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Reduction of Butenes and Butadiene on Pt/C Catalysts Suspended in Aqueous Solution

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The reactions of 1,3-butadiene (C_4'') and three isomeric butenes with deuterium were studied on graphite-supported platinum catalyst in 0.5 *M* D_2SO_4. Dispersion of platinum accelerates the H/D isotope exchange but does not affect the reaction scheme. The D-atom distributions in the reactants and products confirm our earlier conclusion (H. Kita, N. Kubota, and K. Shimazu, *Electrochim. Acta* **26,** 1185 (1981); K. Shimazu and H. Kita, *Electrochim. Acta* **24,** 1085 (1979) that there are two kinds of reaction intermediates in the hydrogenation of C_4'' to the butenes; one gives 1-butene (1-C_4') and *trans*-2-butene (*t*-2-C_4') and the other *cis*-2-butene (*c*-2-C_4'); and these distributions show further that (i) butane is mainly formed from 1-C_4' via two paths; one is the direct hydrogenation of 1-C_4' with the H/D isotope exchange at the vinylic positions of 1-C_4' and the other is the hydrogenation with the double-bond migration, (ii) the latter path accompanies a much more enhanced isotope exchange, and (iii) *t*-2-C_4' and *c*-2-C_4' undergo the exchange, isomerization, and hydrogenation via the same path.

INTRODUCTION

In our laboratory, the hydrogenation of 1,3-butadiene (C_4'') has been studied on platinum (wire or net) in aqueous solution both on open circuit and under potentiostatic polarizations (*1*, *2*). The difference in the hydrogen source, i.e., H_2 molecules in the open-circuit reduction or $H^+ + e^-$ in the electroreduction, has no effect on the reaction mechanism. Common to both cases, the distribution of the reaction products of butane (C_4), 1-butene (1-C_4'), *trans*-2-butene (*t*-2-C_4'), and *cis*-2-butene (*c*-2-C_4') changes critically above or below ca. 80 mV/rhe, where the potential (ϕ) is determined by an elementary step of $H^+ + e^- \rightleftarrows H(a)$ and represents the activity of the adsorbed hydrogen atom, H(a). At $\phi <$ ca. 80 mV, namely, when the catalyst surface is almost fully covered with H(a), C_4 is produced exclusively (>90%), whereas at $\phi >$ ca. 80 mV three isomeric butenes are byproduced in a ratio of C_4 : 1-C_4' : *t*-2-C_4' : *c*-2-C_4' = 50 : 33 : 10 : 7. We have also deduced the presence of two kinds of adsorbed C_4'': one gives 1-C_4' and *t*-2-C_4' and the other *c*-2-C_4', respectively. In the region of $\phi >$ ca. 80 mV, the most stable adsorbed hydrogen atom is inactive but interchanges to the second most stable one and takes part in the hydrogenation process. In the present study, similar experiments were conducted by using graphite-supported platinum catalyst suspended in 0.5 *M* D_2SO_4 in order to examine the effects of the dispersion of platinum and to know the details of the H/D isotopic exchange during the reduction of 1,3-C_4'' and other olefins.

Heterogeneous catalytic hydrogenations on various supported-metal catalysts in solution have been studied extensively, with an electrochemical interest, by Sokol'skii (*3*) and Nagy and Horányi (*4*). They have shown interesting relations between the rate and the potential of the catalysts and discussed the reaction scheme. However, no mechanistic study by using the tracer method has been conducted.

On the other hand, in the heterogeneous

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catalyses in the gas phase the tracer method has been widely used (*5*). For example, Bates *et al.* (*6*) have studied the C_4'' reduction with deuterium on $Pt/\alpha\text{-}Al_2O_3$ and reported that the three isomeric butenes are each formed by the steps, $C_4X_6(a) + X(a) \rightleftarrows C_4X_7(a)$ and $C_4X_7(a) + X(a) \rightarrow C_4X_8$, where $X = H$ or D, and that butene isomerization before desorption does not occur even though adsorbed butyl groups are formed. It is further concluded that in each reaction 50% or more of each butene is formed by the stepwise addition of two X atoms but sites also exist at which fast multiple exchange takes place, and that the sites at which C_4 is formed may be distinct from those at which butene formation occurs.

The present study in liquid phase has an advantage of being carried out with the deuterium content of the adsorbed hydrogen atoms close to unity during the reaction by the reversible step: $H(a) \rightarrow H^+ + e^-$, $D^+ + e^- \rightarrow D(a)$. Another advantage is that one can follow the potential of the catalyst which reflects the activity of the adsorbed hydrogen on Pt under working conditions. Thus one can expect more useful information for understanding the reaction mechanism. The present results reconfirm our previous conclusions (*1, 2, 6*) for the reduction of C_4'' and offer evidence that the dual-pathway mechanism (*7*) of the ethylene reduction holds in the reduction of other olefins.

EXPERIMENTAL

The apparatus used was a closed-circulation system which included a cell of the two-compartment type. One of the compartments was furnished with a reversible hydrogen electrode and connected through a closed greaseless tap and the Luggin capillary to the other compartment. The latter was furnished with a gold-plated probe electrode (apparent area, 0.2 cm^2) (*8*) and an inlet and outlet for reaction gas. The reaction gas was an atmospheric mixture of reactant (ca. 13 mm Hg, 1 mm Hg = 133.3 $N \cdot m^{-2}$), D_2 (ca. 13–63 mm Hg for the reduction of C_4'', and 13–25 mm Hg for other reactants), and He, and circulated through a solution of 0.5 *M* D_2SO_4 (ca. 45 ml). The reactants were C_4'', $1\text{-}C_4'$, $t\text{-}2\text{-}C_4'$, $c\text{-}2\text{-}C_4'$, isobutene ($i\text{-}C_4'$), and 3,3-dimethyl-$1\text{-}C_4'$. They were purified by repeating the distillation under vacuum and by fractional separation with a gas chromatograph (3N purity). Helium and deuterium gas (Showa Denko, Japan, 99.97%) were purified by a commercial purifier (7N purity). The solution was prepared from D_2O (Merck, 99.75%) and concd (96–98%) D_2SO_4 (Merck, 99 D%).

The catalyst was prepared as follows (*9*). The graphite powder (spectroscopically pure, SP-1, 200 mesh, 2 m^2/g, Union Carbide) was immersed in an aqueous nitric acid solution of $Pt(NO_2)_2(NH_3)_2$, slowly dried at 353 K while being stirred; the residue was then heated at 573 K for 2 h in air. The amount of Pt was 0.3 wt% at which the graphite surface was expected to be covered by half of the monolayer provided 10^{15} Pt atoms per square centimeter. The titration of chemisorbed oxygen with H_2 revealed a dispersion of 0.254 by assuming the following reactions: Pt(surface) + $\frac{1}{2}$ O_2 $\rightarrow$ PtO(surface), PtO(surface) + $\frac{3}{2}$ H_2 $\rightarrow$ PtH(surface) + H_2O. A sample of the catalyst, 0.7–1.0 g, was suspended in the solution and reduced in advance of measurement by bubbling D_2 (ca. 13–63 mm Hg). The potential of the catalyst was recorded during the measurements as well as the pretreatment period.

The reaction gas was occasionally sampled for analysis with a gas chromatograph (VZ-7, 5 m, 273 K). After the reaction, the organic gases were collected in a liquid N_2 trap. Each hydrocarbon product was separated gas chromatographically and then subjected to D-atom distribution analysis with a mass spectrometer. Ionization potential was 15.6 eV for C_4 and 2,2-dimethyl-C_4, 11.6 or 13.6 eV for butenes, and 21.7 eV for $i\text{-}C_4$. The natural abundance of ^{13}C and a pattern coefficient of each compound are taken into account in the calculation of the D-atom distribution.

All measurements were conducted at a temperature of 293 ± 1 K.

RESULTS

1. Potential of the Catalyst

The catalyst preheated at 523 K for 2 h in air shows a high potential (ca. 0.8–0.9 V vs rhe) in the 0.5 *M* D_2SO_4 saturated with atmospheric helium. Such a high potential indicates that the platinum is covered with oxygen. The potential of the catalyst is denoted as ϕ_{oc} in what follows where oc refers to the open circuit. When deuterium gas is circulated through the solution, ϕ_{oc} decreases, first gradually and then sharply, to the value expected from the Nernst equation for the hydrogen electrode reaction as shown in Fig. 1. The time course of the potential change reflects slowness of the oxygen layer reduction (0.7–0.8 V) compared with the hydrogen layer formation (ca. 0.4 V) on the platinum.

When the circulation gas is switched to the reaction gas, ϕ_{oc} shifts in the positive direction though the deuterium partial pressure is kept the same. The shift clearly indicates the shortage of deuterium at the catalyst surface and supports our previous conclusion that the hydrogen diffusion controls the overall reaction rate at the present composition of the reaction gas (*1*).

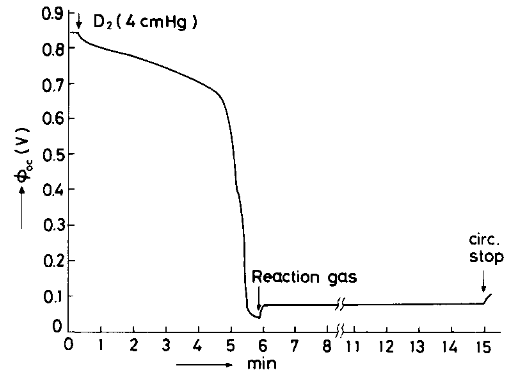


FIG. 1. Potential of the catalyst in 0.5 *M* D_2SO_4 during the pretreatment and the hydrogenation. Catalyst: Pt/C, 0.826 g. Pretreatment: P_D = 40 mm Hg. Hydrogenation: $P_{C_4''}$ = 13 mm Hg, P_D = 40 mm Hg. Potential: referred to the reversible hydrogen electrode in the same solution.

The potential stays constant during the reaction.

This steady value of ϕ_{oc} is a function of deuterium pressure (P_D) and decreases with the increase of P_D. Mean values at P_D = 13 mm Hg observed in the reduction of several reactants are listed in Table 1. The value for C_4'' at P_D = 13 mm Hg is 130 mV and is larger than the others around 100 mV. Hence, adsorption of C_4'' is taken to be the strongest.

2. Reaction Rate and Product Distribution

Under the present experimental conditions, the reaction rate is determined by the

TABLE 1

Potential, Rate Constant, and Product Distribution at Pt/C in 0.5 *M* D_2SO_4 (20 ± 1°C)

Run	Reactant	ϕ_{oc}[a] (mV)	k_D' (mol min^{-1} mm Hg g^{-1})	k_D (mol min^{-1} mm Hg^{-1} Pt cm^{-2})	Product (%)			
					C_4	1-C_4'	*t*-2-C_4'	*c*-2-C_4'
(1)–(3)	C_4''	130	9.4×10^{-8}	3.7 (33)[b] $\times 10^{-11}$	52 (50)	30 (33)	9 (10)	9 (7)
(4)–(6)	1-C_4'	90	8.9×10^{-8}	3.5 (43) $\times 10^{-11}$	78	—	7	15
(7)–(9)	*t*-2-C_4'	100	12.7×10^{-8}	5.0×10^{-11}	96	1	—	3
(10)–(12)	*c*-2-C_4'	105	11.2×10^{-8}	4.4 (43) $\times 10^{-11}$	76 (69)	4 (5)	20 (26)	—
(13)	i-C_4'	110	8.6×10^{-8}	3.4×10^{-11}				

[a] Values obtained at P_D = 13 mm Hg.

[b] Values in parentheses are obtained on a platinum metal (*1*).

diffusion of hydrogen (region H) and expressed as (*1*)

$$v = k_D P_D, \qquad (1)$$

where v is defined as the decrease of reactant in unit time and k_D is the rate constant. Mean values of the rate constants for the reductions of C_4'', 1-C_4', *t*-2-C_4', *c*-2-C_4', and i-C_4' are listed in Table 1 where k_D' is expressed for unit gram of the catalyst and k_D for unit surface area of platinum calculated from the dispersion, respectively. The values in parentheses are for platinum metal (*1*). The rate constant on the present catalyst is approximately a tenth of that on the platinum metal.

Product distribution is also presented in Table 1. In the reduction of C_4'', only a half undergoes the complete hydrogenation to C_4 and the rest desorbs as butenes. Among the three isomeric butenes, 1-C_4' is predominant. Percentages of the products are the same as those observed on the metal. Hence, the reaction mechanism is the same on both catalysts, and therefore butane will be expected to be the main product (>90%) under the condition of the reactant-diffusion control as on the metal.

In the reduction of the butenes, isomerization reaches 22–24% when 1-C_4' and *c*-2-C_4' are the reactants but only 4% when *t*-2-C_4 is the reactant. The product distributions will again be expected to be the same as that on the metal as exemplified by the case of *c*-2-C_4'.

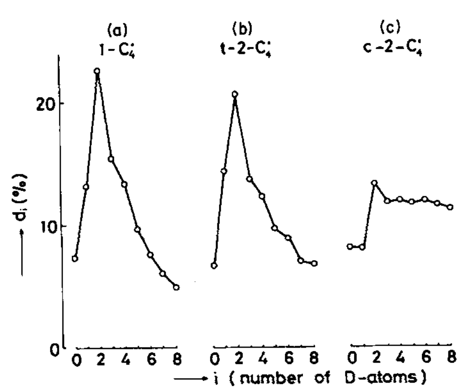


FIG. 2. Averaged D-atom distributions of (a) 1-C_4', (b) *t*-2-C_4' and (c) *c*-2-C_4' from C_4''.

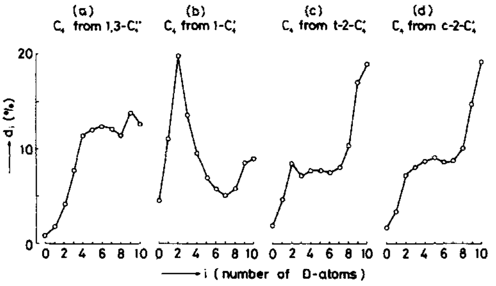


FIG. 3. Averaged D-atom distributions of C_4 from (a) C_4'', (b) 1-C_4', (c) *t*-2-C_4', and (d) *c*-2-C_4'.

3. Isotopic Distribution

(*i*) *Products of the hydrogenation.* Each reduction of C_4'', 1-C_4', *t*-2-C_4', and *c*-2-C_4' was repeated three times. In each reduction, D-atom distributions are reproducible as far as the essential aspects are concerned. However, it must be mentioned that the values of d_0 (the fraction, percentage, of the species which includes no D atom) are less reliable than others because of the possibility that a trace of products which remain in the reactant, unremoved by the purification processes, will appear at d_0.

Figure 2 shows the averaged D-atom distributions of 1-C_4', *t*-2-C_4', and *c*-2-C_4' formed from C_4''. The distributions widen over all the possible deuteroisomers, showing the presence of the rapid H/D exchange during the hydrogenation. More interesting is that the distributions of 1-C_4' and *t*-2-C_4' are very close to each other with a peak at d_2 but that of *c*-2-C_4' is entirely different.

Figure 3 shows the averaged D-atom distributions of C_4 formed from C_4'', 1-C_4', *t*-2-C_2', and *c*-2-C_4'. Butane from C_4'' shows two peaks in its distribution. Two-peak distribution becomes clearer in C_4 from 1-C_4', where d_2 forms a sharp maximum. The other two distributions of C_4 from *t*-2-C_4' and *c*-2-C_4' are very close to each other yet distinctly different from the distribution of C_4 from 1-C_4'. Here, the maximum appears at the per-

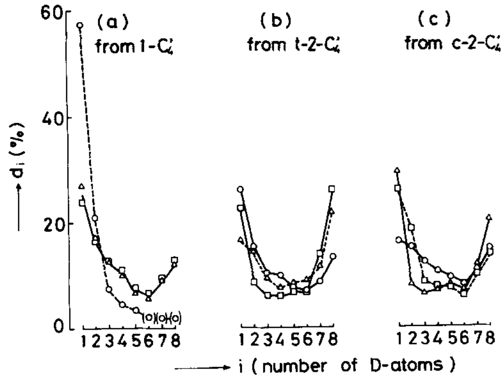


FIG. 4. Averaged D-atom distributions of the isomerization products from (a) 1-C_4', (b) t-2-C_4', and (c) c-2-C_4'. ○: 1-C_4'; △: t-2-C_4'; □: c-2-C_4'. Dashed lines show the distributions of the desorbed reactants. ( ) shows uncertain value.

deuterobutane (d_{10}), showing the occurrence of a much more rapid H/D exchange. However, the presence of the two peaks in their distribution is similar, i.e., the broad one from d_0 to d_6 and the sharp one from d_7 to d_{10}.

(*ii*) *By-products formed by isomerization.* The hydrogenation of each butene accompanies the isomerization (Table 1). Figure 4 shows the averaged D-atom distribution of these isomerization products. The figure also includes the averaged D-atom distribution of each reactant after the reaction (dashed lines). The appearance of the deuterated species in the reactants shows reversibility of the adsorption step of each butene. The ratio of the conversion (%) to the amount of the desorbed (deuterated) reactant (%) reaches 3.3 to 10.5; in other words, the desorption rate of the reactants amounts to 10–30% of the reaction rate. This is different from the case of ethylene reduction where the adsorption step is irreversible (platinum metal) (*10*). The amounts of isomerization product are small compared with the reactant present in the gas phase (conversion, 4–23%) and it is difficult to remove the reactant (d_0) completely from the isomerization products by gas chromatography because of the tailing effect. Hence in Fig. 4, the distribution of the isomerization products was calculated over the deuterospecies from i = 1 to 8, discarding d_0. Similarly, d_0 was discarded in the distribution of the reactants since d_0 is so large ($d_0/\Sigma_{i=1}^{8} d_i > 10$–$100$) that the fractions of deuterospecies from i = 1 to 8 become hardly distinguished when d_0 is included. The fractions d_1 and d_2 of the reactant do not affect d_1 and d_2 of the product isomers because the reactant d_1 and d_2 are sufficiently small in their absolute amounts.

We can comment on Fig. 4 as follows. (1) Among the D-atom distributions of the three reactants, that of 1-C_4' is different from the others. d_i decreases monotonously from d_1 to d_5. Values of d_6–d_8 are negligibly small. (2) The isomerization products from 1-C_4', i.e., t-2-C_4' and c-2-C_4', reveal exactly the same D-atom distribution as each other. (3) All the distributions, except that of reactant 1-C_4', exhibit a V-shape with maxima at terminals d_1 and d_8.

(*iii*) *Products from i-C_4' and 3,3-dimethyl-1-C_4'.* Hydrogenations of i-C_4' and 3,3-dimethyl-1-C_4' were supplemented under the same experimental conditions. D-atom distributions of the products i-C_4 and 2,2-dimethyl-C_4 (an averaged one for i-C_4) are shown in Fig. 5 in comparison with that of C_3 from C_3' previously reported (*11*).

It is noticed that the distribution of i-C_4 consists of two segments, A and B, clearly separated by the exceptionally small amount of d_5. This behavior is exactly the same as that of C_3 where d_6 is the mini-

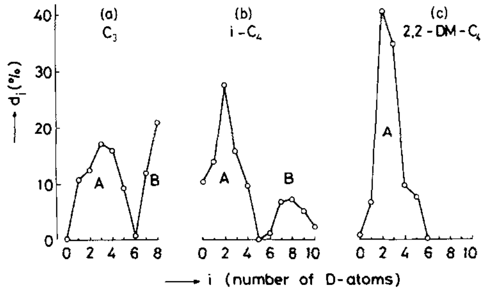


FIG. 5. The D-atom distributions of (a) C_3 from C_3' (*12*), (b) i-C_4 from i-C_4', and (c) 2,2-dimethyl-C_4 from 3,3-dimethyl-1-C_4'.

mum. On the other hand, the distribution of 2,2-dimethyl-C_4 shows only segment A without B.

DISCUSSION

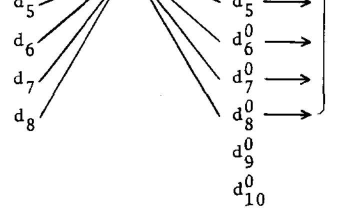
In our previous work on a platinum metal (*1*), we have concluded as follows. The transoid (more than 90%) and cissoid C_4'' in the gas phase dissolve and adsorb on platinum irreversibly. They undergo the hydrogenation while retaining their geometrical configurations as they were. When the hydrogen supply is sufficient (region B), C_4'' is reduced almost quantitatively to C_4 but when insufficient (region H) three isomeric butenes are formed as by-products. The transoidal intermediate (IH) produces 1-C_4' and *t*-2-C_4' and the cissoidal intermediate (IH)′, *c*-2-C_4', respectively. The H/D exchange proceeds by the reversible steps $C_4X_6(a) + D(a) \rightleftarrows C_4X_7(a)$, where x = H or D. Taking the kinetic data into consideration, the step, $C_4X_7(a) + D(a) \rightarrow C_4X_8(a)$, is irreversible. C_4 is produced mainly via adsorbed 1-C_4' in both regions B and H. Step 1, $C_4'(a) + D(a) \rightleftarrows C_4X_9(a)$, is reversible and causes further H/D exchange. The final step, $C_4X_9(a) + D(a) \rightarrow C_4X_{10}$, is irreversible as can be confirmed by the absence of the H/D exchange when C_4 is brought into contact with this catalyst in solution in the presence of hydrogen.

At the present catalyst, hydrogen diffusion is rate determining as is shown by ϕ_{oc}. The product distribution for the present catalyst is the same as that for the platinum metal (Table 1). The D-atom distributions of 1-C_4' and *t*-2-C_4' are very close to each other and distinctly different from that of *c*-2-C_4' (Fig. 2). These results confirm our previous conclusion. The dispersion of platinum affects the reaction rate of the H/D exchange. The mean number of D-atoms in a molecule estimated by $D.N. = \Sigma_i\, i \cdot d_i/100$ is larger in all products than that previously reported on the metal (*1*). Thus the difference in the D-atom distribution between 1-C_4' (and *t*-2-C_4') and *c*-2-C_4' becomes much clearer. The H/D exchange is structure sensitive as in the case of, for example, the nickel-catalyzed reaction of benzene with deuterium in gas phase (*12*). On the other hand, the reaction rate (k_D, Table 1) is smaller by an order of magnitude. The decrease is mainly attributed to an increase in the diffusion layer thickness because the catalyst powder floats during the stirring whereas the metal catalyst stands fixed. Other reasonings based on the change in the chemical nature of the catalyst will not be plausible since the reaction mechanism remains unchanged.

1. Butene Which Produces C_4 in C_4'' Reduction

We estimate below the expected distribution of the deuterospecies in C_4 assuming three paths that C_4 is formed via 1-C_4', *t*-2-C_4', and *c*-2-C_4', respectively. We have observed the D-atom distributions for 1-C_4' from C_4'' and for C_4 from 1-C_4'. Simple multiplication of the two distributions will give the distribution expected for C_4 from C_4'' via 1-C_4'.

The multiplication is exemplified below for d_8-C_4.



Here d_j(1-C_4') is the percentage of the deuterospecies containing *j* D atoms of 1-C_4' formed from C_4'' while $d_i^0(C_4)$ is the percentage of the deuterospecies containing *i* D atoms of C_4 formed from d_0-1-C_4'. Each crossed multiplication gives the possibility for the formation of d_8-C_4.

The multiplication is formulated by taking into account the number of H atoms exchangeable with D as,

$$d_i(C_4) = \frac{1}{100} \cdot \sum_{j=0}^{i} \frac{8-j}{8} \cdot d_j(C_4') \cdot d_{i-j}^{0}(C_4), \quad i = 1, 2, \ldots, 10, \quad (2)$$

where $d_i(C_4)$ is an expected percentage of the deuterospecies containing i D atoms in the butane produced from C_4'' and $(8 - j)/8$ is the atomic fraction of H in the deuterobutene species with j D atoms. In Eq. (2), j cannot exceed 8.

Similar calculation is carried out with respect to the other paths via t-2-C_4' and c-2-C_4'. The calculated results are compared with the experimental distribution in Fig. 6. Here, the latter distribution was that observed at a higher P_D of 63 mm Hg so that ϕ_{oc} is nearly equal to the value in the reduction of the olefins. There is a tendency to have a more accelerated H/D exchange with the increase of ϕ_{oc}. In Fig. 6, it is clearly seen that C_4 is mainly formed via 1-C_4'.

The reactant of C_4'' contains the transoid predominantly (more than 90%) which forms 1-C_4'. Hence, naturally the path via 1-C_4' will become a major route. Second, 2-butenes will be expected to adsorb less strongly than 1-C_4' because of the geometrical hindrance of the two methyl groups in a molecular plane which is parallel to the surface. In 1-C_4', the terminal methyl group will locate normal to the catalyst surface.

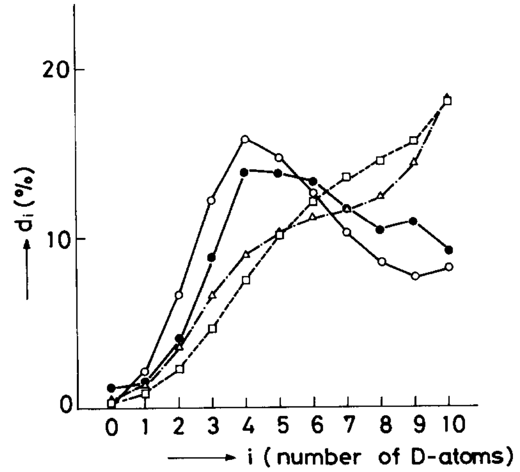


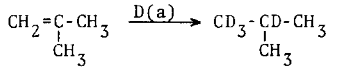
FIG. 6. D-atom distributions estimated by Eq. (2). ○: via 1-C_4'; △: via t-2-C_4'; □: via c-2-C_4'; ●: observed one.

2. From 1-C_4' to C_4

The D-atom distribution of C_4 formed from C_4'' shows two peaks (Fig. 3a) in contrast to a single peak of the half hydrogenation product of 1-C_4'. Hence, a dual path from 1-C_4' to C_4 is expected. Such a situation is more clearly demonstrated when 1-C_4' is used as a reactant (Fig. 3b). These two-peak distributions are found when the deuterium fraction of the adsorbed hydrogen atoms is raised near to unity by the equilibrium step, D(a) $\rightleftarrows$ $D^+ + e^-$, and not at a low deuterium fraction as in the case of the same deuteration in the gas phase on Pt/Al_2O_3 (*13*) where only one maxima at d_1 is reported.

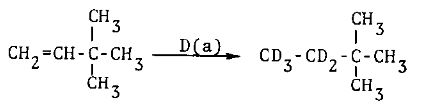
Figure 5 presents other examples of the two-peak distribution. In Fig. 5, segment A is of special interest in that the number of the exchangeable hydrogen atoms is 5 for propane and 4 for i-C_4. The difference in the number is only explained by assuming that the hydrogen atoms at the vinylic positions of the reactants are exchangeable, i.e.,

$$CH_2{=}CH{-}CH_3 \xrightarrow{D(a)} CD_3{-}CD_2{-}CH_3$$



$$\underset{CH_3}{CH_2{=}\underset{|}{C}{-}CH_3} \xrightarrow{D(a)} \underset{CH_3}{CD_3{-}\underset{|}{C}D{-}CH_3}$$

Segment A cannot be derived from the simple associated mechanism which allows the release of a hydrogen atom from all methyl groups of the iso-alkyl intermediate with the same probability and hence can give deuterated species without the sharp minimum at d_6 or d_5. In the case of 3,3-dimethyl-1-C_4' only segment A appears in the product,



$$CH_2{=}CH{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \xrightarrow{D(a)} CD_3{-}CD_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$$

From the above results, one can conclude that segment B is obtained by the reaction path which includes the migration of the double bond. This reaction path must be accompanied by high activity for the H/D exchange as can be seen from segment B where only the highly deuterated species are produced.

With the above in mind, we subtracted from the D-atom distribution of Fig. 3b (C_4 from 1-C'_4) the portion expected as due to the double-bond migration. The latter portion was estimated from Fig. 3b (C_4 from 2-C'_4) with an adjustable parameter. The result is shown in Fig. 7 where the parameter is taken as 0.55. The remaining distribution consists of d_0 to d_5 with almost zero d_6–d_{10}. Hence, we conclude that the remaining distribution is due to the exchange of the hydrogen atoms at the vinylic positions of 1-C'_4.

Therefore, the step of 1-C'_4 + D(a) → C_4X_9(a) should follow parallel paths; one is the direct path from 1-C'_4 to C_4 and the other is the path via the reaction intermediate (X) from 2-C'_4. The above value of the parameter shows that about 55% of C_4 is formed by the latter path.

3. *From 2-C'_4 to C_4*

The reaction intermediate (X) must be common in the isomerization processes since all the isomerization products show a V-shaped D-atom distribution as shown in Fig. 4 and must be the first reaction intermediate from 2-C'_4 since the desorbed reactants of *t*-2-C'_4 and *c*-2-C'_4 also show similar V-shaped distribution.

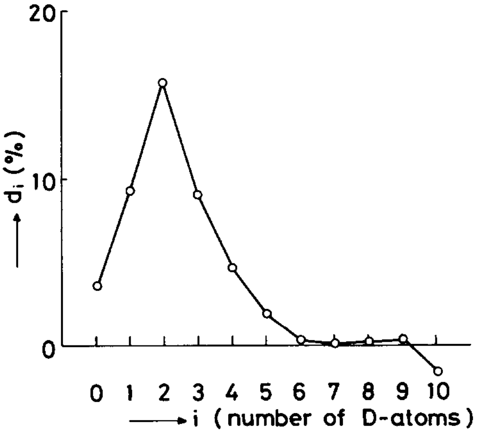


FIG. 7. D-atom distribution expected for C_4 produced by the direct path from (1-C'_4) to C_4.

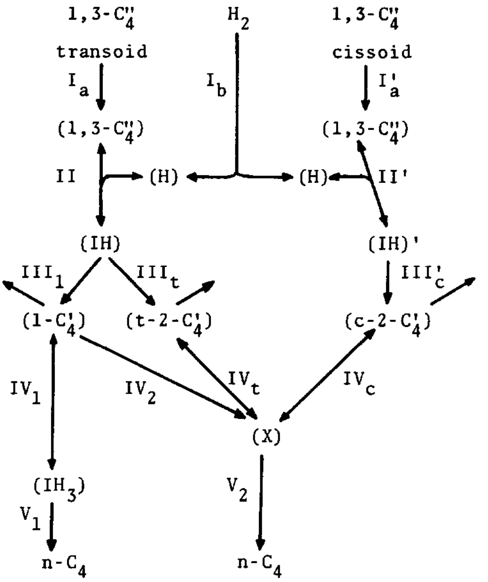


FIG. 8. Reaction scheme. ( ) represents the adsorption state.

In addition, the reaction intermediate (X) is common in the hydrogenation of *t*-2-C'_4 and *c*-2-C'_4 to C_4 since the D-atom distributions of C_4 from *t*-2-C'_4 and *c*-2-C'_4 are essentially the same as each other (Figs. 3c and d).

4. *Reaction Scheme*

The above results are summarized in Fig. 8. C''_4 is reduced to C_4 mainly via (1-C'_4) and step IV_1 or IV_2. Step IV_1 is reversible and accompanies the H/D exchange at the vinylic positions of (1-C'_4). Step IV_2 will be partially irreversible as seen from the results of Figs. 7 and 4a and the product distribution in Table 1. The percentages of 1-C'_4 from *t*-2-C'_4 and *c*-2-C'_4 are much less than the values of *t*-2-C'_4 and *c*-2-C'_4 from 1-C'_4.

Other by-products of *t*-2-C'_4 and *c*-2-C'_4 formed from C''_4 are mainly desorbed from the surface and steps IV_t and IV_c are limited to a great extent under the hydrogenation of C_4''. These by-products in the adsorbed state will be replaced with C_4'' which has the strongest tendency to adsorb. When t-2-C_4' or c-2-C_4' is used as a reactant under the absence of C_4'', steps IV_t and IV_c are reversible as can be seen from Figs. 4b and c. The desorption rate reaches a few tenths of the hydrogenation rate.

Questions now arise as to the nature of the intermediate (X) and the content of step V_2. Undoubtedly step V_2 is not a single step but a multi-one in order to explain the H/D exchange. To solve these questions, further detailed study of the hydrogenation of the butenes is under way.

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