivity was still low. Therefore, a series of experiments with a Ru catalyst was carried out; the results are summarized in Fig. 1. The increase in the concentration of SA depressed the catalytic activity, but improved the selectivity of CHOH until concentration of SA became 40%. The sudden depression of the activity and the selectivity at a high concentration of SA may have been caused by hydrogen sulfide produced by the reduction of SA. Hydrogen sulfide was confirmed by a detector tube and its characteristic unpleasant odor.



Scheme 1.

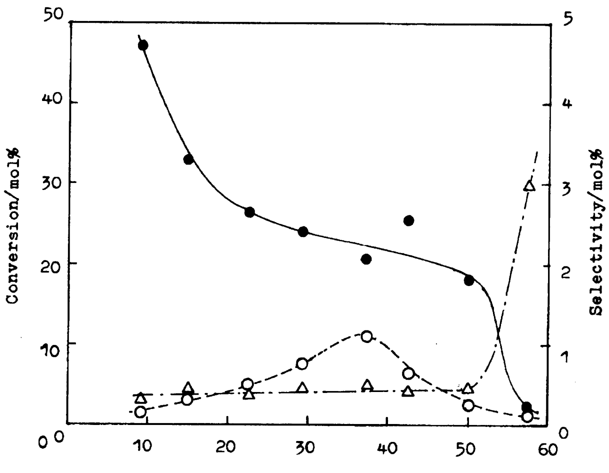


Fig. 1. Effect of the concentration of SA on the conversion of benzene (——●——) and selectivities of CHOH (---○---) and CHE (–·–△–·–). Benzene (2 ml), an aqueous SA (5 ml) and 5%Ru/SiO$_2$ (20 mg) were heated at 100 °C, under 10 atm-G H$_2$, for 20 h.

Preparation of Cyclohexyl Acetate. Ruthenium also exhibited the best catalytic performance in the preparation of CHOAc. The results with a Ru catalyst (2% Ru/PWA) are shown in Fig. 2. An increase in the concentration of acetic acid (AcOH) reduced the activity of the catalyst and enhanced the selectivity of CHOAc. The effects of the reaction time on the conversion and selectivity were studied by using a Ru catalyst (2% Ru/SiO$_2$) and PWA (Fig. 3). Although the conversion increased monotonically with time, the selectivity gradually decreased. These facts imply that the secondary hydrogenolysis of CHOAc to CHA took place. A similar tendency was also observed in the case of the CHOH preparation. To confirm this secondary hydrogenolysis, CHOH and CHOAc were reacted under the same condition as in the above-mentioned reaction (Table 2).

The influence of the AcOH concentration on the conversion and selectivity was checked by using SA. The results are shown in Fig. 4. Depression of the activity by hydrogen sulfide was also observed under a high AcOH concentration (namely, high SA concentration to water) conditions.

Preparation of Chlorocyclohexane. As shown in Table 1, when hydrogen chloride (HCl) was used as an additive reagent, although the hydrogenation rate of benzene decreased greatly, the selectivity of the hydroaddition product was fairly high. It is also worth noting that the best catalyst is not Ru, but Rh or Pd. We studied the influence of the concentration of HCl with platinum metals. Representative results for the Rh catalyst (5% Rh/SiO$_2$) are shown in Fig. 5. The results for noble metal catalysts are listed in Table 3.

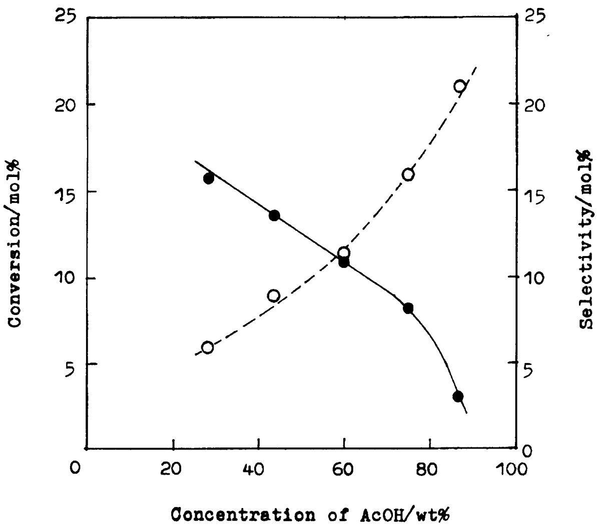


Fig. 2. Effect of the concentration of AcOH on the conversion of benzene (——●——) and the selectivity of CHOAc (---○---). Benzene (2 g), AcOH (0.75—6 ml) and 2%Ru/PWA (200 mg) were heated at 110 °C, under 10 atm-G H$_2$, for 2 h.

Table 1. Preliminary Experiments

Exper. No.	Starting materials[a)] Hydrogenation catalyst/mg		Acid[b)]/ml		Additives ml	Reaction conditions Pressure of H_2[c)] atm-G	Temp °C	Time h	Results /mol% Conversion of benzene	Selectivity of products[d)] CHOH	CHOAc	CHCl	CHE
1	2%Ru/WO_3	20	50%H_2SO_4	2	MeOH 0.4	5	70	24	0.64	1.75			
2	2%Rh/WO_3	20	50%H_2SO_4	2	MeOH 0.4	5	70	3.5	34.5	0.05			
3	2%Pd/SiO_2	20	50%H_2SO_4	2	MeOH 0.4	5	70	24	5.0	Trace			
4	2%Ru/WO_3	100	30%PWA	2		10	95	24	9.5	0.21			
5	2%Ru/SiO_2	20	85%H_3PO_4	2		5	70	24	0.3	None			
6	2%Ru/Al_2O_3	20	50%TSA[e)]	2		5	70	24	1.6	None			
7	5%Ru/C	50	—		AcOH 1	5	75	8.5	17.4		None		
8	5%Ru/C	50	BF_3·2AcOH	0.5	AcOH 1	5	75	4.75	21.5		5.56		
9	2%Ru/SiO_2	50	BF_3·2AcOH	0.5	AcOH 1	5	75	20	0.86		16.7		
10	2%Rh/SiO_2	50	BF_3·2AcOH	0.5	AcOH 1	5	75	3.33	17.4		0.35		
11	2%Pd/SiO_2	50	BF_3·2AcOH	0.5	AcOH 1	5	75	20	11.5		0.71		
12	2%Ir/SiO_2	50	BF_3·2AcOH	0.5	AcOH 1	5	75	1.33	22.1		0.06		
13	2%Pt/SiO_2	50	BF_3·2AcOH	0.5	AcOH 1	5	75	0.5	21.7		0.09		
14	0.2%Ru/SiO_2	100	PWA	0.2(g)	AcOH 3	5	95	30	1.3	Trace	27.4		
15	0.2%Ru/La-Y[f)]	200			AcOH 3	20	180	2	11.0		10.2		12.5
16	5%Ru/SiO_2	200	40%H_2SO_4	5	AcOH 3	10	100	4	7.9	0.7	5.1		6.2
17	2%Rh/SiO_2	200	35%HCl	3	AcOH 3	10	100	17	24.5	0.1	1.2	54.9	0.3
18	2%Ru/SiO_2	50	20%HCl	2		5	70	24	0.09			Trace	
19	2%Rh/SiO_2	20	35%HCl	2		3.5	70	18	0.36			63	
20	5%Pd/SiO_2	200	35%HCl	5		10	100	20	13.1			64.2	

a) With starting materials, 1 ml of benzene (2 ml, in Exper. No. 14—17, and 20) was used. b) The percentage means the concentration of an aqueous solution. c) Total gaseous pressure including the vapor pressure of materials. d) The rest of products is CHA. e) TSA: *p*-toluenesulfonic acid. f) La-Y: La Y-faujasite.

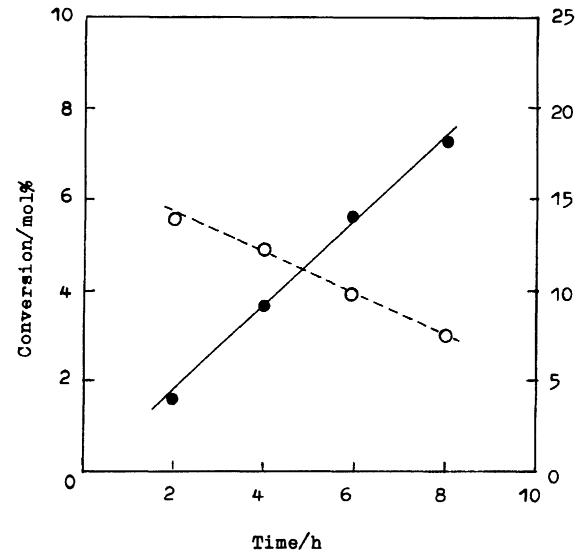


Fig. 3. Effects of the reaction time on the conversion of benzene (—●—) and the selectivity of CHOAc (---○---) over Ru/SiO_2. Benzene (2 ml), PWA (200 mg), AcOH (3 ml) and 2%Ru/SiO_2 (100 mg) were heated at 125 °C, under 20 atm-G H_2, for a time.

It is conceivable that the conversion ratio of benzene at 35 and 10% of the concentration of HCl indicates the relative adsorption strength of HCl to a noble metal. The effects of the hydrogen pressure and temperature on the conversion and selectivity were also studied for a Rh catalyst. The results are shown in Figs. 6 and 7. An increase in the hydrogen pressure resulted in a higher conversion of benzene along with a decrease in the selectivity. Both the conversion and selectivity were increased along with an elevation in the reaction temperature. These facts imply that the apparent activation energy of the addition reaction is larger than

Table 2. Hydrogenolysis of CHOAc and CHOH

Starting materials	Reaction conditions[a)] Temp/°C	Time/h	Yield of products /mol% CHA	CHE
CHOAc	100	7	50.3	8.4
CHOH	150	5	38.8	45.7

a) The starting material (1 g) was heated under 8 atm-G H_2 with 50 mg of 5% Ru/PWA catalyst.

Table 3. Preparation of CHCl over Platinum Metals

Catalyst X mg	Ru 200	Rh 200	Rd 200	Ir 30	Pt 20
Conversion ratio[a)]	0.001	0.10	0.24	0.36	0.41
Selectivity (%) (35% HCl)	—	65	62	14	13

a) Conversion Ratio$=\frac{\text{Conversion at 35\% HCl}}{\text{Conversion at 10\% HCl}}$. Benzene (2 ml), hydrochloric acid (5 ml), and X mg of 5% M/SiO_2 (M=Ru, Rh, Pd, Ir, Pt) were heated at 100 °C, under 10 atm-G H_2, for 20 h.

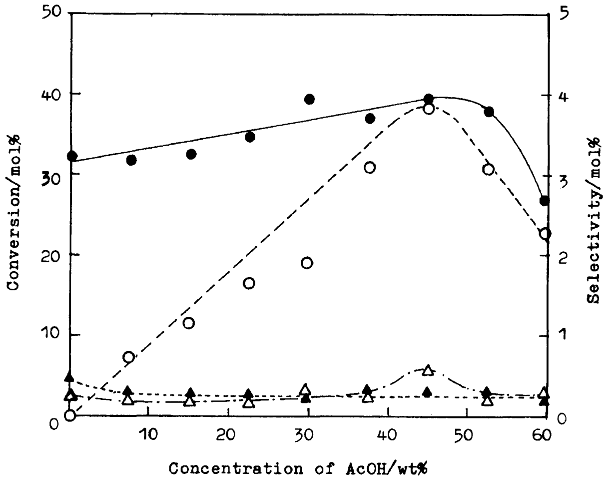


Fig. 4. Effect of the concentration of AcOH on the conversion of benzene (——●——), and selectivities of CHOAc (---○---), CHOH (····▲····), and CHE (–·–△–·–) in aqueous SA. Benzene (2 ml), an aqueous AcOH–SA (AcOH : SA : $H_2O=x\%:20\%:80-x\%$, 5 ml) and 5%Ru/SiO_2 (20 mg) were heated at 100 °C, under 10atm-G H_2, for 2 h.

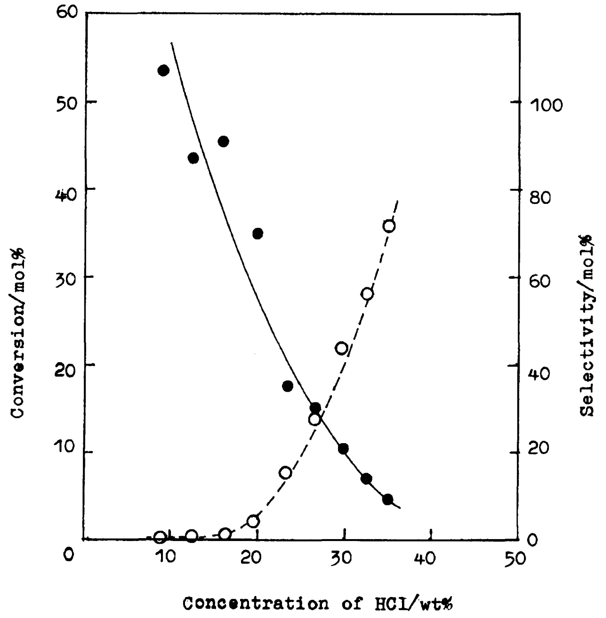


Fig. 5. Effect of the concentration of HCl on the conversion of benzene (——●——) and the selectivity of CHCl (---○---) over Rh/SiO_2. Benzene (2 ml), an aqueous HCl (5 ml), and 5%Rh/SiO_2 (200 mg) were heated at 100 °C, under 10 atm-G H_2, for 20 h.

that of hydrogenation. Under very high temperature conditions, a steep decrease in the benzene conversion was observed. This is attributed to a decrease in the substantial hydrogen partial pressure, because the vapor pressure of materials (water, benzene, and HCl) became not negligible.

Chlorocyclohexane was also obtained from benzene, hydrogen, and gaseous HCl by the catalytic action of a platinum group metal. The results are given in Table 4.

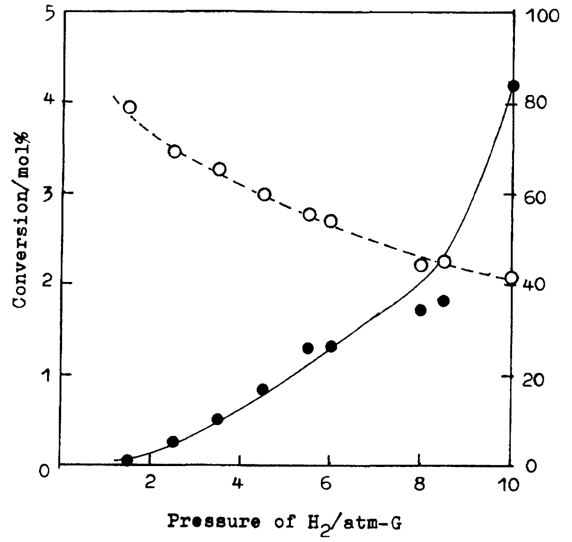


Fig. 6. Effect of the pressure of H_2 on the conversion of benzene (——●——) and the selectivity of CHCl (---○---) over Rh/SiO_2. Benzene (2 ml), 35% aqueous HCl (5 ml) and 5%Rh/SiO_2 (200 mg) were heated at 75 °C, under a certain pressure of H_2, for 20 h.

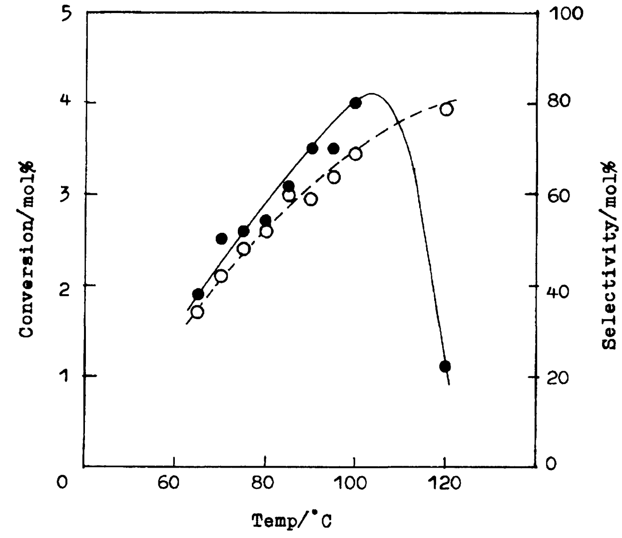


Fig. 7. Effect of the temperature on the conversion of benzene (——●——) and the selectivity of CHCl (---○---) over Rh/SiO_2. Benzene (2 ml), 35% aqueous HCl (5 ml) and 5%Rh/SiO_2 (200 mg) were heated at a certain temperature, under 10 atm-G H_2, for 20 h.

A poisonous activity of gaseous HCl that retards the hydrogenation and accelerates the addition, seems to be smaller than that of aqueous HCl. This difference could be attributed to the molar ratio of HCl to hydrogen in the reaction media. Compared with the solubility of HCl to water, the solubility of hydrogen to water is too small.

It is speculated that water might promote the desorption of CHCl from the surface along with an enhancement of the selectivity, as observed in the acceleration

Table 4. Preparation of CHCl with Gaseous HCl

Catalyst	Results[a)]/mol%	
	Conversion of benzene	Selectivity of CHCl
10%Rh/SiO_2	30.05	1.8
10%Ru/SiO_2	0.35	65.7

a) Benzene (5 ml) and a catalyst (200 mg) were heated at 100 °C, under 50 atm-G H_2–HCl (4 : 1), for 16 h.

of CHE desorption by water.[9,10)] The influence of the reaction time on the conversion and selectivity, by using a Rh catalyst, was also examined (Fig. 8). The conversion increased linearly and the selectivity was constant together with the passage of time. The stability of CHCl under the reaction conditions is a very characteristic feature of this reaction. It exhibits a marked contrast to the cases of CHOH and CHOAc. These facts may be understood from the low solubility of CHCl in the aqueous medium in which the hydrogenation catalyst, that is also a hydrogenolysis catalyst, is present.

Preparation of Bromocyclohexane and Others. The preparation of bromocyclohexane was studied; the results are given in Table 5.

The preparation of iodocyclohexane and cyclohexyl formate were also attempted. However, only a trace amount of each product was detected, because the additive reagent was adsorbed too strongly on the metal.[11,12)]

Alkyl substituted benzenes, instead of benzene, itself, were also used in this reaction and yielded, the corresponding products.

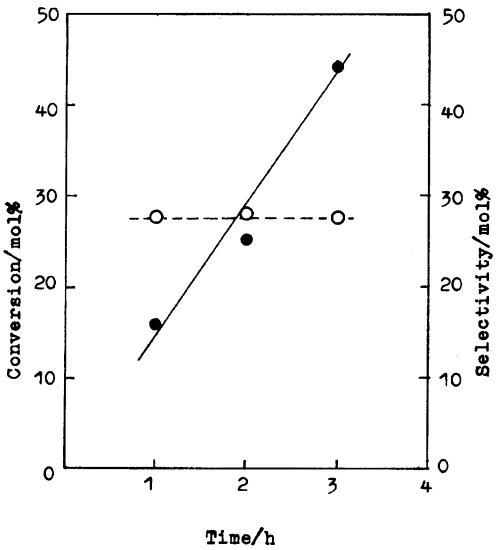


Fig. 8. Effect of the reaction time on the conversion of benzene (—●—) and the selectivity of CHCl (---○---) over Rh/SiO_2. Benzene (2 ml), 35% aqueous HCl (5 ml) and 5%Rh/SiO_2 (200 mg) were heated at 140 °C, under 50 atm-G H_2, for a time.

Table 5. Preparation of Bromocyclohexane

Catalyst	Results[a)]/mol%	
	Conversion of benzene	Selectivity of bromocyclohexane
5%Rh/SiO_2	0.09	43.0
5%Pd/SiO_2	0.04	32.6
5%Ir/SiO_2	2.60	14.8
5%Pt/SiO_2	43.61	2.5

a) Benzene (2 ml), 40% aqueous HBr (5 ml), and the catalyst (200 mg) were heated at 100 °C, under 10 atm-G H_2, for 20 h.

Mechanism of the Reaction. It became obvious that the conversion and selectivity depended drastically on the concentration of HCl in the CHCl preparation (Fig. 5). Plots of the conversion against the concentration of HCl strongly suggest that HCl acts as a poison, as shown by Baltzly[11)] and Rylander.[12)] Hydrogen chloride seems to be competitively adsorbed on the hydrogen active sites of the catalyst surface. This facilitates the addition reaction of HCl to an intermediate CHE. Also, it became obvious that the extent of the concentration dependence differs according to the kind of the noble metal (Table 3). The results giving in Table 3 show that there is the following sequence of the adsorption strength of HCl on platinum metals:

$$\mathrm{Ru} \gg \mathrm{Rh} > \mathrm{Pd} > \mathrm{Ir} > \mathrm{Pt}. \qquad \text{(I)}$$

This sequence is similar to that of ethylene desorption reported by Bond and Wells,[13)] though the driving force of the adsorption of HCl on platinum metals may be quite different from that of the adsorption of ethylene. If benzene is adsorbed on platinum metals in the same manner as ethylene, HCl must be competitively adsorbed on those active sites where hydrogen, but not benzene, is adsorbed. This is because when the hydrogen pressure was raised, adsorbed, the conversion increased along with a decrease in the selectivity (Fig. 6); and when the concentration of HCl was raised, the conversion decreased along with an increase in the selectivity (Fig. 5).

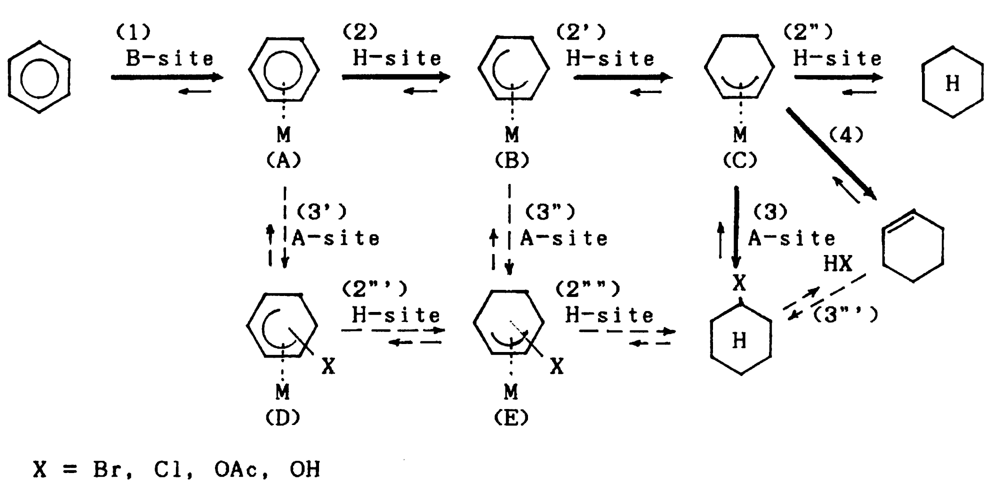
From the data given above, another sequence for the adsorption strength of additive reagents on the noble metals can be summarized as follows. The extent of the decrease in the conversion was used as an index of the adsorption strength:

$$\mathrm{HI},\ \mathrm{HCOOH} \gg \mathrm{HBr} > \mathrm{HCl} \gg \mathrm{AcOH},\ \mathrm{H_2O}. \qquad \text{(II)}$$

The reaction may be illustrated by the following mechanistic scheme (Scheme 2):

In this scheme, benzene is chemisorbed on a "B-site". Hydrogenation of chemisorbed benzene (derivatives) proceeds by a reaction with the "H-site", where hydrogen is chemisorbed. An addition to chemisorbed benzene (derivatives) takes place by a reaction with an "A-site", where an additive reagent is chemisorbed.

Benzene is ordinarily hydrogenated by steps (1), (2),



Scheme 2. Reaction scheme.

(2′) and (2″), to give CHA as a sole product. Cyclohexene seems to be desorbed from the intermediate (C) by step (4) to some extent under the specified conditions.[1—3] Cyclohexylbenzene is likely produced by step (3) (X=Ph) from intermediate (C) in the hydrodimerization.[4—6]

In the present reaction, it is well understood that the key intermediate (C) appears to give the addition product: X-cyclohexane (X=Cl, Br, OAc or OH) by step (3). Although the addition may be thought to proceed at an early step, this possibility must be negligible, because no polyaddition product was detected and the cyclohexadiene intermediate (B) should be more unstable than intermediate (C). It may also be supposed that the addition product is obtained from the reaction of desorbed CHE with an additive reagent in the liquid phase. However, this process must also be negligible, because the ratio of an addition product to CHE in the reaction products was too high compared with the ratio in the liquid-phase reaction. It is conceivable that a noble metal catalyst adsorbs an additive reagent.

The surroundings of the key intermediate (C) are critically important in determining the activity and selectivity of the catalyst, similarly to the hydrodimerization described by Slaugh and Leonard.[5]

It is very interesting that the optimal noble metal catalyst differs by the kind of additive reagent. To obtain an hydroaddition product effectively, it is necessary to be well ballanced between the hydrogenation and addition reaction simultaneously. In other words, the balance of reaction (2)—(2″) and reaction (3) is important. In the case of a weak adsorbate (AcOH or water), Ru, which is the strongest adsorbent, showed the best catalytic performance. Hydrogenation took place predominately when a weaker adsorbent, for example Rh, was used as the catalyst. Rhodium or Pd, which is a medium-strong adsorbent showed the best catalytic performance in the hydroaddition of HCl or hydrogen bromide, which is a medium-strong adsorbate. Ruthenium, the strongest adsorbent, adsorbed too tightly the additive reagent, resulting in an extremely low conversion. Since Ir and Pt are the weakest adsorbents, they gave high conversion and low selectivity. Namely, hydrogenation predominated over hydroaddition.

The fact that Ru is the best catalyst for the production of CHE from benzene by a partial reduction, is also understandable. The sequence of ethylene desorption from a noble metal[13] may reasonably assume to accord with the sequence of that of CHE.

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