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Study of Chemisorption and Hydrogenation of 1-Butene on Platinum by Temperature-Programmed Desorption

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The temperature-programmed desorption (TPD) chromatograms of 1-butene from platinum black comprised four peaks, A, B, C, and D, with peak maxima at about 265, 390, 580, and higher than 770 K, respectively. Peak A was identified to be 1-butene with a trace amount of *n*-butane. Peaks B and C were the mixtures of 1-butene and propylene. Peak D was methane. The methane and propylene were formed from chemisorbed 1-butene by decomposition as the temperature was raised during the subsequent TPD. The reactivities of various types of chemisorbed hydrogen previously detected by TPD were also investigated with regard to the hydrogenation of 1-butene. Two types of chemisorbed hydrogen, presumed to be present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms and in the bridge form of molecular hydrogen, were found to react with 1-butene.

INTRODUCTION

The existence of four different chemisorbed species of hydrogen (α, β, γ, and δ) on platinum surface has previously been detected by the temperature-programmed desorption (TPD), with peak maxima at about 170, 250, 360, and 570 K, respectively (*1*). The TPD chromatogram with four peak maxima has been confirmed by Verbeek and Sachtler (*2*). These chemisorbed species were tentatively assumed to correspond to two types of molecularly chemisorbed hydrogen: one in linear form (α) and the other in a bridge form (β), and two types of hydrogen atoms: one adsorbed right on top of metal atoms (γ) and the other in the interstices between the metal atoms (δ). The differences in the reactivity of them have been investigated for the H_2–D_2 exchange reaction (*3*), and for the hydrogenation of ethylene (*4*), and of propylene (*5*). The reactivity, however, was not necessarily the same: β-hydrogen not involved in the H_2–D_2 exchange reaction did react with ethylene and propylene to form ethane and propane, respectively (*4, 5*). It is therefore of importance to investigate more deeply on the matter.

In the present study, 1-butene has been employed as the reactant, because it is the lowest olefin that can be hydrogenated and isomerizated, in addition to the simple extension in the carbon chain of reactant olefin molecules, to investigate on the difference in the reactivity of the forms of chemisorbed hydrogen.

The isotope exchange of reactant olefins during the hydrogenation in the presence of deuterium has been interested by many investigators (*6*). The information on the matter can contribute on the mechanism of hydrogenation of olefins. If the reactant olefin molecules are more rapidly exchanged than hydrogenated, the deutero-olefin molecules may be stably chemisorbed on the surface. In the previous cases with ethylene (*4*) and propylene (*5*), the deutero-olefin molecules chemisorbed could not be measured. Since the chemi-

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sorbed state is the intermediate state in the course of the reaction, the information on the chemisorbed species is of importance.

In the present study, the chemisorbed species have been removed by TPD technique and collected for further analysis in order to obtain the information on the reaction mechanism.

EXPERIMENTAL METHODS

Apparatus and materials. The apparatus used was the same as that used previously (*4*). It consisted basically of two parts: an adsorption and reaction system, in which the adsorption and reaction were measured in a conventional manner, and a TPD system, in which adsorbed gas was later desorbed into a carrier-gas stream (N_2 or He) by means of the programmed heating of the catalyst. The concentration of the desorbed gas was measured and recorded by means of a thermal conductivity detector. The catalyst used was the platinum black in the same lot previously employed (*4*). Its surface area, was 3.2×10^3 cm^2/g and the amount used was 1.80 g. The initial reduction and the treatment of catalyst between the experiments have also been described previously (*4*).

Cylinder hydrogen (99.975%) supplied by the Osaka Hydrogen Company was stored in a reservoir for use as a reactant after having been passed over platinized silica at 720 K and then through a liquid-nitrogen trap. The same cylinder hydrogen could also be fed through to the reactor for the reduction of the catalyst. Matheson's deuterium (99.5%) passed through a liquid-nitrogen trap was also used as a reactant. 1-Butene obtained from Tokyo Kasei Kogyo Company, Ltd., was purified by repeated distillation *in vacuo;* the purity was confirmed by means of gas chromatography to be more than 99%. High-purity helium (99.995%) and high-purity nitrogen (99.999%), obtained from the Seitetsu Kagaku Company, Ltd., were used as carrier gases for TPD after having been passed through a molecular sieve trap.

Procedure. In a typical experiment with 1-butene a known amount of 1-butene was adsorbed for 15 min at the experimental temperature. The reactor was then cooled to 238 K with the 1-butene present in the gas phase, and kept for 90 min. Following this, the carrier gas, helium, was diverted from the bypass into the reactor in order to remove the 1-butene in the gas phase, and then after 5 min the catalyst was heated in a programmed manner. The heating was stopped at about 800 K, after which the catalyst was kept in the helium stream for 20 min at the same temperature before cooling. A more detailed desorption of the TPD method has been given elsewhere (*7*). Reproducible results were usually obtained by this procedure. When the results were not reproducible, however, the catalyst was treated with oxygen to oxidize any organic contamination, and was then again reduced by hydrogen. This treatment improved the reproducibility considerably.

In the hydrogenation of 1-butene, various types of chemisorbed hydrogen were first prepared by the TPD technique described previously (*1, 3, 8*), and then 1-butene was admitted to the reaction system to start the reaction. Helium was added to dilute the 1-butene when the circulating pump in the reaction system was operated. After the reaction, all the system except for the reactor was evacuated through a liquid-nitrogen trap to collect any condensable hydrocarbons, which were transferred to a sampler for analysis. The carrier gas was then diverted into the reactor, and any materials adsorbed on the catalyst were removed by TPD.

The reactants, the reaction mixtures, and the desorption products were identified by gas chromatography. The deutero-hydrocarbons obtained after the reaction were analyzed by means of a JEOL JMS D-100 mass spectrometer. Before subjecting the reaction mixtures to mass-spectrometric analysis, if possible, they were separated gas chromatographically to avoid any mutual interference of the mass spectra.

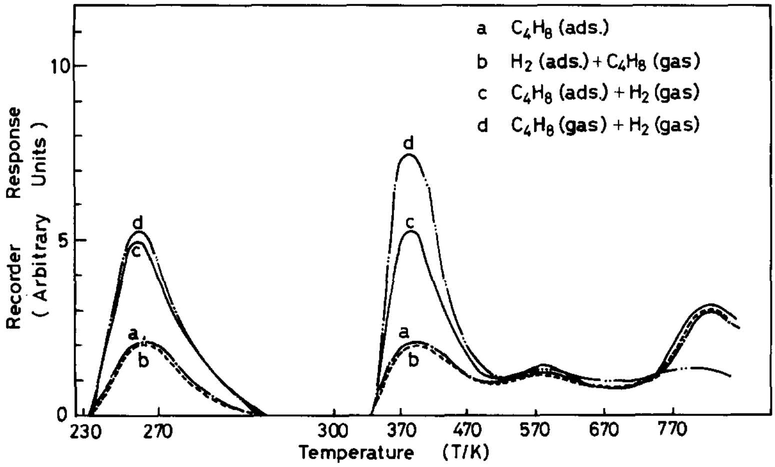

FIG. 1. TPD chromatograms of 1-butene on platinum. (a) 1-C_4H_8 only was adsorbed. (b) H_2 was preadsorbed and 1-C_4H_8 was subsequently admitted. (c) 1-C_4H_8 was preadsorbed and H_2 was subsequently admitted. (d) 1-C_4H_8 and H_2 were simultaneously admitted.

RESULTS AND DISCUSSION

Temperature-Programmed Desorption

Figure 1 shows some typical TPD chromatograms taken after the 1-butene had been adsorbed on the platinum black in the absence or presence of hydrogen as indicated, with helium used as the carrier gas. The pressure of the 1-butene or hydrogen admitted was ca. 5×10^2 Pa, and the reaction temperature was 238 K. These four TPD chromatograms resemble each other, characteristically being composed of four peaks appearing at about 265, 390, 580, and higher than 770 K. These peaks are referred to as A, B, C, and D in the order of appearance with increase in the temperature. By gas chromatographic analysis, peak A was identified to be 1-butene with trace amount of *n*-butane. Peaks B and C were identified as the mixtures of 1-butene and less amount of propylene. Peak D was methane. It is suggested that the butane was formed by the self-hydrogenation of chemisorbed 1-butene, where hydrogen was absent. The methane and propylene may be formed by decomposition from the chemisorbed 1-butene heated by TPD. In order to observe the desorbing hydrogen more clearly, nitrogen was used as the carrier gas for the TPD; only δ-hydrogen was observed in the TPD chromatogram. The other forms of hydrogen may have been removed from the surface when 1-butene was admitted, probably by the surface hydrogenation to *n*-butane. The possibility of the displacement in the chemisorption by 1-butene, however, cannot be excluded at this stage. On the surface, therefore, only the admitted 1-butene along with δ-hydrogen was chemisorbed in the form of 1-butene and/or *n*-butane.

It is not very clear at this stage whether the *n*-butane in the peak A, where hydrogen was present, is a result of the self-hydrogenation, or of the desorption of *n*-butane formed by hydrogenation, or both.

Reactivity of Chemisorbed Hydrogen

Table 1 shows the results of the surface hydrogenation experiments with hydrogen preadsorbed on the platinum black in various forms (the surface reactant), and with gaseous 1-butene subsequently admitted into the reaction system (the gas-phase reactant). No gaseous hydrocarbon other than 1-butene and *n*-butane was observed under the present experimental conditions; the isomerization of 1-butene and of *n*-bu-

TABLE 1

Hydrogenation of 1-Butene on Platinum Black[a]

Series	Surface reactant			Gas-phase	
	Type of chemisorbed hydrogen and estimated amount[b] (mm^3, STP)			Reactant pressure of 1-butene (10^2 Pa)	Product *n*-Butane formed (mm^3, STP)
	β	γ	δ		
A	—	—	—	6.8	0.1
B	—	—	3.9	6.4	0.1
C	—	7.7	2.6	6.3	2.9
D 1	12.3	9.6	6.2	6.5	4.1
D 2	30.5	8.7	6.0	6.8	5.3

[a] Catalyst weight, 1.80 g. Reaction temp., 238 K, and reaction time, 90 min.

[b] Estimated from TPD chromatograms in comparable experiments.

tane could not be detected. The amounts of *n*-butane formed in Series B with δ-hydrogen agreed well with that in Series A, in which *n*-butane was formed by a self-hydrogenation reaction. Apparently, δ-hydrogen hardly reacts with the gas-phase reactant under the present experimental conditions.

In Series C, with δ- and γ-hydrogen preadsorbed on the surface, however, relatively larger amounts of *n*-butane were produced than in Series B. In the TPD chromatogram obtained after 1-butene was admitted to the preadsorbed hydrogen, where nitrogen was used as the carrier gas, the γ-hydrogen disappeared, while δ-hydrogen was still present in almost the same amount. It is, therefore, clear that γ-hydrogen is involved in the hydrogenation.

In Series D, in which β-, γ-, and δ-hydrogen were preadsorbed, the formation of *n*-butane was again observed. The contribution of β-hydrogen to the hydrogenation, however, was not clear at this stage, because the amounts of *n*-butane formed were still smaller than those of γ-hydrogen.

To elucidate the point, the preadsorbed hydrogen was partially displaced by deuterium before 1-butene was introduced, and the deutero-*n*-butanes formed by hydrogenation were then analyzed. The participation of the different types of chemisorbed hydrogen was consequently elucidated. For the sake of simplicity, the word "hydrogen" in the present paper will hereafter stand for both isotopes, protium and deuterium, and, where necessary, the individual isotopes will be designated as H and D. The types of surface used were: (1) δ-Hydrogen was displaced by deuterium, and γ- and β-hydrogen were protium (βH–γH–δD); (2) δ- and β-hydrogen were deuterium, and γ-hydrogen was protium (βD–γH–δD); (3) δ-Hydrogen was protium, and β- and γ-hydrogen were deuterium (βD–γD–δH). The method of preparation was described previously (*8*); the isolation of different types of chemisorbed hydrogen was confirmed by separate TPD experiments.

Table 2 shows the results of hydrogenation: the type of surface employed, the amounts of hydrogen preadsorbed and those of the individual deutero-*n*-butanes formed by the hydrogenation are shown. The reactions were carried out at 238 K for 90 min. In the mass spectra of 1-butene, the reactant, the $m/e > 56$ could not be observed, the ^{13}C contribution having been corrected; the H–D exchange between sur-

TABLE 2

Hydrogenation of 1-Butene with Labeled Hydrogen Chemisorbed on Platinum[a]

Type of surface employed	Amounts of hydrogen preadsorbed[b] (mm^3, STP)			Pressure of C_4H_8 (10^2 Pa)	Deutero-*n*-butanes formed (mm^3, STP)					
	β	γ	δ		d_0	d_1	d_2	d_3	d_4	Total
βH–γH–δD	15.9	10.9	6.3	6.1	11.1	—	—	—	—	11.1
βD–γH–δD	14.7	11.1	5.6	6.9	12.1	0.7	—	—	—	12.8
βD–γD–δH	8.1	7.7	5.0	6.3	5.4	1.3	0.4	0.1	—	7.2

[a] Catalyst weight, 1.80 g. Reaction temp., 238 K, and reaction time, 90 min.

[b] Estimated from TPD chromatograms in comparable experiments.

face deuterium and gaseous 1-butene could not be detected.

Obviously, 1-butene was deuterated to deutero-*n*-butanes over the βD–γH–δD, and βD–γD–δH surface, but not over the βH–γH–δD surface. These results agree quite well with the above suggestions that δ-hydrogen does not, and γ-hydrogen does, participate in the hydrogenation. The results also suggest the participation of β-hydrogen, which was not detected before. The total amount of deutero-*n*-butanes formed over the βD–γD–δH surface was larger than that over the βD–γH–δD surface under similar experimental conditions, and γ-hydrogen is seemingly more reactive than β-hydrogen. Over the βD–γD–δH surface, *n*-butane-d_0 was formed, suggesting that the self-hydrogenation of 1-butene took place even when hydrogen was present.

After the reaction, 1-butene molecules adsorbed on the surface was removed by TPD technique, and then analyzed by means of the mass spectrometer. The mass spectrometric analysis of reactant olefins chemisorbed and removed by TPD could not be succeeded in the previous cases with ethylene and propylene (*4, 5*), because the amounts of olefins desorbed were too small to be transferred to the sampler for analysis. The results of 1-butene are shown in Table 3; deutero-1-butenes were observed. Since the deutero-1-butenes were not observed in the gas phase, the results suggest that the hydrogenation of chemisorbed 1-butene is easier than the desorption of chemisorbed 1-butene.

In peak A, any deutero-1-butene was not observed in the case with βH–γH–δD surface. The result suggest that δ-deuterium does not react with 1-butene to form deutero-1-butenes below 290 K. The formation of deutero-1-butenes observed in the case with βD–γH–δD surface was therefore due to the participation of β-deuterium. In the case with βD–γD–δH surface, the participation of β-deuterium is obvious, but that or γ-deuterium cannot be excluded. The deutero-1-butenes observed may be formed on the surface with β-deuterium at 238 K. Because the hydrogenation of 1-bu-

TABLE 3

1-Butenes Desorbed from Platinum Surface

Type of surface employed	TPD peaks	Deutero-1-butenes formed (mm^3, STP)					
		d_0	d_1	d_2	d_3	d_4	Total
βH–γH–δD	A	1.7	—	—	—	—	1.7
	B	1.2	—	—	—	—	1.2
	C	0.5	0.1	—	—	—	0.6
βD–γD–δH	A	1.7	0.1	0.1	—	—	1.9
	B	0.7	0.3	0.2	0.1	—	1.3
	C	0.4	0.1	0.1	—	—	0.6
βD–γH–δD	A	2.1	0.1	—	—	—	2.2
	B	1.3	0.1	0.1	—	—	1.5
	C	0.6	0.1	—	—	—	0.7

tene admolecules are more rapid than the desorption as mentioned above, the possibility of their formation during TPD is excluded.

In peak B, deutero-1-butene was not observed in the case with βH–γH–δD surface. Since peak B appeared between 350 and 500 K, and since δ-hydrogen, peak δ, appeared between 470 and 670 K, δ-deuterium does not suggestively participate in the H–D exchange reaction with 1-butene.

In the case with βD–γD–δH surface, the total amount of deutero-1-butenes observed was the greatest. The result can be reasonably explained by the participation of γ-deuterium.

Small amounts of deutero-1-butenes were observed in the case with βD–γH–δD surface, where γ-hydrogen was protium. The result can be explained in such a way that the deutero-1-butenes was formed from β-deuterium and 1-butene at the lower temperature and subsequently desorbed by the rise of temperature. The deutero-1-butenes formed by this way may be also included in the case with βD–γD–δH surface.

Peak C appeared between 500 and 600 K, where δ-hydrogen mostly desorbed. In the case with βH–γH–δD surface, therefore, the deuterium atoms in deutero-1-butenes observed obviously came from δ-deuterium, which is only deuterium source.

The amount of deutero-1-butenes observed in the case with βD–γH–δD surface agreed with that with βH–γH–δD. The result suggests that the deuterium atoms in the deutero-1-butenes came from δ-deuterium alone. No contribution of β-deuterium on deutero-1-butenes in peak C is accordingly concluded.

In the case with βD–γD–δH surface, some amounts of deutero-1-butenes were observed. The result suggests that the deuterium atoms in the deutero-1-butenes came from γ-deuterium alone, and that deutero-1-butenes formed at the lower temperature subsequently desorbed by the rise of temperature during TPD, since β-deuterium does not contribute on the deutero-1-butenes in peak C as mentioned above.

The mass spectrometric analysis of *n*-butane in peak A, of propylene in peaks B and C, and of methane in peak D was not carried out, because the amounts of *n*-butane and of propylene were too small to be separated from 1-butene by gas chromatography, and because the vapor pressure of methane was too low to be separated from the carrier gas by condensation.

Since the chemisorbed *n*-butane is the precursor of the gaseous *n*-butane, *n*-butane in peak A may probably contain deutero-*n*-butanes, in case deutero-*n*-butanes were observed in the gas phase. If any deuteropropylenes and/or deuteromethanes are observed, they are reasonably considered to be formed from the chemisorbed deutero-1-butenes by the decomposition during TPD. The deutero-1-butenes, however, do not necessarily give the deuteropropylenes and the deuteromethanes, which may depend on the degree of deuteration and the mechanism of decomposition of the chemisorbed deutero-1-butenes.

On the mechanism of the hydrogenation of olefins, extensive studies have been reported (*6*, *9*, *10*). In the hydrogenation of ethylene over platinum catalyst, Bond–Wells mechanism may be accepted. According to the ir study by Soma (Soma–Noto) (*10*), π-adsorbed ethylene was easily hydrogenated at such low temperature as 195 K, and no hydrogenated species remained on the surface. The observation is consistent with the present result that the hydrogenation of 1-butene was more rapid than the desorption. Accordingly, the following scheme of the hydrogenation of 1-butene may be suggested. 1-Butene is first chemisorbed on the surface and rapidly exchanged with the surface deuterium, without desorbing from the surface. The deutero-1-butenes formed are stably chemisorbed on the surface with π-bond. Then, the deutero-1-butenes are hydrogenated to deuterobutanes and desorbed from the surface.

The four types of chemisorbed hydrogen were tentatively assigned on the basis of the previous results (*1*) and the postulates of other workers (*11–16*). The γ- and δ-hydrogen were assigned to the weakly and strongly chemisorbed hydrogen atoms so far proposed. The α-hydrogen was assigned to the linearly chemisorbed hydrogen molecules. The β-hydrogen was the intermediate between α- and γ-hydrogen. Later, Primet *et al.* (*17*) and Dixon *et al.* (*18, 19*) independently proposed their assignment on the basis of the ir studies. Dixon *et al.* deduced the existence of five kinds of hydrogen adsorption. Type I is physisorption, and the other four types, II–V, were corresponded to α–δ hydrogen.

It has previously been presumed that γ-hydrogen is present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms, and that β-hydrogen is molecular hydrogen chemisorbed in a bridge form (*1*). The difference in the reactivity may, accordingly, be due to the chemisorbed state, whether or not the H–H bond has been split. In the H_2–D_2 exchange reaction, β-hydrogen is not reactive, but it is reactive in the hydrogenation of olefins, and in the H–D exchange between the surface deuterium and 1-butene. It is, accordingly, probable that a different tendency would be shown depending upon the sort of reaction; the explication of the other reactions awaits further investigations.

CONCLUSION

While some of the information could perhaps be obtained otherwise, the TPD technique in many cases can be used with unique advantage. Although the information that 1-butene is more strongly chemisorbed than hydrogen on a catalyst had already been suggested on the basis of kinetic data (*9*), it was more clearly shown by TPD, and in addition, the amounts of chemisorbed species could be estimated. Using isotopes, the individual chemisorbed species can be differently labeled, and the reactivity of each is separately measurable. The participation of various types of chemisorbed hydrogen in the 1-butene hydrogenation was similar to that in the hydrogenation of ethylene and of propylene. γ-Hydrogen, presumed to be present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms and β-hydrogen, presumed to be molecular hydrogen chemisorbed in a bridge form, were found to be involved in the 1-butene hydrogenation. The information on the chemisorbed deutero-1-butenes during the reaction revealed by the labeled TPD technique, suggests the following scheme of hydrogenation: 1-butene chemisorbed was first exchanged with deuterium to form deutero-1-butenes, and before desorbing from the surface, the deutero-1-butenes were hydrogenated to form deuterobutanes.

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