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Saw-toothed Distributions of Deuterium in Butenes Formed by 1,3-Butadiene Deuteration on a Pt/Al_2O_3 Catalyst in D_2SO_4

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Saw-toothed distributions of deuterium are observed in butenes produced by the deuteration of 1,3-butadiene on Pt/Al_2O_3 catalysts suspended in 0.5 M D_2SO_4. The nature of the saw-tooth is sensitive to the purity of the solution and to the deuterium content of the solution. On the basis of the N-profiles (the distributions of hydrogen equilibrated with surface H/D pool) deduced from the observed distributions of deuterium in butenes, the saw-tooth distribution is explained by the reaction mechanism where *cis*- and *trans*-1-methyl-π-allyls are reaction intermediates for the formation of *cis*-2-butene and the other isomers of 1-and *trans*-2-butenes respectively.

The heterogeneous catalytic hydrogenation of 1,3-butadiene in the gas phase has widely been studied on various transition-metal catalysts from the 1960's, for example, on Pt,[1-4] Pd,[1-3,5] other noble metals,[1-4] Co[6-8], and Ni.[6,8,9] However, only a few of these studies have used an isotopic tracer method. The deuteration of 1,3-butadiene on Pt catalysts has been reported only by Bates *et al.*[3] Their reaction mechanism includes mono- and di-π-bonded butadiene as the raction intermediates. 1,3-Butadiene is first chemisorbed in the mono-π-bonded form and then some of the adsorbed 1,3-butadiene becomes the di-π-bonded one in an irreversible way. Thereafter, these adsorbed butadienes, in equilibrium with the corresponding adsorbed butenyl intermediates, are converted to butenes. Their discussion was based on the N-profiles calculated from the distribution of the deuterium in the products.

One must mention that in gaseous catalytic deuteration, deuterium up-take is limited to a lower extent because of the lower deuterium-fraction in adsorbed hydrogen atoms, f_D, due to both the slow rate of the exchange reaction of the adsorbed hydrogen with D_2[3,10] and the smaller ratio, D in D_2 gas/H in butadiene. This limitation is entirely removed in the case of the reaction in a deuterated acid solution.[11] That is, f_D is raised nearly to unity through the fast equilibrium step; $D(a) \rightleftharpoons D^+ + e^-$ on Pt, and the ratio of D in solution/H in butadiene is extremely large. Thus, the reaction products in a solution of deuterated acid are expected to acquire many more deuterium atoms and to provide more concrete information for the elucidation of the reaction mechanism. We have already reported the deuteration of 1,3-butadiene on Pt/graphite[11] and Pt-net,[12] of ethylene[13] and propene[14] on Pt in a 0.5 M D_2SO_4 solution. The deuteration of cyclopentene in solutions of tetrahydrofuran (THF) containing D_2O with and without 5% D_2SO_4 or in the other solutions of CH_3COOD, CH_3OD, $(CH_3)_3COD$, and $DOCH_2CH_2ND_2$–CH_3OD has been studied by Phillipson and Burwell,[15] but here the f_D's are lower than that in a deuterated acid solution, and hence the average number of deuterium atoms taken up in the product cyclopentane was much smaller, even though the addition of D_2O to THF accelerated the deuterium-exchange reaction.

In the present investigation, the deuteration of 1,3-butadiene on a Pt/Al_2O_3 catalyst was conducted in 0.5 M D_2SO_4 purified by the preelectrolysis. We will present a new saw-toothed distribution of deuterium in butenes and discuss the reaction mechanism.

Experimental

Catalysts. The Pt/Al_2O_3 (0.5 wt% Pt) used in this study was a *reference catalyst* supplied by the Catalysis Society of Japan and was prepared as follows.[16] The γ-alumina (BET surface area, 174 m^2/g; pore volume, 0.66 ml/g) was impregnated in an aqueous solution of H_2PtCl_6 and then dried overnight. After calcination at 450 °C for 3 h in O_2, the catalyst was reduced in a H_2 stream at 300 °C for 3 h and then recalcinated at 600 °C for 3 h. The dispersion of Pt has been measured by means of the CO, H_2, and O_2 adsorption methods by several investigators and found to be *ca.* 0.6, though slightly scattered.[16]

Reaction Procedure. The catalyst (0.1—0.2 g), heated at 250 °C for 1 h in a H_2 stream, was suspended in 0.5 M D_2SO_4 and rereduced by bubbling D_2 (Showa Denko, 7N-purity, 99.97D%, P_D=13 mmHg, 1 mmHg=133.3 N·m^{-2}) through the solution. The reaction gas was mixture of 1,3-butadiene (4N-purity, P_R=14 mmHg), D_2(P_D=7 or 28 mmHg) and He (7N-purity) at a total pressure of 1 atm. The reaction was conducted by circulating the reaction gas through the solution at 20±1 °C. Our previous work has shown that, under these conditions, the diffusion of D_2 to the catalyst surface is rate-determining.[11,12] No reaction occurred under these conditions without the catalyst.

Solution. The solution of 0.5 M D_2SO_4 was prepared from D_2O (Showa Denko, 99.75D%) and sulfuric acid-d_2 (Merck 99D%). The deuterium content of the solution was estimated from its specific gravity. Unless otherwise stated, the solution was subjected to preelectrolysis overnight (anodically and then cathodically, several mA). The AES and XPS of the Pt electrode used for the preelectrolysis were run on an ESCA 3 Electron Spectrometer (VG Scientific, Ltd.) to detect any impurity picked up from the solution. Both the purity and the deuterium content of the solution greatly influenced the results. These effects will be discussed in the text.

Analysis. The analyses of the products were conducted gas-chromatographically and mass-spectrometerically, as has been described previously.[11]

[†] 1 M=1 mol dm^{-3}.

Results and Discussion

Saw-toothed Distribution. Table 1 presents the saw-toothed distributions of deuterium in butenes produced from 1,3-butadiene on 0.5 wt%Pt/Al_2O_3 in pre-electrolyzed 0.5 M D_2SO_4 with a high deuterium content (99.7D%). The saw-toothed shape is most clear in *trans*-2-butene and least clear in *cis*-2-butene, while the latter product shows the most enhanced deuterium-exchange among the three isomers. Such saw-toothed distributions are independent of the conversion, at least up to 20%. As has been stated above, each butene takes up much more deuterium atoms than it does in gaseous deuteration on Pt catalysts. For example, the average deuterium number, DN, ($\sum_{i=1}^{8} i\cdot X_i$, X_i is the fraction of the d_i-species) of *cis*-2-butene in Table 1 is 5.2, while, it is 2.1 in the gaseous deuteration.[3] However, the product distributions are very close to each other; butane: 1-butene: *trans-2*-butene: *cis*-2-butene=44:34:11:12 in this work and 44:36:10:10 at 15 °C in a gaseous reaction.[1] This fact indicates that the reaction mechanism is almost the same for both systems. The present saw-toothed distributions have also been observed in our separate experiments on such other catalysts as 5 wt% Pt/Al_2O_3, 0.5 wt% Pt/SiO_2, Pt/TiO_2, and Pt/Nb_2O_5 in a deuterated solution.[17] Therefore, it is concluded that the kind of supports and the amount of doped Pt have no effect on the reaction mechanism.

The saw-toothed shape is sensitive to the solution purity and the deuterium content of the solution. When the solution is used repeatedly without the pre-electrolysis (this was the case in our previous work on Pt/graphite[11]), the saw-tooth becomes less clear. Such a situation is reproduced in the present catalyst as exemplified by the distribution of deuterium in *trans*-2-butene in Fig. 1 (-○-). The overnight pre-electrolysis of the same solution makes the saw-toothed shape clearer, as is shown in Fig. 1 (-△-), indicating that a trace of impurity interferes with the appearance of the saw-toothed shape. In order to check on the impurities removed, the surface of the Pt electrode used for the preelectrolysis was examined by means of the AES and XPS. Both spectra show the peaks of carbon, oxygen, and sulfur. Since the peak intensity of carbon and oxygen is much the same as that on clean Pt foil, neither kind of atom comes from the solution. The presence of sulfur is easily understood, as it comes from SO_4^{2-} in the solution, not from the impurity. The complete absence of the other kinds of atoms in the spectra leads us to assume organic compounds as the impurities in the solution, since organic compounds will be decomposed during the anodic polarization, while inorganic compounds will be deposited through discharge during the cathodic polarization. However, a possibility would remain that the impurity is so small an amount of the inorganic compound that it cannot be detected by means of the AES and XPS. Further

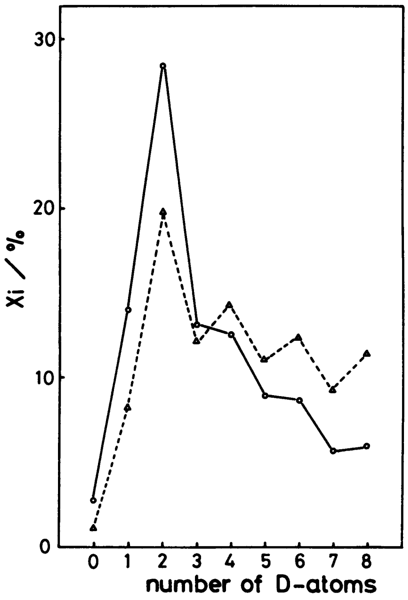


Fig. 1. Distribution of deuterium in *trans*-2-butene formed by the deuteration of 1,3-butadiene on Pt/Al_2O_3 in 0.5M D_2SO_4 of 98.5D%.
The solution; without (○) and with (△) preelectrolysis. P_R=14 mmHg, P_D=28 mmHg. Total conversions are 5.1% for ○ and 7.8% for △.

TABLE 1. DISTRIBUTION OF DEUTERIUM IN BUTENES OBTAINED BY THE HYDROGENATION OF 1,3-BUTADIENE ON Pt/Al_2O_3 IN 0.5 M D_2SO_4 OF 99.7 D%, CALCULATED DISTRIBUTIONS AND N-PROFILES
P_R=14 mmHg, P_D=7 mmHg, total conversion; 2.0%

Product	$i=$	0	1	2	3	4	5	6	7	8	DN	f_D
1-butene	found (X_i)	0.8	5.9	22.5	15.6	15.9	12.4	9.6	7.8	9.4	4.1	
	calcd (X_i)	0.2	4.6	22.7	15.6	16.7	12.6	9.5	8.0	9.0		
	N-profile (N_i)	0.0	0.0	23.0	13.0	17.0	13.0	12.0	0.0	21.0		0.90
trans-2-butene	found (X_i)	1.2	6.4	21.0	11.9	14.4	10.9	12.8	8.5	12.9	4.4	
	calcd (X_i)	0.2	4.0	22.0	12.5	14.9	11.0	12.6	10.0	12.7		
	N-profile (N_i)	0.0	0.0	23.0	10.0	16.0	8.0	16.0	0.0	27.0		0.91
cis-2-butene	found (X_i)	1.6	3.7	12.9	9.3	10.7	11.2	13.1	14.2	23.4	5.2	
	calcd (X_i)	0.0	1.8	13.0	8.9	10.0	11.2	13.4	14.2	23.5		
	N-profile (N_i)	0.0	0.0	13.0	8.0	9.0	9.0	15.0	0.0	42.0		0.93

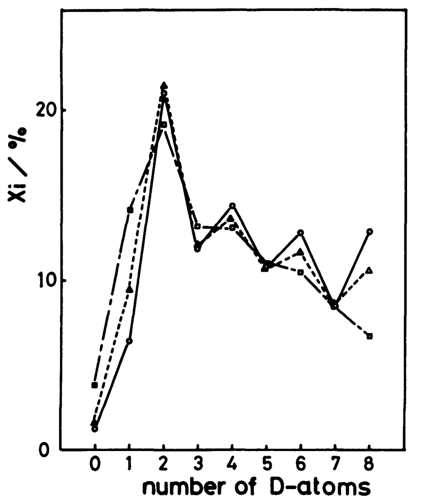


Fig. 2. Distribution of deuterium in *trans*-2-butene formed by the deuteration of 1,3-butadiene on Pt/Al_2O_3 in 0.5M D_2SO_4 of 99.7 D% (○), 97.6 D% (△), and 94.2 D% (□). All the solutions were subjected to the preelectrolysis overnight. P_B = 14 mmHg, P_D = 7 mmHg. Total conversions are 2.0% for ○ and 2.5 % for △ and □.

examination is required for the solution of this problem.

The saw-tooth also tends to be smoothed by decreasing the deuterium content of the solution (Fig. 2). In the solution of 94.2 D%, only the shoulders can be seen at butene-d_4 and -d_6. Though both factors - the solution purity and deuterium content of the solution- influence the saw-toothed shape very much, the lack of the saw-toothed shape in the previous work is taken predominantly as being due to the impurity factor, for the decrease in the deuterium content upon repeated use is not large enough to smoothen out the saw-toothed shape.

Isotopically exchanged 1,3-butadiene was not detected after the reaction. Therefore, it is concluded that there is an irreversible adsorption of 1,3-butadiene on the Pt surface.

Simulation by N-profile. The N-profiles of butenes were calculated in order to discuss the reaction mechanism. The N-profile consists of N_0, N_1, ⋯, N_8, where N_i represents the fraction of the butene in which i hydrogen positions have been equilibrated with the surface H/D pool. The fraction of molecules in which m out of i equilibrated atoms are deuterium, $X_m(i)$, is given by the standard binomial formula as;

$$X_m(i) = {}_iC_m f_D^m (1-f_D)^{i-m}$$

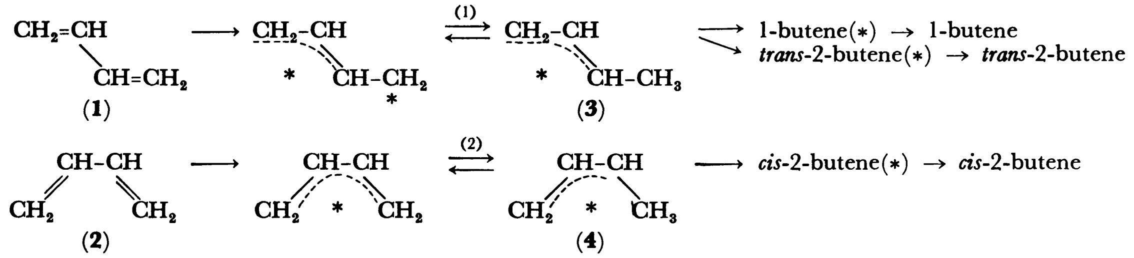
Thus, the fraction of d_m-species, X_m, is calculated as;

$$X_m = \sum_{i=m}^{8} X_m(i)\cdot N_i$$

The N-profile is determined so that X_m, m=0, 1, ⋯, 8, can best fit the observed distribution of deuterium by adjusting N_2, N_3, ⋯, N_8 (N_0=N_1=0 because the two hydrogen or deuterium atoms are necessarily taken up in butenes).

The N-profiles thus calculated are shown in Table 1, together with the experimental and the calculated X_m distributions of deuterium. The first thing to notice is that each experimental distribution is satisfactorily reproduced by the X_m calculated based on the N-profile listed in the third row for each butene. The N-profiles of 1-butene and *trans*-2-butene resemble each other. Maxima appear at N_2, N_4, and N_8. N_6 appears as a clear maximum for *trans*-2-butene, but only as a shoulder for 1-butene. N_7 is exceptionally small in both cases. Thus, the N-profiles of 1-butene and *trans*-2-butene also reflect the characteristic features of the maxima (or shoulder) at N_2, N_4, N_6, and N_8. On the other hand, the N-profile of *cis*-2-butene presents three maxima, at N_2, N_6, and N_8, without N_4.

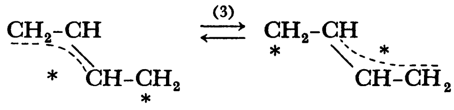
N-profile and Reaction Mechanism. The above features of N-profiles are explained by the following reaction mechanism including the reaction intermediates, **3** and **4** proposed by Bates *et al.*[3] for the same reaction, but on Pd/Al_2O_3 in the gas phase;



A molecule of 1,3-butadiene in the gas phase which exists in the *s-trans* **1** or *s-cis* **2** form is adsorbed irreversibly on the surface by delocalizing its π-electrons with the same geometrical configuration. The adsorbed *s-trans*-butadiene is converted to either 1-butene or *trans*-2-butene through *trans*-1-methyl-π-allyl **3**, whereas the *s-cis*-butadiene is converted only to *cis*-2-butene through *cis*-1-methyl-π-allyl **4**. Interconversions between the two kinds of adsorbed butadienes and between *trans*- and *cis*-1-methyl-π-allyls are not allowed because of the double-bond-like nature of the internal C–C bond. The lack of these interconversions is in accordance with the clear difference in the distribution of deuterium between *trans*- and *cis*-2-butene. This difference can not be accounted for by either σ- or π-bonded butadiene, since these adsorbed butadienes allow a rotation of the other vinyl group around the axis of the internal C–C bond and, hence, mutual interconversion between the *trans* and *cis* forms. The σ-bonded butadiene is not likely to be present, as is seen from the negative shift of the work function caused by the butadiene adsorption on Pt(100) and Pt(111).[18]

It must be expected on the basis of the above mechanism that a good correlation exists between the molar fraction of *cis*-2-butene in the products and that of *s-cis*-1,3-butadiene in the gas phase, because *cis*-2-butene is the only product from *s-cis*-1,3-butadiene (butane comes from the *s-trans via* 1-butene[11]). The former molar fraction is 12%, while the latter has been reported to be 3—7%.[19] The correlation is not bad if one takes into account the small modification in the stability of *s-cis*-1, 3-butadiene at the adsorption.

In the above mechanism, the *s-trans* route produces d_4 species by H/D exchange only through Step (1) and d_6 species through Step (1) and also the following Step (3), first proposed by Bates *et al.*[3];

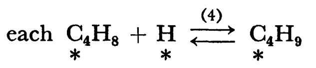


The relative rate of the hydrogenation of species **3** to the reverse of Step (1) for 1-butene formation is somewhat faster than the case of *trans*-2-butene formation. Thus, no distinct maximum is observed at N_6 for 1-butene.

On the other hand, the *s-cis* route gives the N_6-species of *cis*-2-butene through the single step of the reversible Step (2), because the two terminal methylenes in the adsorbed *s-cis*-butadiene are equivalent. Thus, the maximum at N_4 for *cis*-2-butene is diminished.

In addition to N_4 and N_6, considerable amounts of N_3 and N_5 are obtained. This can be readily explained by the slowness of the reverse rates of Steps (1) and (2).

The high fraction of N_8 and the zero amounts of N_7 for all the butenes suggest the presence of another sequence which causes an extremely fast H/D exchange over a molecule. The above mechanism can not explain the formation of N_8-species. One possible explanation could be that the butyl intermediate accelerates the H/D exchange by the following, reversible step;



$$\text{each } \underset{*}{C_4H_8} + \underset{*}{H} \overset{(4)}{\rightleftarrows} \underset{*}{C_4H_9}$$

where $\underset{*}{C}_4H_9$ includes the two possible butyls bonded at either of the carbon atoms of the double bond. Thus, all the hydrogen atoms in the molecule become H/D exchangeable through Steps (1) to (4). The admission of the adsorbed butyl, however, will undoubtedly cause the hydroisomerization of butenes, which is not the case in the hydrogenation of 1,3-butadiene.[11] Further investigation of the details will be required.

The above mechanism is different from that on Pt/Al_2O_3 in the gas phase proposed by Bates *et al.*[3], where *mono*- and *di*-π-bonded butadienes were proposed. Interconversion between these two π-bonded butadienes was taken not to be readily reversible. Their discussion was based on the N-profiles, which differed for the respective butenes, though the observed distribution of deuterium in 1-butene was very similar to that of *trans*-2-butene, but different from that of *cis*-2-butene, as in our results. Therefore, their N-profiles had to lead to a different mechanism. Since the f_D in the gas-phase deuteration is rather low, it is essentially difficult to calculate the N-profile accurately from the distribution of deuterium in less deuterated products, though a somewhat saw-toothed figure can be noticed in their N-profile calculated for *trans*-2-butene. On the other hand, the present system can provide highly deuterium-exchanged products which ensure an accurate N-profile, and it enables us to elucidate the reaction mechanism more precisely.

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