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Hydrogenation of 1,3-Butadiene on Pd in Sulfuric Acid Solution

I. Kinetic Study

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Hydrogenation of 1,3-butadiene on Pd foil in 0.5 *M* sulfuric acid solution was studied by deuterium tracer method. Hydrogen atoms were supplied from H_2, H_{diss} (hydrogen dissolved in Pd), and $H^+ + e^-$ (electroreduction). The difference in the hydrogen source did not affect reaction rate, distribution of products and distribution of deuterium in each products. They were only a function of the catalyst (electrode) potential and common conclusions were derived independent of the hydrogenation methods. In region H (H_2 diffusion to the surface is rate controlling), only butenes are formed. On the other hand, in region R (1,3-butadiene diffusion is rate controlling), butenes are further hydrogenated to butane of the main product (>50%). In region I (intermediate region between H and R), all the products are formed, though the amount of butane is relatively small because of a strong adsorption of 1,3-butadiene which replaces the butenes once formed on the surface. In this region, distributions of deuterium in 1- and *trans*-2-butenes are the same and different from that of *cis*-2-butene. Butane is the most deuterium-exchanged species with the average deuterium number of ca. 5. The reaction mechanism discussed includes: (i) 1-butene and *trans*-2-butene are formed via *syn*-1-methyl-π-allyl from *transoid*-1,3-butadiene and *cis*-2-butene via anti-1-methyl-π-allyl from *cisoid* one, (ii) the individuality of these routes is kept during the reaction, and (iii) butane is produced mainly via 1-butene. This mechanism is the same as that on Pt/graphite in sulfuric acid solution (H. Kita, K. Shimazu, Y. Kakuno, and A. Katayama-Aramata, *J. Catal.* **74**, 323 (1982)) and except for (iii) on Pd catalysts in the gas phase (E. F. Mayer and R. L. Burwell Jr., *J. Am. Chem. Soc.* **85**, 2881 (1963); A. J. Bates, Z. K. Leszczyński, J. J. Phillipson, P. B. Wells, and G. R. Wilson, *J. Chem. Soc.* 2435 (1970)).

INTRODUCTION

We have examined the hydrogenation of lower unsaturated hydrocarbons such as ethylene (*4*), propene (*1, 5*), butenes (*1, 6*), 1,3-butadiene (*1, 6, 7*), and 2-butyne (*8*) on platinum catalysts (electrodes) in aqueous acid solution and confirmed that the electrochemical approach is powerful on providing new information, not available in heterogeneous catalytic hydrogenation in the gas phase, e.g., the saw-toothed distribution of deuterium in butenes from 1,3-butadiene (*9*), the high reactivity of the weakly adsorbed hydrogen (*7*), and the two maxima distribution of deuterium in paraffins from butenes (*1, 10*). This information ought to be due to the characteristic advantages of the electrochemical system. (i) The catalyst potential during the reaction reflects the activity of adsorbed hydrogen. (ii) Its adsorption state and amount are readily observed *in situ* by using a potential sweep method. (iii) In D_2O solution, the fraction of deuterium of the surface hydrogen atoms is attained at about unity during the reaction through the step, $D(a) \rightleftarrows D^+ + e^-$, and hence highly deuterated products are formed.

On account of these advantages, the electrochemical method is now applied to the study of the hydrogenation of 1,3-butadiene on Pd.

No work has been reported as to the hydrogenation of 1,3-butadiene on Pd in electrochemical system, though Young *et al.* (*11*) conducted the hydrogenation of 1,3-butadiene on Pd in 95% ethanol and found a highly selective formation of butenes (94%).

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Other works reported are mainly on Pt. There are a few reports on the hydrogenation of ethylene on Pd electrode. Burke *et al.* (*12*) observed the potential and electrical resistance changes during the reaction and concluded that the reaction rate is governed by diffusion of ethylene. Sakellaropoulos and Langer (*13*) studied the kinetics on partially wettable porous Pd electrode and concluded that ethyl radical is formed by two steps: $C_2H_4(a) + H^+ + e^- \rightarrow C_2H_5(a)$ and $C_2H_4(a \text{ or } g) + H(a) \rightarrow C_2H_4(a)$. However, no mechanistic study by deuterium tracer method has been reported on the electrochemical system.

On the other hand, heterogeneous catalytic hydrogenation of 1,3-butadiene in gas phase has widely been studied on various catalysts in view of the selective hydrogenation. Mechanistic studies by deuterium tracer method were conducted by Meyer and Burwell (*2*) and Wells *et al.* (*3, 14–16*) in the 1960s. They proposed half-hydrogenated species with delocalized π-orbitals under the same initial conformations on Pd catalysts. Interconversions between *trans*- and *cis*-forms was not allowed. After these works, few mechanistic works on Pd catalysts in the gas phase have been reported.

The present paper describes the results obtained by the electrochemical and deuterium tracer methods. These data enable us to discuss the reaction mechanism in more detail than in the case of the catalytic hydrogenation in the gas phase. Furthermore, effect of the hydrogen source, i.e., H_2 gas, H_{diss} (the dissolved hydrogen in Pd), and H^+ (in solution) + e^-, is examined.

EXPERIMENTAL

Catalyst and pretreatment. Smooth Pd foils (99.98% purity, Tanaka Noble Metals Ind. Co. Ltd.) were mainly used as catalysts (working electrodes). Their apparent surface areas were 24.5 and 11.1 cm^2. The foils were electrochemically preoxidized at 1.4 V vs rhe (reversible hydrogen electrode) for 5 min in 0.5 *M* sulfuric acid solution and subjected to one-and-half triangular potential pulses in a range from 0.3 to 1.4 V, and then reduced at 0.3 V for 5 min. Unless a voltammogram for the clean surface was obtained, the foils were reoxidized at 1.4 V. The above oxidation (*17*) and even the reduction process (*18*) causes a dissolution of palladium as Pd^{2+} and gives the solution itself an activity for the isomerization of butenes by Pd^{2+} (*19*). Thus, the solution was replaced by another fresh 0.5 *M* H_2SO_4 after the treatment. Second reduction of the foils at 0.3 V for 5 min was then applied before reaction. In the isotopic studies in 0.5 *M* D_2SO_4, Pd foil was pretreated in another cell of 0.5 *M* D_2SO_4 in a similar manner and then transferred into a test cell. Hydrogenation by H_{diss} was conducted on Pd foil either cathodically polarized or kept in contact with hydrogen gas prior to use.

In order to examine the adsorption states of hydrogen on Pd, Au electrode covered with a monolayer of Pd (Pd/Au) was prepared because at a Pd metal foil a large oxidation peak of the dissolved hydrogen on voltammogram veils a small peak of adsorbed hydrogen. A Au foil (12 cm^2, 99.98% purity, Tanaka Noble Metals Ind. Co. Ltd.) was first activated at 1.8 V for 30 s and then cathodically polarized for a desired time in 0.5 *M* sulfuric acid solution of 6.5×10^{-5} *M* $PdSO_4$. After the transfer of Pd/Au electrode to a test cell, no further pretreatment was conducted.

Apparatus and cell. Reaction was carried out at room temperature in a closed circulation system with a test cell of three-compartment type, or a cell in which two counter electrode compartments faced both the sides of the working electrode through anion-exchange membranes. Each compartment was filled with 0.5 *M* H_2SO_4 (or D_2SO_4). All the potentials were referred to rhe in the same solution.

Potential was controlled with a potentiostat (Yanagimoto Mfg. Co., Ltd. V-8) and a function generator (Nichia Keiki Co., Ltd., S-5A).

Gases and solutions. 1,3-Butadiene was purified up to 4 *N* purity by a fractional separation with a gas chromatograph. Helium, hydrogen, and deuterium (Showa Denko, 99.97 D%) were purified up to 7 *N* purity with commercial purifiers (LW-06SC and RT-025, Japan Pionics Co., Inc., for He and for H_2 and D_2, respectively). The reaction gas was an atmospheric mixture of 1,3-butadiene, H_2 (or D_2), and He. In the cases of electroreduction and hydrogenation by H_{diss}, reaction gas was a mixture without H_2.

Solution of 0.5 *M* H_2SO_4 was prepared from the guaranteed reagent (Wako Pure Chemical Co., Ltd.) and triply distilled water. Solution of 0.5 *M* D_2SO_4 was prepared from D_2O (Merck, 99.75 D%) and sulfuric acid-d_2 (Merck 99 D%) and subjected to preelectrolysis overnight in order to remove impurities in the solution.

Analysis of products. The reaction gas was occasionally sampled for analysis with a gas chromatograph (VZ-7, 5 m, 273 K). After the reaction, gaseous products were collected with a liq. N_2 trap and separated into each product by a gas chromatograph for a mass spectrometric analysis. Low ionization voltages were applied in order to minimize an error caused by the fragmentation.

RESULTS

1. *Kinetics and Distribution of Products*

Electroreduction. Figure 1 presents a relation between electrode potential, ϕ, and current density, i, at 5 min under the potentiostatic electroreduction. A current at a given potential, e.g., 0.1 V, under He (hydrogen evolution) increases to a large extent by the introduction of 1,3-butadiene, indicating an occurrence of the reduction of 1,3-butadiene. There exists a linear relation between log i and ϕ (the Tafel relation) at $\phi > 0.16$V (named region H) with a slope of 0.07 V/decade.

Time variation of the gas composition also gives the reaction rate. Initial rate thus obtained, v(mol · min^{-1} · cm^{-2}), is trans-

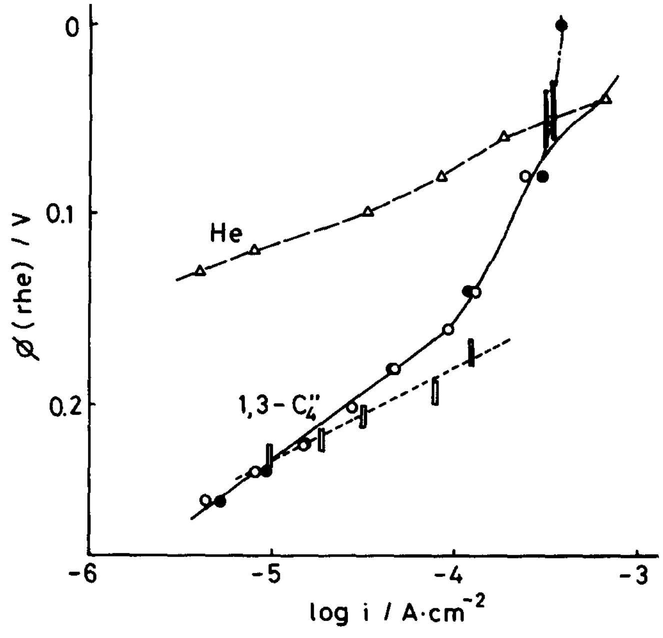


FIG. 1. Relations between ϕ and log i (at 5 min) in the electroreduction of 1,3-butadiene (○, P_R = 22 mm Hg) and under He atmosphere (△) on Pd electrode. ●, ▯, and ▮ represent the initial reaction rates estimated from the products under electroreduction, in the hydrogenation by H_2 and by H_{diss}, respectively. The latter two are plotted against ϕ_{oc}.

formed into a current density, i_c, by the following equation,

$$i_c \text{ (ampere} \cdot \text{cm}^{-2}) = F \frac{v}{60} \{2S + 4(1 - S)\} \quad (1)$$

where F is the Faraday constant and S is the selectivity of butenes defined as

$$S = \frac{\text{amount of butenes}}{\text{amount of butenes + amount of butane}} \quad (2)$$

and compared with the observed current density in Fig. 1 (●). Agreement is satisfactory in region H, showing a current efficiency of 100%. At lower potential of $\phi < 0.08$ V (named region R), i_c becomes almost independent of the electrode potential.

The reaction rate, v, is of first order at 0 V and zeroth order at $\phi > 0.16$ V in the 1,3-butadiene pressure. These dependences imply that the electrode surface is covered mainly with hydrogen in region R whereas with the species from 1,3-butadiene in region H, respectively. This is confirmed from voltammograms taken on Pd/Au (Fig. 2). When the electrode potential is swept in the positive direction, the oxidation current of the adsorbed hydrogen appears in a potential range of $0 < \phi < 0.6$ V. Figures 2a and b show the oxidation current–potential relations when the potential is swept from 0 and 0.2 V, respectively. Dashed and solid curves represent the voltammograms under the absence and the presence of 1,3-butadiene. Comparison of these curves clearly shows the presence (Fig. 2a) and absence (Fig. 2b) of the adsorbed hydrogen atoms during the electroreduction of 1,3-butadiene at 0 and 0.2 V, respectively.

Rate constant at 0 V is calculated from log v-log P_R plot (P_R, the partial pressure of 1,3-butadiene) as 3.5×10^{-9} mol · min^{-1} · cm^{-2} · mm Hg^{-1}, which is close to the rate constant for the diffusion of 1,3-butadiene, 5.9×10^{-9} mol · min^{-1} · cm^{-2} · mm Hg^{-1} (*6*). Therefore, it is concluded that the diffusion of 1,3-butadiene controls the reaction rate in region R.

Potential dependence of the reaction rates for the respective products is shown in Fig. 3. In region H, butane does not form at all and 1-butene is the main product. As the electrode potential shifts in the negative direction, the rate of each butene formation decreases; especially that of 1-butene formation is sharply affected in a potential range of $0.08 < \phi < 0.16$ V (region I). At $\phi \leq 0.08$ V, butane becomes a main product. The distributions of products are summarized in Fig. 4 where the selectivity of butane formation, (1-S), and the relative ratios among the three isomeric butenes of 1-, *trans*-2-, and *cis*-2-butene are plotted

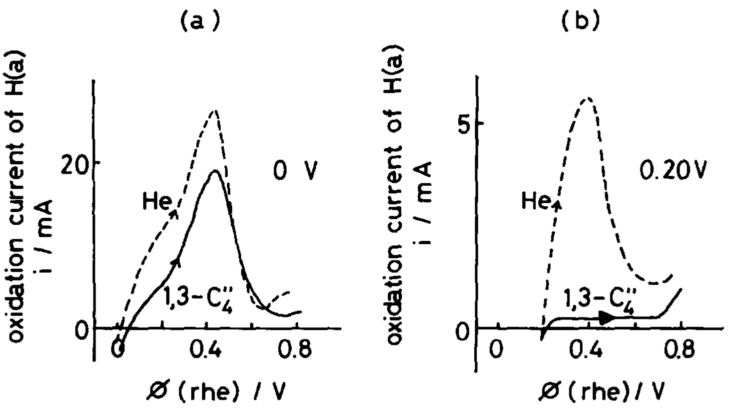


FIG. 2. Voltammograms on Pd/Au electrode during the electroreduction of 1,3-butadiene (—) and under He atmosphere (---) at (a) 0 V and (b) 0.20 V. Sweep rate; 1.0 V · sec^{-1}.

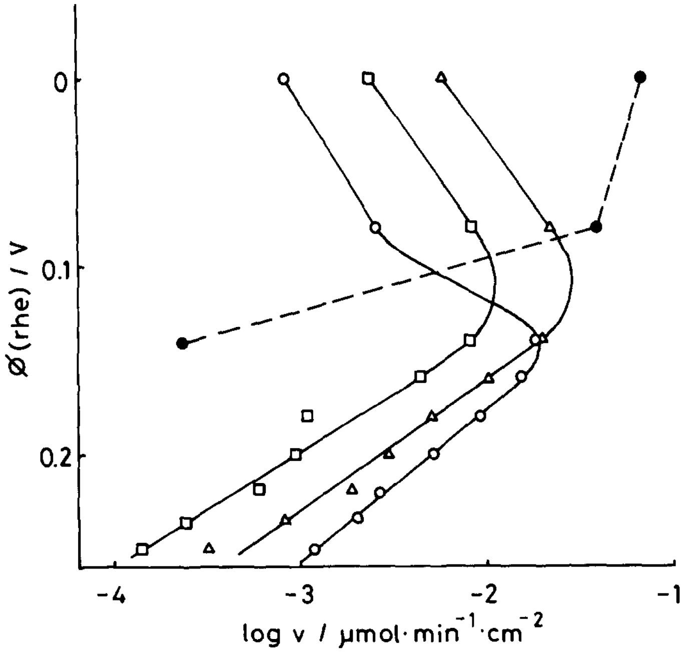


FIG. 3. Potential dependence of the reaction rate for the formation of each product on Pd electrode. ●, Butane; ○, 1-butene; △, *trans*-2-butene; □, *cis*-2-butene.

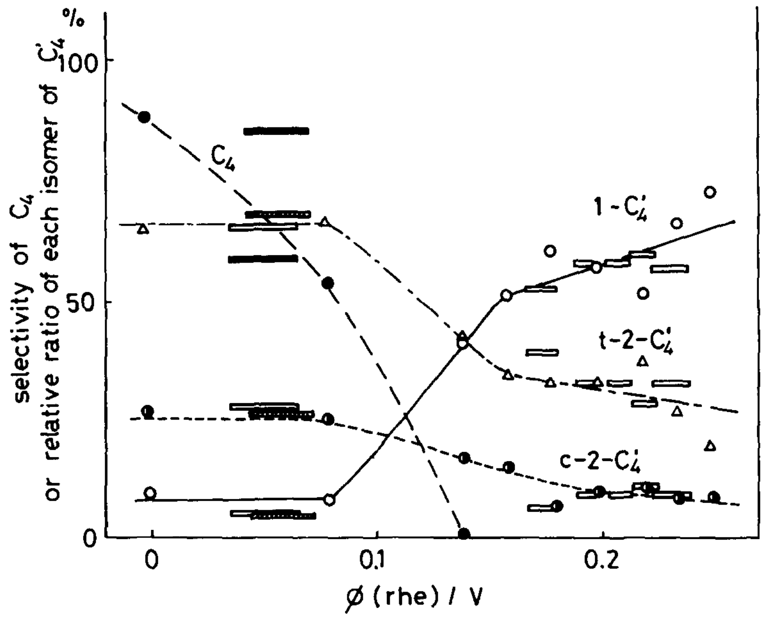


FIG. 4. Distribution of products in the electroreduction (●, ○, △, ◑), the hydrogenation by H_2 (▬, ▭), and by H_{diss} (▬, ▥) of 1,3-butadiene. ●, ▭ ; selectivity of butane, ○, ▭ , ▥ ; relative ratio of 1-butene, △, ▭ , ▥ ; *trans*-2-butene, □, ▭ , ▥ ; *cis*-2-butene.

against the electrode potential. The relative ratios are 57 : 32 : 11 at 0.2 V and 9 : 65 : 26 at $\phi \leq 0.08$ V. In the latter potential range, the butenes are minor products with $S < 0.1$.

Hydrogenation by H_2. Reaction rate is proportional to P_H (the partial pressure of H_2) when P_H is relatively low. Rate constant is 3.2×10^{-10} mol · min^{-1} · cm^{-2} · mm Hg^{-1} which is equal to the rate constant for the diffusion of H_2, 3.3×10^{-10} mol · min^{-1} · cm^{-2} · mm Hg^{-1} (*6*). On the other hand, the reaction rate at higher P_H is in good agreement with the limiting diffusion rate of 1,3-butadiene.

Potential of the catalyst called open circuit potential, ϕ_{oc}, provides an information concerning the activity of the adsorbed hydrogen. Relation between ϕ_{oc} at 5 min and P_H is shown in Fig. 5. At lower P_H, there is a linear relation as

$$\phi_{oc}\ (\mathrm{mV}) = \mathrm{const} + 43 \log P_H, \qquad (3)$$

and ϕ_{oc} is much more positive than that under the absence of 1,3-butadiene but H_2. Thus, the value of ϕ_{oc} reflects a hydrogen-deficient surface state.

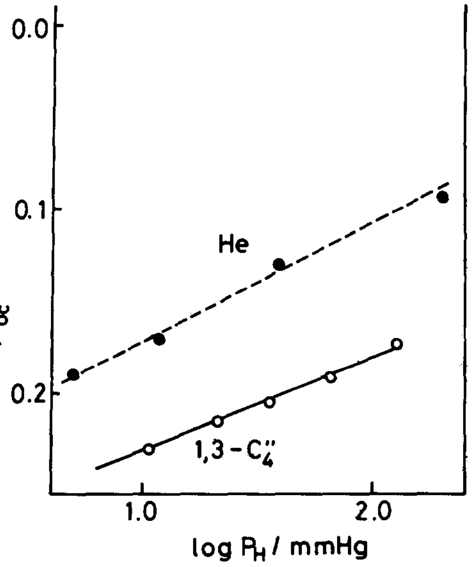


FIG. 5. Open circuit potential of Pd electrode at 5 min in the presence (○) and absence (●) of 1,3-butadiene (P_R = 22 mm Hg) as a function of P_H.

The above results on the reaction rate and ϕ_{oc} lead to the conclusion that the diffusion of H_2 or 1,3-butadiene controls the reaction rate according as lower or higher P_H, respectively.

Reaction rates in terms of current density is plotted against ϕ_{oc} in Fig. 1 (dotted line). The reaction rate in the hydrogenation by H_2 is slightly faster than that of electroreduction in region H. However, no difference in the distribution of products is observed between both the reactions as shown in Fig. 4 (▬,▭). Therefore, the difference in the source of hydrogen atoms, H_2 or $H^+ + e^-$, has little influence on the reaction mechanism. Hereafter the names of region H, I, and R are used accordingly as ϕ or $\phi_{oc} \geq 0.16$, $0.16 \sim 0.08$, and ≤ 0.08 V, respectively.

Hydrogenation by H_{diss}. Contact of 1,3-butadiene with the Pd foil loaded with dissolved hydrogen causes a potential shift in the positive direction by the consumption of the dissolved hydrogen. The reaction is started with a lower initial ϕ_{oc} (<50 mV) to ensure a sufficient H_{diss}. The reaction rate (▮ in Fig. 1) and the distribution of products (▬,▭ in Fig. 4) are similar to those measured in region R with the other hydrogen sources. Therefore, it is also concluded that the rate-determining step is the diffusion of 1,3-butadiene in the lower potential region.

2. Competitive Hydrogenation between 1,3-Butadiene and Butene

In contrast to Pt catalysts, Pd shows the highly selective formation of butenes from 1,3-butadiene in region H and even in region I. In order to clarify the high selectivity, the competitive hydrogenation between 1,3-butadiene and butene was examined at a typical potential of 0.14 V where both butenes (*20*) and 1,3-butadiene are hydrogenated. Figure 6a shows changes of the reactant partial pressures with time. Arrows in the figure indicate the introduction of 1,3-butadiene or *cis*-2-butene. After the first dose of *cis*-2-butene, 1,3-butadiene was

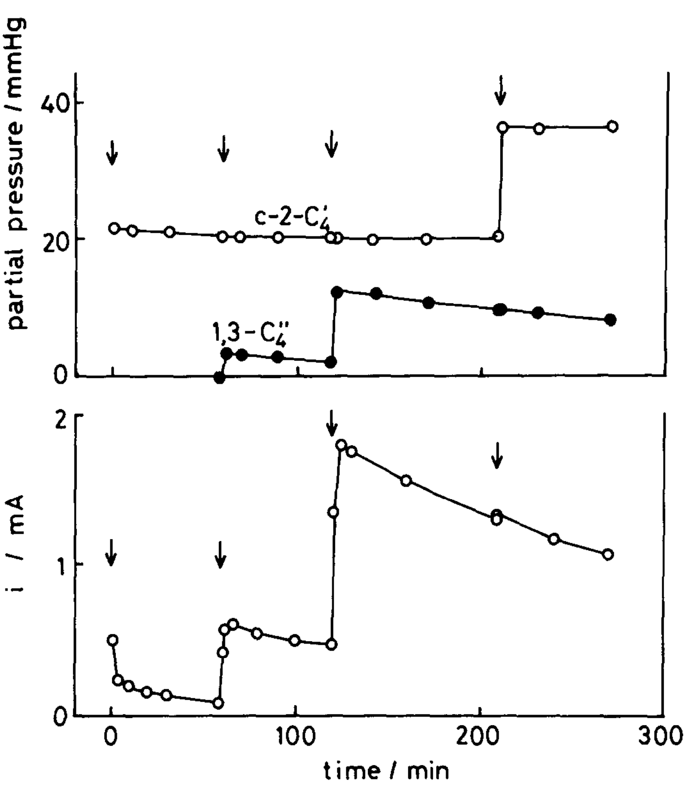


FIG. 6. Time course of the competitive hydrogenation between 1,3-butadiene and *cis*-2-butene on Pd electrode at 0.14 V. Changes of (a) the partial pressure of 1,3-butadiene (●) and *cis*-2-butene (○), and (b) current.

successively added (second and third arrows, P_R = 3.4 and 9.7 mm Hg). The pressure decrease of *cis*-2-butene ceases completely but that of 1,3-butadiene continues with time. The subsequent addition of *cis*-2-butene (fourth arrow) causes no change; neither the reaction of 1,3-butadiene is disturbed nor the hydrogenation of *cis*-2-butene is initiated. The corresponding current change is presented in Fig. 6b which reflects the situation much more clearly, a large increase by 1,3-butadiene but not at all by *cis*-2-butene (fourth arrow).

Initially mixed reaction gas of 1,3-butadiene and *cis*-2-butene leads to similar results, i.e., 1,3-butadiene of only 3.5% accelerates the current density and that of 20% give almost the same value as 1,3-butadiene alone of the equal partial pressure. When 1,3-butadiene exceeds 25%, the reaction of *cis*-2-butene is completely suppressed. Thus, it is concluded that 1,3-butadiene preferentially adsorbs on the surface and undergoes the hydrogenation. However, a preliminary test shows that this tendency is somewhat weakened when 1-butene is mixed with 1,3-butadiene, indicating somewhat stronger adsorption of 1-butene than *cis*-2-butene.

3. *Isotopic Studies: Deuteration of 1,3-Butadiene*

First, we examined a dependence of the distribution of deuterium (D distribution) in products on reaction time by repeating separate electroreductions at different reaction times (0.12 V). The D distributions in 1-butene and *trans*-2-butene do not change at least up to a conversion of 10% of 1,3-butadiene. However, the D distribution in *cis*-2-butene slightly changes with the conversion; average deuterium number, defined as

D.N. = $\sum_{i=1}^{n} i \cdot X_i$ where n is the number of hydrogen in a molecule and X_i is the fraction of d_i species ($C_4H_{n-i}D_i$), changes from 2.9 to 2.7 with the increase of the conversion from 0.6 to 8.4%. However, this change is small and does not affect intrinsic features of the D distribution.

Electroreduction. Results obtained at 0.18 and 0.12 V, are listed in Table 1. They are almost the same with each other. A maximum appears at d_1 species for the respective butenes and all the D.N.'s are approximately two in contrast to the higher values of 3 ~ 4 on Pt net in 0.5 M D_2SO_4 (*6*). One can notice that among the three isomeric butenes, *cis*-2-butene is most and 1-butene least deuterium-exchanged in all cases.

Deuteration by D_2. Run 3 (P_D = 55 mm Hg, ϕ_{oc} = 186 ~ 172 mV, S = 1.0) in Table 1 gives similar results to those obtained by the electroreduction at nearly the same potential, run 1 (ϕ = 180 mV, S = 1.0). One will notice common features in runs 4 and 5 that the D distribution in *trans*-2-butene is the same as that in 1-butene, indicating the participation of a common intermediate for the formation of these two butenes and that *cis*-2-butene is much more deuterium-exchanged than the others. Run 5 will be grouped in region I rather than region R because a value of S is smaller than 0.50. The D distribution in *cis*-2-butene is largely affected by P_D; the higher P_D is, the larger D.N. is.

Deuteration by D_{diss}. Run 6 (S = 0.59) is to be compared with run 5 (S = 0.62) because of the close values of S. There is no difference between them, though the dissolved deuterium gives somewhat smaller D.N. than D_2 does. As in the case of the deuteration by D_2, D distributions in *trans*-2-butene and 1-butene are close to each other.

Hydrogenation by H_2. 1,3-Butadiene was hydrogenated in 0.5 M D_2SO_4 by H_2 instead of D_2. Compared with D_2 (run 4), the deuterium uptake is suppressed to a great extent (run 7). However, both 1-butene and *trans*-2-butene exhibit the same D distribution and *cis*-2-butene has a higher D.N. than the other butenes as in the other cases.

D-Distribution in butane. Independent of the source of hydrogen, butane exhibits a simple cone-like D distribution (runs 2, 4 ~ 6 in Table 1) in contrast to the two maxima distribution on Pt in 0.5 M D_2SO_4 (*1*). D.N.'s (4 ~ 6) are smaller than that on Pt as in the case of butenes.

DISCUSSION

The present discussion is based on a model that the hydrogenation occurs through the interaction of adsorbed hydrogen atoms with adsorbed 1,3-butadiene or its derivatives independent of the source of hydrogen of H_2, $H^+ + e^-$, or H_{diss}. The reasons are as follows. Direct association of proton through the discharge step,

$$C_4H_6(a) + H^+ + e^- \rightarrow C_4H_7(a)$$

$$C_4H_7(a) + H^+ + e^- \rightarrow C_4H_8(a)$$

is excluded by the fact that the distribution of products and the D distribution in products under electroreduction are intrinsically identical with those of the hydrogenation on open circuit where the process takes place undoubtedly via the adsorbed hydrogen atoms. Independence of the hydrogen source is only understood by allowing the participation of H(a), a common species formed by the following steps,

$$H_2 \rightarrow 2H(a)$$

$$H^+ + e^- \rightarrow H(a)$$

$$H_{diss} \rightarrow H(a).$$

1. Kinetics

Hydrogenation by H_2. As stated above, the reaction rate in region H is controlled by the diffusion of H_2 to the catalyst surface. The kinetics of surface process under such a condition can be examined by the catalyst potential, ϕ_{oc}, which reflects the activity of the adsorbed hydrogen during the reaction. Namely, the potential is deter-

TABLE 1

Distributions of Deuterium in Products Formed by the Hydrogenation of 1,3-Butadiene on Pd Electrode

Run	Conditions	Conv. (%)	S	Product	x_i (%)											D.N.
					0	1	2	3	4	5	6	7	8	9	10	
1	ϕ = 0.18 V	3.3	1.00	1-Butene	19.5	24.7	19.6	16.4	11.5	5.8	1.9	0.5	0.0			2.0
				trans-2-Butene	22.3	23.3	16.7	15.3	12.9	7.2	2.0	0.3	0.0			2.0
				cis-2-Butene	19.2	21.0	16.6	15.4	13.3	8.9	4.1	1.3	0.2			2.3
2	ϕ = 0.12 V	0.6 ~ 7.5	0.99	Butane	4.5	8.4	12.1	13.2	14.0	12.4	11.4	9.3	5.8	4.7	4.2	4.5
				1-Butene	22.3	25.4	19.9	15.4	9.9	4.9	1.8	0.4	0.0			1.9
				trans-2-Butene	19.6	21.4	18.3	17.3	13.1	7.3	2.4	0.5	0.1			2.2
				cis-2-Butene	16.6	18.7	17.0	16.6	14.4	9.9	4.8	1.7	0.3			2.5
3	P_D = 55 mmHg	4.6	1.00	1-Butene	17.1	22.7	19.2	16.5	12.4	7.5	3.3	1.0	0.2			2.3
	ϕ_{oc} = 186 ~ 172 mV			*trans*-2-Butene	14.9	20.8	18.0	17.3	14.8	9.8	3.7	0.7	0.1			2.4
				cis-2-Butene	15.2	19.4	16.9	15.8	14.0	10.4	5.8	2.1	0.4			2.6
4	P_D = 164 mmHg	11.2	0.91	Butane	2.9	9.8	15.0	17.1	17.4	15.5	11.3	6.6	2.8	1.0	0.6	3.9
				1-Butene	17.2	21.9	19.5	16.3	12.1	7.7	3.9	1.3	0.2			2.3
	ϕ_{oc} = 133 ~ 102 mV			*trans*-2-Butene	19.5	21.4	17.9	15.4	11.9	7.9	4.3	1.5	0.3			2.3
				cis-2-Butene	10.2	16.1	17.6	17.8	16.0	12.1	7.0	2.6	0.5			2.9
5	P_D = 357 mmHg	22.8	0.62	Butane	0.4	2.0	7.1	14.3	16.9	14.6	12.8	10.2	8.9	7.7	5.1	5.4
				1-Butene	9.0	23.6	31.0	14.4	10.0	5.0	3.1	2.2	1.6			2.4
	ϕ_{oc} = 102 ~ 30 mV			*trans*-2-Butene	4.9	22.2	27.2	11.7	10.7	8.3	5.9	4.6	4.5			3.0
				cis-2-Butene	3.3	7.4	15.4	17.5	15.1	13.7	10.4	9.0	8.1			4.1
6	D_{diss}	6.9	0.59	Butane	1.5	3.3	5.8	9.3	12.4	13.0	13.7	12.8	11.9	9.3	7.0	5.8
				1-Butene	22.7	24.1	25.7	12.0	7.3	3.9	2.4	1.2	0.8			1.9
				trans-2-Butene	13.2	22.5	23.8	11.6	9.5	6.9	5.4	3.8	3.3			2.6
				cis-2-Butene	7.3	14.3	19.7	18.6	13.2	10.0	7.4	5.1	4.4			3.0
7	P_H = 164 mmHg	5.1	0.98	Butane	76.9	17.3	4.3	1.2	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.3
	ϕ_{oc} = 138 ~ 123 mV			1-Butene	92.1	7.1	0.8	0.0	0.0	0.0	0.0	0.0	0.0			0.0
				trans-2-Butene	90.3	8.4	1.1	0.2	0.0	0.0	0.0	0.0	0.0			0.1
				cis-2-Butene	85.5	12.4	1.7	0.3	0.0	0.0	0.0	0.0	0.0			0.2

mined by the following step which is always in equilibrium at the present condition of zero net current,

$$\mathrm{H}^+ + e^- \rightleftarrows \mathrm{H(a)} \qquad (4)$$

and is expressed as

$$\phi_{\mathrm{oc}} = \mathrm{cost} - \frac{RT}{F} \ln a_{\mathrm{H(a)}} \qquad (5)$$

where $a_{\mathrm{H(a)}}$ represents the activity of the adsorbed hydrogen. From Eqs. (3) and (5), and the first-order dependence of the reaction rate on P_{H}, we obtain the rate expression as

$$v = \mathrm{const} \cdot a_{\mathrm{H(a)}}^{1.6}. \qquad (6)$$

The reaction order of 1.6 reflects a complex nature of the kinetics but a value larger than unity excludes the possibility that the first addition of H(a) determines the reaction rate. Second or later addition will be rate controlling. This is supported by the occurrence of multiple deuterium exchange in butenes.

In many literature works, the reaction order is determined by using a total amount of the adsorbed hydrogen measured by voltammograms like Fig. 2. On Pt (*21*) and Pd (*22*) surface, however, several kinds of adsorbed hydrogen exist and some of them are inactive for the hydrogenation of 1,3-butadiene on Pt in 0.5 *M* H_2SO_4 (*7*), of olefins on Pt (*23*), and of benzene on Pt/Al_2O_3 (*24*) in the gas phase. Therefore, it will not be correct to search the reaction order by using a total amount of the adsorbed hydrogen. In the present work, the reaction order is obtained by using the potential-determining hydrogen which is active for the hydrogenation on Pt (*7*) and Pd (*22*) in region H.

Electroreduction. The reaction rate of electroreduction is somewhat smaller than that of the hydrogenation by H_2 in region H and the Tafel slope is 70 mV/decade. This difference shows a presence of a small bias on step 4 since the slope is expected to be 120 or ≤60 mV/decade according as step 4 is rate determining or in equilibrium. The difference in the rate is relatively small and D distributions in products are very similar to those obtained in the hydrogenation. Hence, the reaction mechanism will be taken to be the same in both the cases.

2. *Selective Formation of Butenes*

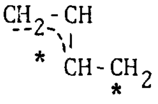
As stated above, 1,3-butadiene is strongly adsorbed in comparison with butenes on Pd surface. This is the reason why the formation of butane from 1,3-butadiene is suppressed in region I though the hydrogenation of butenes can proceed (*20*). Butenes once formed from 1,3-butadiene are readily replaced by 1,3-butadiene and desorbed from the surface. Furthermore, a decrease in the activity of H(a) by the strong adsorption of 1,3-butadiene reduces a chance for the butenes to be further hydrogenated. This is the case called "thermodynamic selectivity" by Bond *et al.* (*25*). At lower potential, the hydrogen activity is high and 1,3-butadiene supply to the surface is not sufficient (region R), so that the butenes are subjected to the further hydrogenation to butane before the desorption.

The above explanation cannot be applied in region H because butenes can not be hydrogenated in this potential range. In our subsequent paper (*22*), we will conclude that four kinds of the adsorbed hydrogen exist on Pd surface (H_{-1}, H_{-2}, H_{-3}, and H_{-4} in the sequence from weakly to strongly adsorbed hydrogen) and that H_{-3}, present in region H, is active for the hydrogenation of 1,3-butadiene but not of butenes. This is the direct reason for the selective formation of butenes in region H.

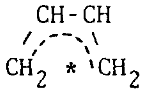
3. *Reaction Mechanism for the Formation of Butenes*

In regions I and H, 2-butenes are formed by 1:4 addition without isomerization. Reasons are as follows: (i) The D distribution in *trans*-2-butene is in agreement with that in 1-butene while entirely different from that in *cis*-2-butene in region I. If the isomerization plays an important role, both the D distributions in *trans*- and *cis*-2-butenes are expected to coincide each other and their D.N.'s are larger than 1-butene as in the case of hydroisomerization (*20*). (ii) The ratio of *trans*-2-butene to *cis*-2-butene in the hydrogenation of 1,3-butadiene is about 3 which is in contrast with 1.2 for the hydroisomerization (*20*). (iii) Butenes formed prefer to desorb because of their weak adsorbability. (iv) No formation of butane in region H gives a drawback for the existence of the adsorbed butyl radical required for the hydroisomerization.

First, we discuss the reaction mechanism in region I in the hydrogenation by H_2 and H_{diss}. No difference in the D distribution between 1-butene and *trans*-2-butene suggests that both are formed through the same route. Furthermore, the fact that the D distribution in *trans*-2-butene is quite different from that in *cis*-2-butene excludes the conformational interconversions among the adsorbed species. Therefore, the following species **(I)** and **(II)**, which hardly undergo the conformational interconversion because of the double-bond-like nature of internal C—C bond,



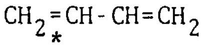
(I)



(II)

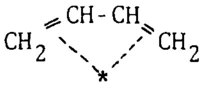
must be proposed for the adsorption states of *transoid*- and *cisoid*- 1,3-butadiene, respectively, as in the case on Pt catalysts in 0.5 *M* H_2SO_4 (*1*) and on Pd/Al_2O_3 in the gas phase (*2, 3*). These species are formed by delocalizing the π-electrons of 1,3-butadiene.

Other adsorbed species of mono **(III)** and bi-π-bonded butadiene **(IV)**, in which the double bonds retain their individuality,



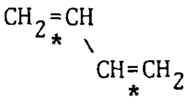
$$\underset{*}{CH_2}{=}CH{-}CH{=}CH_2$$

(III)



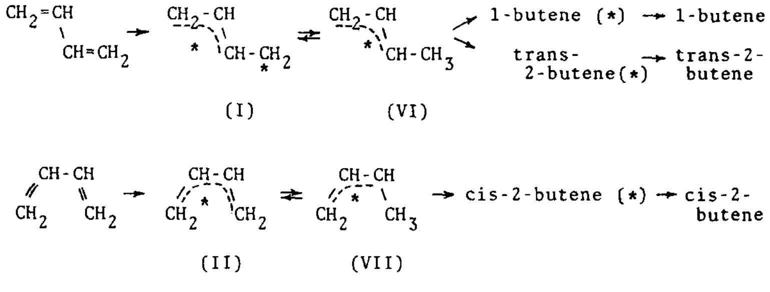
(IV)

have been reported as the adsorbed species on Pd/Al_2O_3 in the absence of hydrogen by ir spectroscopic study (*26*). Mono-π-bonded species can be precursor only of 1-butene. Therefore, if this species play an important role, D distribution in 1-butene has to be quite different from the others which is not the case. Furthermore, one cannot find any reason for suppressing the conformational interconversion among **(IV)** and the species:



(V)

This interconversion will then give rise to the identical D distributions in *trans*- and *cis*-2-butenes which is also not the case. Thus, **(III)** ~ **(V)** are ruled out. Consequently, the same reaction mechanism as on Pt/graphite in 0.5 *M* H_2SO_4 (*1*) and on Pd catalysts in the gas phase (*2, 3*) is proposed.



Scheme I

Both 1-butene and *trans*-2-butene are formed from *transoid*-1,3-butadiene through *syn*-1-methyl-π-allyl **(VI)** and *cis*-2-butene from *cisoid*-1,3-butadiene through anti-1-methyl-π-allyl **(VII)**, respectively. The restriction on the conformational interconversion between **(VI)** and **(VII)** is expected as in the case of **(I)** and **(II)** and explains the different D distribution between *cis*-2-butene and the other butenes.

The same reaction mechanism will hold in region H though the D distribution in *trans*-2-butene somewhat deviates from that of 1-butene.

4. *Butene Which Produces Butane in Region I*

D distribution in butane is simulated by the previous method (*1*) for the respective paths via 1-butene, *trans*-2-butene, and *cis*-2-butene. For example, the distribution via 1-butene is obtained by the multiplication of the two D distributions in 1-butene from 1,3-butadiene and in butane from 1-butene (*20*), i.e.,

$$X_i(C_4) = \sum_{j=0}^{i} \frac{8-j}{8} \cdot X_j(C_4') \cdot X^0_{i-j}(C_4), \quad i = 1, 2, \ldots, 10 \qquad (7)$$

where $X_i(C_4)$, $X_j(C_4')$, and $X^0_{i-j}(C_4)$ are the expected fraction of d_i-butane, the fraction of d_j-butene from 1,3-butadiene and of d_{i-j}-butane from d_0-butene, respectively, and $(8 - j)/8$ is the atomic fraction of H in d_j-butene. In Eq. (7), j cannot exceed 8. A similar treatment applies to the other paths via *trans*-2-butene and via *cis*-2-butene.

The distributions thus calculated from the data by the electroreduction (0.12 V), are compared with the observed one in Fig. 7. It is clearly seen tht the distribution via 1-butene reproduces the experimental results and hence butane is mainly formed via 1-butene. This is supported by the fact that the negative shift of ϕ from 0.14 to 0.08 V causes a large decrease in the rate of 1-butene formation but not much in the rates of 2-butene formation. An easier hydrogenation of 1-butene is probably due to its stronger adsorbability. Terminal double bond will make its interaction with the surface stronger in a crowded environment because of the lesser steric hindrance of the alkyl group compared with the case of the internal double bond. The stronger adsorption of 1-butene on Pd catalyst is observed in their catalytic oxidation reaction (*27*).

5. *Comparison with the Results in the Gas Phase*

Hydrogenation of 1,3-butadiene was studied on 0.03% Pd/Al_2O_3 by Meyer and Burwell (*2*), and on Pd wire (*15*), 5 molar% Pd/α-Al_2O_3 (*3, 14*) and Pd–Au alloy on pumice (*16*) by Wells *et al.* in the gas phase. The present reaction mechanism is intrinsically the same as both authors', except that Meyer and Burwell did not specify precisely the binding nature of the adsorbed intermediate and that Wells *et al.* permitted the formation of 1-butene via cisoidal route in Scheme 1. We excluded the formation of 1-butene via cisoidal route because of the definite difference in the D distributions between 1-butene and *cis*-2-butene. Wells *et al.* reported a high *trans*/*cis* ratio of ~10 (*3, 14–16*) different from the present ratio of ~3. In our work, the ratio of the sum of 1-butene and *trans*-2-butene to *cis*-2-butene (~10) becomes close to *transoid*/*cisoid* ratio for 1,3-butadiene in the gas phase.

Though *trans*/*cis* ratio in the present study (i.e., in aqueous solution) is different from that in the gas phase, the reaction mechanisms in both the systems are regarded as intrinsically identical. Therefore, we conclude that the bonding nature between the metal and the hydrocarbon plays an important role and the electric field and the ionic environment have little effect on the reaction mechanism.

On the analogy with Pt, we first expected that the fraction of deuterium in surface H/D pool is kept about unity during the reaction and hence the products would be much more isotopically exchanged than those in the gas phase catalysis. The present study,

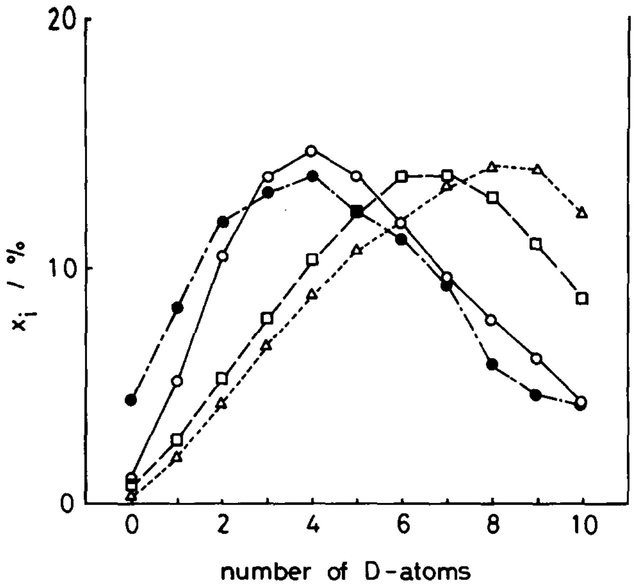


FIG. 7. Expected D distributions in butane from 1,3-butadiene via 1-butene (○), via *trans*-2-butene (△), and via *cis*-2-butene (□) on Pd electrode. Observed distribution (●).

however, shows a rather limited enhancement in the exchange and that when H_2 is used instead of D_2, D.N.'s diminish to a great extent as shown in run 7 (Table 1). These observations indicate that the rate of the exchange reaction of the adsorbed hydrogen with D^+ in solution is slow compared with the rate of hydrogenation. As a result, the fraction of deuterium in surface H/D pool becomes lower. Such a situation holds in regions H and I but not in region R. In region R products are much more deuterium exchanged. The results on the deuteration in region R will be reported in the subsequent paper (*22*).

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