

Effect of Steric Strains upon the Hydrogenation of Olefins and Acetylenes on Pd/SiO₂ and Pt/SiO₂

HAROLD H. KUNG AND ROBERT L. BURWELL, JR.

Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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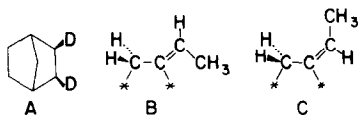
Cyclopentene, di-*t*-butylacetylene, 3-hexyne, *cis*- and *trans*-di-*t*-butylethylene, bicyclo[2,2,1]heptene, and bicyclo[2,2,2]octene were hydrogenated with H₂ and with D₂ in a liquid-phase, batch reactor at 20°C on Pd/SiO₂ and Pt/SiO₂. The effect of the presence of unsaturated hydrocarbon on the reaction, H₂ + D₂ → 2HD, was also investigated. In hydrogenation of the acetylenes, *trans*-ene and alkane were formed via α,α,β-triadsorbed alkane and this path was promoted by relief of intraadsorbate strain in the adsorbed acetylene during hydrogenation of di-*t*-butylacetylene. Hydrogenations of the *cis*- and *trans*-di-*t*-butylethylene proceeded by different mechanisms because of intraadsorbate strain in the adsorbed *cis*-ene. The ratio of isomerization to hydrogenation in the reaction of the *cis*-olefin with H₂ was very much larger than usual because of the large adsorbate-surface strain in the adsorbed *trans*-ene. Adsorbed hydrogen was in preequilibrium on neither catalyst and adsorbed olefin was not in preequilibrium on Pt/SiO₂ and probably not on Pd/SiO₂ except perhaps for *trans*-di-*t*-butylethylene. The effect of the two kinds of steric strain on rates of hydrogenation is analyzed.

INTRODUCTION

Steric strains resulting from interaction between an adsorbate and the surface of a heterogeneous catalyst have been known for many years to affect the form in which a molecule adsorbs and, consequently, the product proportions in many hydrogenations (1, 2). Two particularly simple examples of the effect of adsorbate-surface strain follow. In reactions of bicyclo[2,2,1]heptene, the side of the double bond toward -CH₂-CH₂- bridge is much more hindered than that toward the -CH₂- bridge (3). In consequence, reaction between deuterium and bicycloheptene on palladium leads to the *exo*-dideuterobicycloheptane (A) (3). In the hydrogenation of methylallene on palladium, the adsorbed form B is hindered by interaction between the surface of the metal and the methyl group. Therefore, form C is favored and the

thermodynamically less favored *cis*-2-butene heavily predominates over *trans*-2-butene in the products (4).

In addition, steric strain within adsorbed species (intraadsorbate strain) or within the reactant olefin can influence product selectivity. Thus the ratio *trans*-/*cis*-2-butene in the product of hydrogenation of 1,3-butadiene on palladium much exceeds the equilibrium ratio (4). The effect of these two kinds of strain upon rates of hydrogenation is much less clear. For example, ring strain in bicycloheptene¹ (5) would be substantially alleviated in adsorbed bicycloheptene. On the other hand, there must be some adsorbate-surface strain in the adsorbed olefin even when adsorption is on the *exo* side because of interaction between the surface and the methylene bridge. What role do these two kinds of strain play in making the hydrogenation of bicycloheptene one of the fastest known for olefins (6, 7)? Certainly in some cases in which the adsorbate-



¹ The enthalpy of hydrogenation of *norbornene* is 25 kJ more negative than that of cyclohexene; see Turner *et al.* (5).

surface strain is large, hydrogenation is slow, for example, that of *trans*-di-*t*-butyl-ethylene (8). However, the rate of hydrogenation of bicyclo[2,2,2]octene is nearly as fast as that of bicycloheptene (6) and here adsorption must involve a form like the *endo* side of bicycloheptene.

Both types of steric strain appear in the hydrogenations of di-*t*-butylacetylene and the *cis*- and *trans*-olefins derived therefrom (8, 9). This system coupled with bicycloheptene and bicyclooctene seemed to offer prospects of providing mechanistic information of a type not ordinarily available. This paper reports the results of the investigation of the hydrogenations of these compounds from a mechanistic point of view.

EXPERIMENTAL METHODS

The purification of reagents employed has been described (9) except for the following. Bicyclo[2,2,1]heptene was refluxed with potassium and distilled therefrom three times. The operations were conducted under an atmosphere of nitrogen. Bicyclo[2,2,2]octene was treated similarly once and then further purified by preparative gas chromatography. When deuterium was used for hydrogenation, it was admitted to the system through a silica gel trap cooled to -196°C .

The 0.104% Pt/SiO₂ catalyst was prepared by ion exchange of Pt(IV) ammine on Davison Grade 59 silica gel, 400+ mesh (9). As measured by hydrogen chemisorption at 25°C (10), the percentage exposed was 105%. Accuracy in this number is low because of the small content in platinum which was chosen to avoid diffusional limitations. The 0.037% Pd/SiO₂ catalyst was prepared by ion exchange using tetrammine palladium dichloride and 270- to 400-mesh Grade 59 silica gel which had been pretreated as previously described (9). The product was washed, dried at 120°C, reduced in hydrogen at 300°C for 19 hr, purged with helium for 2 hr, and cooled in helium. The percentage exposed of the Pd was measured by chemisorption of deute-

rium at 60°C from neon carrier using a pulse technique (10). The percentage exposed was 31%.

Hydrogenations were run in a constant-volume, batch apparatus previously described (9) using 1.0 cm³ of cyclohexane as solvent, 0.05–0.1 cm³ of unsaturated hydrocarbon, and 10–60 mg of catalyst. The temperature was 20°C; the pressure was 1 atm unless otherwise stated. The reaction apparatus had a volume of about 2.1 liters and consisted of a large, thermostated gas reservoir connected to a reactor of about 24 cm³. Liquid unsaturated hydrocarbons were injected into the reactor neat, but solid hydrocarbons (bicycloheptene and bicyclooctene) were injected as solutions in cyclohexane. The pressure fall resulting from consumption of hydrogen was about 1% of the total pressure. It was measured by means of a capacitance manometer and recorded.

As before, runs with various unsaturated compounds were sandwiched between runs with cyclopentene by means of successive injections of reactants. That is, after the pressure fall terminated, the agitation of the reactor was stopped, a new sample of unsaturated hydrocarbon was injected, and agitation was started again to begin a new run. The agreement between the two cyclopentene runs established that the runs were free from the effects of extrinsic poisons. Previous work (9) also establishes that the hydrogenation runs were free from the influence of mass transport.

In some experiments using deuterium, the hydrogenation was interrupted at 25–60% conversion, a sample was removed, separated by gas chromatography, and the various isolated components were analyzed mass spectrometrically on a Consolidated 21-104 mass spectrometer using a nominal ionizing voltage of 10 V.

In some cases, hydrogenation was effected with a roughly equimolar mixture of H₂ and D₂ by injecting 12 cm³ of D₂ into the reactor vessel (whose volume was 24 cm³) after a reaction had been prepared for a

conventional hydrogenation. The injected D_2 displaced H_2 from the reactor bulb, but because of mixing during the injection the ratio D_2/H_2 in the reactor was somewhat less than unity. Injection was immediately after the injection of unsaturated hydrocarbon and at a stage when the apparatus had already been filled with H_2 . The run was interrupted after 3–5 cm^3 of $H_2 + D_2$ had been consumed. The gas mixture in the reactor was analyzed for H_2 , HD, and D_2 by gas chromatography on a $FeCl_3/Al_2O_3$ column in the apparatus of Kenneth S. Stec (11).

RESULTS

Table 1 lists turnover frequencies N_t in molecules reacted per second per surface atom of Pt or Pd and the deuterium isotope effect on the rates. A second injection of a reactant led to the same rate vs time as the original injection, as shown in Fig. 1. The kinetic orders in cyclopentene and di-*t*-butylacetylene were both 0.0 on Pt/SiO₂ and 0.20 and 0.28, respectively, on Pd/SiO₂. Kinetic orders were obtained by fitting the form (concentration of olefin or acetylene, a) to the best value of a , but the use of the initial rates for the hydrogenation of cyclopentene in the range 0.06 to 0.5 M led to the same kinetic order. The apparent orders in bicyclooctene increased with total

TABLE 1
Rates of Hydrogenation of Various Compounds^a at 20°C, 1 atm

Catalyst	N_{cp}^b	N_{dtba}/N_{cp}	N_{bch}/N_{cp}	N_{bco}/N_{cp}	r_{H_2}/r_{D_2}	
					bch	bco
Pt/SiO ₂	6.5	0.34	2.2	2.1	1.2	1.43
Pd/SiO ₂	44	0.47	1.8	2.0	1.25	1.30

^a Cyclopentene, cp; di-*t*-butylacetylene, dtba; bicyclo[2.2.1]heptene, bch; bicyclo[2.2.2]octene, bco.

^b Turnover frequency of cyclopentene at 0.5 M . N_{dtba} is at 0.4 M , N_{bch} at 0.15 M , and N_{bco} at 0.2 M .

^c The ratio of the rates of hydrogenation in hydrogen and in deuterium at the concentrations given in footnote b .

pressure. At pressures of 1.0, 1.5, and 2.0 atm the kinetic orders in bicyclooctene were 0.10, 0.11, and 0.16, respectively, on Pt/SiO₂ and 0.18, 0.25, and 0.36 on Pd/SiO₂. At [bicyclooctene] = 0.2 M the kinetic orders in H_2 and D_2 were both about unity. The effect of hydrogen pressure was not investigated on the other unsaturated hydrocarbons. The kinetic order in bicycloheptene was zero on Pt/SiO₂ and 0.13 on Pd/SiO₂.

Initial product distributions in the hydrogenations of di-*t*-butylacetylene, *cis*-di-*t*-butylethylene, and 3-hexyne are presented in Table 2. Table 3 presents the isotopic distribution patterns of alkane and unreacted olefin resulting from the hydrogenation of several olefins with deuterium. The isotopic distribution patterns of the alkane

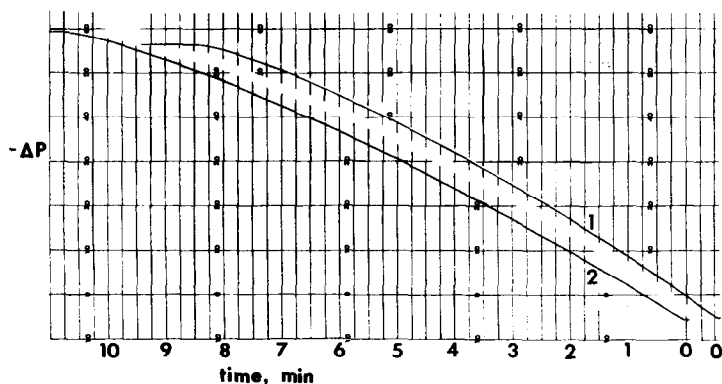


FIG. 1. Decrease in pressure in arbitrary units on the y-axis vs time on the x-axis for two successive injections of 0.06 cm^3 of cyclopentene on 34.22 mg of Pd/SiO₂. The recording traces have been put close together to facilitate comparison. The concentration of cyclopentene in run 2 is 1/1.06 that in run 1. Both curves are fitted by a form $k[C_5H_8]^{0.2}$ and k is the same in both cases.

TABLE 2
 Initial Product Distributions in the Hydrogenations of Various Compounds

Catalyst	Reactant	<i>cis</i> -ene (%)	<i>trans</i> -ene (%)	ane (%)	(<i>t</i> -ene + ane)/ <i>c</i> -ene
Pd/SiO ₂	dtba ^a	68	27.2	4.8	0.47
	3-hexyne	93.2 ^b	2.4 ^b	2.8	0.06
	<i>c</i> -dtbe ^c		95	5	
Pt/SiO ₂	dtba	70	21	9	0.43
	3-hexyne	81 ^d	6 ^d	13	0.23
	<i>c</i> -dtbe ^e		90	10	

^a Di-*t*-butylacetylene.

^b *cis*- and *trans*-3-hexene. There was also about 0.8% *cis*-2-hexene and 0.8% *trans*-2-hexene.

^c *cis*-Di-*t*-butylethylene. N_i (hydrogenation + isomerization) was initially about 70 at 1.2M. The accuracy is low since N_i could not be accurately measured from the rate of consumption of hydrogen.

^d *cis*- and *trans*-3-hexene. There was less than 0.5% *cis*-2-hexene.

^e N_i was initially about 3, but see footnote *c*.

were fitted to the following statistical model that has been described in detail in Ref. (12): it is assumed that the *effective* ratio D^*/H^* in the adsorbed pool had some

average value in a given run, that two hydrogen atoms of alkane had been equilibrated with the adsorbed pool in the fraction of alkane N_2 , three hydrogen atoms

 TABLE 3
 Reaction of Deuterium with Olefins^a

Catalyst	bch		bco		<i>t</i> -dtbe	
	Pd	Pt	Pd ^b	Pt ^c	Pd ^d	Pt ^e
Conv. (%) ^f	50		57		33	
ane- <i>d</i> ₄ (%)	0	0.0	0.0	1.3(1.3)	0.0	0.0
ane- <i>d</i> ₃ (%)	0	2.0	0.6(0.6)	4.3(4.3)	2.1(2.1)	1.8(1.9)
ane- <i>d</i> ₂ (%)	100	93.8	90.3(89.7)	78.9(78.3)	89.0(88.3)	85.8(84.9)
ane- <i>d</i> ₁ (%)	0	4.2	9.1(9.4)	14.4(15.4)	8.8(9.3)	12.2(12.7)
ane- <i>d</i> ₀ (%)	0	0	0.0(0.4)	1.0(0.8)	0.0(0.2)	0.0(0.5)
<i>d</i> _{av} ^g	2.0	1.98	1.92	1.90	1.94	1.90
ene- <i>d</i> ₁ (%) ^h	0	0	2.6	2.0	2.0	2.0

^a Bicycloheptene bch; bicyclooctene, bco; *trans*-di-*t*-butylethylene, *t*-dtbe.

^b The values in parentheses result from $D^*/H^* = 0.93/0.07$, $N_3 = 0.007$, and $N_2 = 0.993$.

^c $D^*/H^* = 0.91/0.09$, $N_4 = 0.0192$, $N_3 = 0.0498$, and $N_2 = 0.9310$.

^d $D^*/H^* = 0.95/0.05$, $N_3 = 0.0245$, $N_2 = 0.9755$.

^e $D^*/H^* = 0.93/0.07$, $N_3 = 0.023$, $N_2 = 0.977$.

^f Percentage hydrogenated at time of sampling.

^g Average number of atoms of deuterium in the alkane.

^h Percent of olefin exchanged to *d*₁. Olefin-*d*₂ was always undetectable.

had been equilibrated in the fraction N_3 , and four in N_4 . N_0 and N_1 are necessarily zero and N_4 was made nonzero only when necessary. Of course, alkane- d_0 and alkane- d_1 will be nonzero when $D^*/H^* < \infty$. Alkane- d_0 can result, for example, from reaction of $2H^*$ with unexchanged adsorbed olefin and such alkane- d_0 is counted in N_2 . The values calculated from this model give good fits to the data as shown in Table 3.

The ratio of hydrogenation to isomerization during the hydrogenation of *cis*-di-*t*-butylethylene was independent of conversion and of whether H_2 or D_2 was used. This same value of the ratio also applied to the reaction of H_2 and *cis*-di-*t*-butylethylene- d_2 (made by addition of D_2 to di-*t*-butylacetylene on a Pt/ Al_2O_3 catalyst of high percentage exposed (9), actual isotopic content, d_2 90, d_1 8.2, d_0 1.8%). Table 4 presents the isotopic analysis of products and reactant in reaction between D_2 and the *cis*-ene at several conversions. Di-*t*-butylethane- d_3 amounted to about 19% of total alkane on both catalysts, but accuracy in the isotopic distribution pattern of alkane was low because the amount of alkane was low, the alkane isolated by gas chromatography was contaminated with *trans*-ene, and the parent peak of alkane was weak.

In an otherwise empty reactor, an equimolar mixture of $H_2 + D_2$ was converted

TABLE 4
Reaction of *cis*-Di-*t*-butylethylene with Deuterium

	Pd/SiO ₂		Pt/SiO ₂	
	20	38.9	74.9	34.6
Conv., % ^a	20	38.9	74.9	34.6
<i>t</i> -ene- d_1 , % ^b	9.0	13.4	20	58.8
<i>t</i> -ene- d_0 , %	91.0	86.6	80	41.2
<i>c</i> -ene- d_0 , %	—	100	100	100
ane- d_{av} ^c	—	0.85	—	1.34

^a Percentage conversion of reactant, isomerization + hydrogenation.

^b Percentage of *trans*-di-*t*-butylethylene- d_1 in total *trans*-ene. The content in *trans*-ene- d_2 was always negligible.

^c The average number of deuterium atoms in di-*t*-butylethane.

TABLE 5

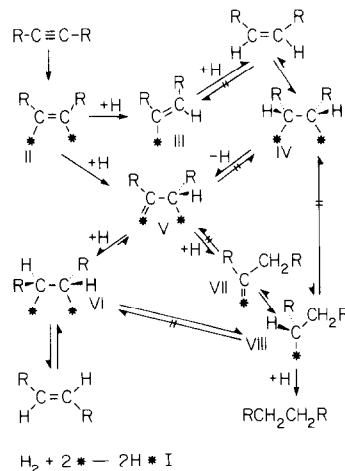
Isotopic Exchange between H_2 and D_2 in the Presence of Solvent but in the Absence of Unsaturated Hydrocarbon

Catalyst	Amount (mg)	Time (min)	H ₂ (%)	HD (%)	D ₂ (%)
Pd/SiO ₂	28.4	2	55.1	4.8	40.1
		8	54.9	16.6	28.4
Pt/SiO ₂	16.58	1	50.5	11.3	38.2
		4	51.2	24.7	24.0

nearly to equilibrium within 1 min by 10 mg of either catalyst. In the presence of cyclohexane solvent as well as of catalyst but in the absence of unsaturated hydrocarbon, rates were much slower, as shown in Table 5. In the absence of catalyst, the rate was negligible. The results of reaction between $H_2 + D_2$ and bicycloheptene, bicyclooctene, and 3-hexyne are shown in Table 6 and di-*t*-butylacetylene in Table 7.

DISCUSSION

The reactions shown in Scheme 1 can reasonably accommodate our results. Intermediates II, IV, and VI are shown as σ -complexes. If cluster complexes are the



SCHEME 1. Two parallel bars crossing an arrow indicate that the reaction is inhibited by intraadsorbate or adsorbate-surface strain when R is *t*-butyl. A short arrow indicates a process of a rate which is small when R is *t*-butyl.

TABLE 6

Effect of Various Unsaturated Hydrocarbons upon the Rate of Equilibration of Hydrogen and Deuterium

Catalyst	Weight (mg)	Conv. ^a (%)	Time (min)	Composition					
				Gas			Alkane ^b		
				H ₂ (%)	HD (%)	D (%)	D ₀ (%)	D ₁ (%)	D ₂ (%)
				Bicyclo[2,2,2]octene					
Pd/SiO ₂	7.20	42	4	62.6	0.2	36.2	46.0	44.4	9.6
							(47.1)	(43.0)	(9.9)
Pt/SiO ₂	15.30	40	2.7	56.8	4.7	38.5	39.7	47.3	13.0
							(40.4)	(46.3)	(13.3)
				Bicyclo[2,2,1]heptene					
Pd/SiO ₂	18.62	25	1.7	68.8	0.9	30.3	46.8	38.1	15.1
							(40.7)	(46.2)	(13.1)
Pt/SiO ₂	35.46	25	1.8	60.0	4.4	35.6	37.5	44.3	18.1
							(34.9)	(48.2)	(16.9)
				3-Hexyne					
Pd/SiO ₂	26.7	20	10	65.4	1.1	33.5			
Pt/SiO ₂	34.7	8	10	59.2	3.6	37.2			

^a Loss of reactant (%).^b D_i is percentage of alkane-d_i. The values in parentheses are those computed for a statistical distribution of deuterium.

best analogy to surface complexes on group VIII metals, II is probably the best simple representation of adsorbed RC≡CR (13). However, some π-bonding may be involved in II, and IV and VI may even be mainly π-bonded. The discussion will be based on the relative magnitudes of the

intraadsorbate strain and the adsorbate-surface strain in the various surface species, which are determined by the geometry of the adsorbate.

In a π-complex in which olefin is bound to a single site, there is lengthening of the C=C bond and bending back of the four

TABLE 7

Reaction of H₂ + D₂ with Di-t-butylacetylene

Catalyst	Weight (mg)	Conv. ^a (%)	Time (min)	Composition						
				Gas			Alkenes ^b			
				H ₂ (%)	HD (%)	D ₂ (%)	D ₀ (%)	D ₁ (%)	D ₂ (%)	
Pd/SiO ₂	27.51	41	9	54.4	24.3	21.3	<i>cis</i> :	49.8	41.7	8.5
								(50.1)	(41.3)	(8.6)
							<i>trans</i> :	46.7	43.4	9.9
							(47.0)	(43.0)	(10.0)	
Pt/SiO ₂	36.85	32	10.5	51.8	34.1	14.1	<i>cis</i> :	52.8	39.3	7.9
								(51.9)	(40.3)	(7.8)
							<i>trans</i> :	45.4	43.4	11.1
							(45.2)	(44.1)	(10.8)	

^a In loss of reactant (%).^b The values in parentheses are those for a statistical distribution.

substituent groups away from the site (14). Thus, the hydrocarbon portion of the adsorbed olefin would have a similar geometry both in a π -complex form and in that of representations IV and VI which are disubstituted alkanes, or, more precisely, eclipsed α,β -diadsorbed alkanes where "adsorbed" signifies that a hydrogen atom has been substituted by a surface site (15). We shall attempt to present conclusions which are independent of present uncertainty as to the "electronic" details of the structures of IV and VI and of whether binding is in atop positions or in positions centered between two or more surface atoms.

When R is *t*-butyl, many of the intermediates will have abnormally high energies and some of the reactions among intermediates will become negligible in rate. The reaction sequences will be considerably simplified with interesting consequences. In addition, the absence of hydrogen atoms α to >C=C< eliminates any possibility of allylic intermediates.

Two kinds of strain energies appear when R is *t*-butyl. Intraadsorbate strain will result from repulsion between the two *t*-butyl groups. Because of such repulsion, the enthalpy of *cis*-di-*t*-butylethylene is ~ 42 kJ greater than that of the *trans* isomer (16). In converting the olefin to IV (and independent of whether IV is a π -complex or an eclipsed diadsorbed alkane), bending back the substituents will increase intraadsorbate strain and lengthening the C–C bond will decrease it. Overall it appears likely that the intraadsorbate strain will increase and the strain may even result in some rotation about the central C–C bond. Bending back the substituents will also generate strain in II vs di-*t*-butylacetylene. Intraadsorbate strain in III should be about equal to that in the *cis*-olefin. The rotation of 60° about the C–C bond in going from *cis*-olefin to V should substantially reduce intraadsorbate strain. Finally in VI, intraadsorbate strain should be zero (and independent of whether VI is a π -complex or an eclipsed

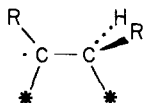
diadsorbed alkane). In the above discussion we assign zero strain to the *trans*-olefin and to alkane in the *trans* conformation.

The second form of strain, adsorbate–surface strain between *t*-butyl groups and the surface, is of the type between the methyl group of methylallene and the surface in form B. It should appear to varying degrees in all of the adsorbed intermediates but most seriously in VI. Adsorbate–surface strain in IV and V can probably be alleviated somewhat by tilting so as to elevate the *t*-butyl groups from the surface. Such tilting must be present in adsorbed bicyclooctene but is impossible in VI. Accordingly, adsorption of *cis*-di-*t*-butylethylene should be hindered but that of the *trans* isomer should be hindered much more. In competitive hydrogenations on platinum, adsorption of cyclopentene is preferred to that of the *cis*-olefin by a factor of at least 1000 but the presence of the *cis*-olefin almost completely inhibits adsorption of the *trans*-olefin (8).

Approach of di-*t*-butylacetylene to the surface will generate adsorbate–surface strain and II must involve substantial adsorbate–surface strain. In the molecular complex between this acetylene and $\text{M}_2(\text{CO})_6$ where M is Fe or Co (17), the carbon atoms of the $\text{C}\equiv\text{C}$ unit and a carbon atom from one of the methyl groups on each *t*-butyl group are nearly in a straight line. If this structure was to exist on a more densely packed surface plane, the two non-bonded methyl carbon atoms would be as close to the surface as the bonded carbon atoms of the $\text{C}\equiv\text{C}$ unit and at least one of the hydrogen atoms of each of the two methyl groups would be even closer. It has been conjectured that the adsorbate–surface strain in II is partly alleviated by extractive chemisorption in which one or two surface platinum atoms of the adsorption complex are lifted above the surface plane (8, 9).

Hydrogenations of disubstituted acetylenes on group VIII metals give *cis*-ene as the major initial product despite the fact

that *trans*-ene is favored thermodynamically. It has been generally assumed for many years that *cis*-ene results from the sequence $RC\equiv CR \rightarrow II \rightarrow III \rightarrow cis\text{-ene}$, in which no opportunity for the formation of *trans*-ene and alkane arises. The question has been, how are the minor initial products (*trans*-ene and alkane) formed? Bond, Dowden, and Mackenzie (18) suggested that they arise through the intermediate,



In view of thermodynamic difficulties in forming such a free radical and of the subsequent discovery of alkylidene complexes of transition metals which involve $M=C$ bonds, formulation of this complex as V seems preferable. The mechanistic consequences are the same.

It has been proposed that an atom of hydrogen could add to an adsorbed carbon atom from a direction opposite to the surface:



Such a reaction could lead to the formation of *trans*-ene from acetylenes. It now appears unlikely that this process is ever very rapid (19), but it is particularly unlikely when R is t-butyl, since the t-butyl group blocks the direction necessary for the approach of a hydrogen atom.

Comparison of the Hydrogenations of Di-t-butylacetylene and 3-Hexyne

In applying the scheme to the case in which R = t-butyl, we shall assume that an increase in adsorbate-surface strain would make the rates of $VIII \rightarrow VI$ and $VII \rightarrow V$ negligible and that increase in intraadsorbate strain would make the rates of $V \rightarrow IV$ and $VIII \rightarrow IV$ negligible. What would be the effect of these restrictions upon the hydrogenation of the acetylene with R = t-

butyl as compared with that in which R = ethyl where intraadsorbate strain would be small?

The ratio $(II \rightarrow V)/(II \rightarrow III)$ should be larger for R = t-butyl because relief of the large intraadsorbate strain in II will promote $II \rightarrow V$. The ratio can be measured by the following ratio of initial yields, (*t*-ene + ane)/*c*-ene. On our model, the equality will be exact for R = t-butyl because $V \rightarrow IV$ is "forbidden" and the initial concentration of *cis*-ene is low. When R = ethyl, $V \rightarrow IV$ can lead to the formation of a little *cis*-ene and the ratio of initial yields will slightly underweigh the given ratio of rates. However, even when R is ethyl, IV has some intraadsorbate strain analogous to that which makes the equilibrium ratio *cis*-ene/*trans*-ene considerably less than unity. Thus, $(V \rightarrow IV)/(V \rightarrow VI)$ should be rather small. These conclusions accord with the data of Table 2. The ratio (*t*-ene + ane)/(*c*-ene) is unusually large for R = t-butyl, much larger than for R = ethyl. The very weak adsorption of *trans*-di-t-butylethylene should favor desorption of VI vs reaction of VI to VIII. This would make *t*-ene/ane larger for R = t-butyl as was indeed observed.

The Hydrogenation of Cis- and Trans-di-t-butylethylenes

When R = t-butyl, the scheme leads to an unusual mechanistic situation: the hydrogenations of *cis*- and *trans*-enes proceed by different mechanisms.

In the hydrogenation of *trans*-di-t-butylethylene, formation of an isomeric olefin being thermodynamically impossible and $VIII \rightarrow V$ being forbidden, hydrogenation should proceed by the simplest variant of the Horiuti-Polanyi mechanism,

ene \rightarrow diadsorbed (VI)

\rightarrow monoadsorbed (VIII) \rightarrow ane

with the reverse of the middle step being forbidden. On the simplest sequence this irreversibility would lead alkane- d_2 to be

the only product of reaction between D_2 and the *trans*-ene. In fact (Table 3), a very small amount of alkane- d_3 is formed and probably via trace formation of V or VII. As required by the scheme, unreacted *trans*-ene is unlabeled or almost so. Nearly exclusive formation of alkane- d_2 is rare in reaction between D_2 and olefins (12) on group-VIII metals. However, bicycloheptene exhibits similar simplicity in mechanism and results (Table 3). Here, no isomeric olefins are possible and reversibility of $IV \rightarrow VIII$ would have no isotopic consequences. Reaction of bicyclooctene with D_2 approaches the simplicity of the other two olefins.

On platinum catalysts, the ratio of isomerization to hydrogenation during the hydrogenation of olefins usually amounts to only a few percent (6, 12). The hydrogenation of *cis*-di-*t*-butylethylene is unusual in that the ratio is extraordinarily large, 90/10 on Pt/SiO₂ and 95/5 on Pd/SiO₂ (Table 4). The conventional Horiuti-Polanyi mechanism for isomerization, *cis*-ene $\rightarrow IV \rightarrow VIII \rightarrow VI \rightarrow trans$ -ene, would be forbidden because $VIII \rightarrow VI$ would involve a large increase in adsorbate-surface strain. Rather, isomerization would proceed via the sequence *cis*-ene $\rightarrow IV \rightarrow V \rightarrow VI \rightarrow trans$ -ene, and the large yield of *trans*-ene would result from the weakness of adsorption of *trans*-ene in VI. Although at least one hydrogen atom of the *trans*-ene formed during reaction between D_2 and *cis*-di-*t*-butylethylene should be equilibrated with the surface D^*/H^* pool, much *trans*-ene- d_0 was formed and particularly with Pd/SiO₂ (Table 4). This results from the ratio D^*/H^* being small, unlike the case in the reaction between D_2 and the *trans*-ene. With *cis*-ene, considerable H^* is formed by $IV \rightarrow V$, desorption of HD is suppressed by the presence of IV and V, and the rate of adsorption of D_2 is low because of the low yield of ane. Thus, much $V \rightarrow VI$ involves the addition of H rather than of D. The yield of *trans*-ene- d_1 increases with increasing conversion. D^*/H^* increases with con-

version as the reaction slows consequent to the kinetic order in *cis*-ene being finite. Once made, *trans*-ene does not further react as long as any *cis*-ene remains unreacted. At least with Pd/SiO₂, D^*/H^* appears to be larger in formation of alkane than in formation of *trans*-ene. Presumably, then, V is formed at two different surface sites, one giving mostly isomerization and the other, isomerization and hydrogenation. Such a situation has been observed in the hydrogenation of other olefins on palladium and platinum catalysts (7, 12).²

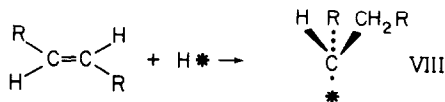
In the hydrogenation of the *cis*-ene, the ratio *trans*-ene/alkane was the same in the presence of hydrogen, in that of deuterium, and in the hydrogenation of *cis*-ene in which the two vinylic hydrogen atoms had been replaced by deuterium. Since $IV \rightarrow VIII$ and $IV \rightarrow V$ should have different kinetic isotope effects, isomerization and hydrogenation both appear to proceed via V. Further, since $VI \rightarrow trans$ -ene and $VI \rightarrow VIII$ would have different kinetic isotope effects, alkane should mainly be formed via $V \rightarrow VII$ since this step and $V \rightarrow VI$ should exhibit the same kinetic isotope effect.

There appears to be no evidence as to whether the rate of $V \rightarrow VII$ is significant for cases other than R = *t*-butyl. However, as judged by the isotopic exchange patterns of cyclopentane exchanged with D_2 , the rate ratio $(VIII \rightarrow VII)/(VIII \rightarrow IV)$ is negligible for exchange on Pd but important on Pt (20-22). $VIII \rightarrow VII \rightarrow VIII$ can transfer the position of adsorption on cyclopentane from one side of the ring to the other.

One might imagine that, when R = *t*-butyl, adsorbate-surface strain would be so

² The isomerization of 1-butene on Pd/Al₂O₃ produced predominantly 2-butene- d_0 . Bond and Wells (20) interpreted this as resulting from some isomerization process in which a hydrogen atom was transferred intramolecularly during isomerization. Some 2-butene- d_0 must have been made by the mechanism of the present paper and it seems reasonable and much simpler to assume that all was made by this mechanism.

large as to make any contributions from VI negligible. The *trans*-ene would then undergo hydrogenation by reactive adsorption,

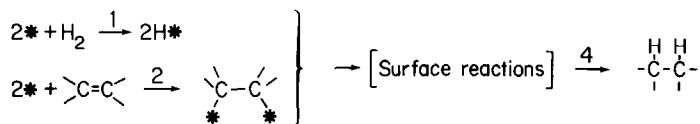


followed by further reaction with H*. The ratio *cis*/*trans*-ene in the hydrogenation of *cis*-di-*t*-butylethylene would depend upon the gain (VIII + H* \rightleftharpoons *cis*-ene) or the loss (VIII \rightleftharpoons *trans*-ene + H*) of an atom of hydrogen from VIII. This situation appears

incompatible with the absence of a kinetic isotope effect on the product ratio. However, arguments based upon such kinetic isotope effects may not be entirely conclusive.

The Question of Preequilibrium during Hydrogenation

An exact treatment of the kinetics of the hydrogenation reactions of this paper would involve allowance for the reverse rates of the adsorptions of hydrogen, r_{-1} , and of unsaturated hydrocarbons, r_{-2} , in the conventional scheme.



However, one may ask which is the closest approximation to the correct treatment, (a) the assumption that the reverse rates are fast enough so that the adsorptions may be treated as representing preequilibria, i.e., the reaction may be adequately approximated by a Langmuir-Hinshelwood mechanism (15), or (b) the assumptions that the reverse rates are so slow that the adsorptions may be treated as irreversible.

The reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ was too fast to follow in our system in the absence of solvent and unsaturated hydrocarbon ($N_t > \sim 200 \text{ sec}^{-1}$). In the presence of solvent the rate was slower: for formation of HD, N_t was 21 on Pt/SiO₂ and 26 on Pd/SiO₂ (Table 5). The slower reaction may be related to some coverage of metal by some form of adsorbed cyclohexane and to the fact that, at equilibrium, the ratio of the concentration of hydrogen in solution to that in the gas phase is 0.1 (24). At similar rates of consumption of hydrogen during

hydrogenations in solution on these catalysts, the concentration gradients of H₂ have been shown not to influence the rate of hydrogenation significantly. However, the reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ involves gradients both of H₂ + D₂ in and of HD out. The diffusion uninfluenced rate might be somewhat larger than the values given above.

As shown in Table 6, the presence of bicyclooctene, bicycloheptene, or 3-hexyne drastically reduced the rate of the reaction, $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$, as had been previously noted for ethylene (25) and 2-butyne (26). In these runs, r_1 was much greater than r_{-1} , r_4 (the rate of hydrogenation) was only a little less than r_1 , and preequilibrium cannot have existed for hydrogen. As previously found for $\text{H}_2 + \text{D}_2 + 2\text{-butyne}$ (26), the isotopic distribution was random in products from hydrogenations with $\text{H}_2 + \text{D}_2$ (Tables 6 and 7). In the framework of the scheme, H* and D* must have been randomized on the surface be-

fore adding to the surface organometallic complexes.³

The value of r_{-1} was several times greater than the equivalent of r_4 for the hydrogenation of di-*t*-butylacetylene with $H_2 + D_2$ (Table 7), the system was closer to a preequilibrium in hydrogen, but r_1/r_{-1} was still significantly different from unity. With the very weakly adsorbed *trans*-di-*t*-butylethylene, the approach to a preequilibrium in hydrogen may well have been good. In addition, in this case, the kinetic order in olefin was about 0.4 (8) and the degree of approach to a preequilibrium in olefin may also have been good. However, as the strength of adsorption of the olefin increases, the rate constant for its desorption decreases and the kinetic order in olefin approaches zero. It seems very unlikely that r_2/r_{-2} will approach unity or that r_{-2}/r_4 will usually be large for a zero-order reaction. Furthermore, the low degree of isomerization which ordinarily accompanies hydrogenation on platinum accords with the view that r_{-2}/r_4 is small in most hydrogenations on this catalyst. On platinum, then, we doubt that either step 1 or step 2 is often in preequilibrium. Hussey rejected preequilibrium in adsorption of olefin on related grounds (6). In sum, to a good approximation, one can view the rate of most hydrogenations on platinum as simply proportional to the rate at which hydrogen strikes the sites available to it. Madon, O'Connell, and Boudart have proposed (primarily for the hydrogenation of cyclohexene) that on platinum catalysts (1) the adsorption of hydrogen is nearly irrevers-

³ Siegel *et al.* (27a) proposed a scheme for reactions between hydrocarbon and hydrogen on the surface of metals which is based on analogies with mononuclear organometallic catalysts rather than with cluster compounds. Intermediates are adsorbed and react at a single metal atom and hydrogen migration is considered to be slow. The mobility of hydrogen atoms is fast on clean surfaces (27b), but this fact does not establish the case for surfaces covered with hydrocarbon. Should the mononuclear analogy prove correct, the conclusions of the present paper would transfer to the Siegel scheme with little change.

ible, but (2) the adsorption of olefin can be treated as a preequilibrium (28). We accord with item (1) but not with (2). They also proposed that the chemisorption of hydrogen occurs not on the surface of "platinum but on the chemisorbed hydrocarbon species which almost completely cover the metal." A recent publication from this laboratory (29) provides evidence which favors the opposite conclusion, that hydrogen is adsorbed directly on the surface of platinum.

Similar considerations apply to preequilibrium in reaction 1 on palladium. The ratio r_{-1}/r_4 is much less than unity and even smaller than on Pt/SiO₂ (Tables 6 and 7). On the other hand, in general, the ratio isomerization/hydrogenation is much larger on palladium than on platinum (19, 30) and in many cases the order of magnitude of the ratio is one. It is doubtful that such a value is large enough to correspond to a proper preequilibrium in olefin. Furthermore, if, as appears likely, hydrogenation and isomerization proceed primarily on separate sets of sites, the ratio would be much smaller at the sites which primarily lead to hydrogenation, and preequilibrium would not be established for hydrogenation. For an opposite view on this matter see Ref. (31).⁴

⁴ Gonzo and Boudart (31) have interpreted the hydrogenation of cyclohexene on Pd/SiO₂ as involving preequilibrium in both hydrogen and olefin. Their techniques and those of the present paper were similar and some of their catalysts were prepared by ion exchange on Davison Grade 62 silica gel which has a texture very close to that of Grade 59. However, their loadings were much larger than ours, 0.57 to 4.88% Pd. At 35°C, their turnover frequencies were about 7 sec⁻¹. From Ref. (30), the rate of hydrogenation of cyclopentene is about twice that of cyclohexene. Thus, their turnover frequency appears to be substantially less than ours. Further, on another Pd/SiO₂ by ion exchange, 0.029% Pd and percentage exposed of 53%, we found the turnover frequency to be 32 sec⁻¹ at 20°C. Gonzo and Boudart reported that the kinetic order in cyclohexene was zero whereas we found that in cyclopentene to have a small positive order in agreement with Ref. (30). We examined several other Pd/SiO₂ catalysts and all gave small positive orders. In

The Effect of Strain upon Rates

The effect of strain upon rates of hydrogenation must be complicated. To consider just the hydrogenation of olefins: Side effects of strain might influence the number of sites available for step (1). Strain may directly affect r_2 and r_{-2} and the rate of conversion of adsorbed olefin to monoadsorbed alkane, step (3) and its reverse. With most olefins, r_{-3}/r_4 is large enough to lead to the formation of substantial multiply exchanged alkane but not to the equilibration of most of the hydrogen atoms in product alkane (12).

Relief of strain in formation of adsorbed olefin (as with bicycloheptene) will increase r_2 and the competitive effectiveness of an olefin. However, on platinum, hydrogenation is zero order in most simpler olefins, coverages by hydrocarbon intermediates are near unity, and there should be no influence of r_2 upon r_4 (which equals the rate of hydrogenation). Naively, one might expect all such hydrogenations to have the same rate after adjustment for the area occupied by adsorbed olefin. The situation then differs from that in the hydrogenation of olefins by diimide treated by Garbisch (32) where the equivalent of r_2 is the rate-limiting process. On platinum, strain may influence both the concentration of monoadsorbed alkane (VIII) and k_4 for its conversion to alkane. In the hydrogenation of bicycloheptene and even more so in that of bicyclooctene, both k_3 and k_4 should be

augmented by release of surface-adsorbate strain vs k_3 and k_4 for cyclopentene. Consequently, bicycloheptene and bicyclooctene hydrogenate faster than cyclopentene. A similar explanation can be advanced for the fact that di-*t*-butylacetylene hydrogenates a little more rapidly than 3-hexyne even though the latter completely inhibits the hydrogenation of the former acetylene in competitive hydrogenations (8, 9).

In the preceding paragraph, adsorbate-surface strain was considered to lead to augmented reactivity of adsorbed olefin. However, if strain becomes large enough, rates of hydrogenation will decrease from two effects. First, coverage by hydrocarbon intermediates will fall below unity. Second, the reactivity of VI will decrease on the conventional argument based on a volcano-shaped curve for rate vs strength of adsorption, i.e., both too strong and too weak adsorption lead to reduced reactivity. The first effect clearly applies to *trans*-di-*t*-butylethylene and the second probably does also. However, a very large adsorbate-surface strain is needed for the appearance of such effects, because, even with bicyclooctene, hydrogenation is zero order in olefin and $H_2 + D_2 \rightarrow 2HD$ is heavily inhibited.

One might expect strength of adsorption and k_2 to parallel the enthalpy of hydrogenation. Indeed, the first three compounds in Table 8 have large enthalpies of hydrogenation and are good competitors. However, cyclohexene is a poor competitor even though its enthalpy of hydrogenation exceeds that of cyclopentene. Here, the parallel between enthalpy and rate of hydrogenation is inappropriate since diadsorbed cyclohexane is restricted to an eclipsed conformation whereas cyclohexane itself is in a chair conformation (7). The enthalpy of hydrogenation of cyclohexene to the twist boat conformation of cyclohexane is only 90.4 kJ mole⁻¹ and one should not expect cyclohexene to be a good competitor vs cyclopentene where both cyclopentane and adsorbed cyclopentene have the same con-

addition, R. J. Pellet in this laboratory observed that the order in cyclopentene was about +0.2 on several Pd/Al₂O₃ catalysts prepared from Pd(NH₃)₂(NO₂)₂ and Catapal alumina at loadings of about 0.05%. For a catalyst with a percentage exposed of 30%, N_i was 33 sec⁻¹. Although the experiments of Ref. (30) may have been influenced by concentration gradients of hydrogen in the catalyst pores, we doubt that they were influenced by concentration gradients of olefin (9). Further, the kinetic order in the very slowly hydrogenating cyclooctene was +0.24. We can offer no secure explanation for the discrepancies between our work and that of Gonzo and Boudart.

TABLE 8
Relative Rates of Hydrogenation at 20°C

Olefin ^a	Pt ^b	Pd ^c	$-\Delta H_{\text{hyd}}^d$
bch	2.2	1.9	138.5
bco	2.1	2.0	118.0
cp	(1.0)	(1.0)	108.8
ch	0.9 ^e	0.5	113.4 ^f
co	0.08 ^e	0.05	96.2

^a Bicycloheptene, bch; bicyclooctene, bco; cyclopentene, cp; cyclohexene, ch; *cis*-cyclooctene, co.

^b Rates relative to cyclopentene on Pt/SiO₂ from this paper except ch and co are for 0.52% Pt/Al₂O₃ at 25°C, Ref. (6).

^c Rates relative to cyclopentene on Pd/SiO₂ from this paper except ch and co are for 0.57% Pd/Al₂O₃ at 25°C, Ref. (28).

^d $-\Delta H$ of hydrogenation in kJ mole⁻¹ at 25°C in HOAc (J. L. Jensen, *Progr. Phys. Org. Chem.* 12, 189, 1976).

^e In competitive hydrogenations, the relative rate of hydrogenation of co to ch is 2.2, i.e., $\ln(A_0/A)/\ln(B_0/B) = 2.2$, Ref. (7).

^f If the enthalpy of cyclohexane constrained to a twist boat conformation is 23 kJ mol⁻¹ greater than that in the chair form (M. Squillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, *J. Amer. Chem. Soc.* 97, 3244, 1975), then the enthalpy of hydrogenation of cyclohexene to the twist boat form is 90.4 kJ mol⁻¹.

formation. By the same token, k_{-3} should be smaller for monoadsorbed cyclohexane than for monoadsorbed cyclopentane (12) and, indeed, on Pt/Al₂O₃, hydrogenation with deuterium leads to a cyclopentane which is much more extensively exchanged than is cyclohexane (12).

The origin of the behavior of cyclooctene is less clear. Its hydrogenation is slow, but it wins in competition with cyclohexene. It is probable that the concentration of monoadsorbed cyclooctane is low during hydrogenation and this would correlate with the comparatively large ratio, (exchanged olefin)/(alkane), observed in the hydrogenation of cyclooctene with deuterium on Pt/Al₂O₃ (12). The low concentration of monoadsorbed cyclooctane may result from some stabilization of the diadsorbed species by some particular van der

Waals interaction between adsorbate and surface in the diadsorbed form. In addition, diadsorbed cyclooctane should be stabilized by the fact that it can exist both in the *cis* and the *trans* form, IV and VI (21). Thus, k_2 is larger for cyclooctene than for cyclohexene but k_3 is much smaller.

Siegel *et al.* (33) have treated rates of catalytic hydrogenation along the lines employed by Garbisch for hydrogenation by diimide. In the olefins considered in that work, effects of strain were much smaller than in the present work where olefins were chosen which introduced unusually large effects of strain more clearly to expose the effect of strain.

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