Homogeneous Hydrogenation of Unsaturated Compounds Catalyzed by Pd Complexes

II. Deuteriogenation of Mono- and Diolefins

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Catalysis of deuterium addition to ethylene, 3-methyl-1-butene, and isoprene by unpretreated and oxygen pretreated $(\phi_2PCH_2P\phi_2)_3Pd_2$ was studied. With the monoolefins, monoexchange was faster than isomerization, diexchange and deuteriogenation in the presence of unpretreated catalyst. With the oxygen pretreated catalyst, deuteriogenation became faster than exchange and isomerization. In the case of isoprene, deuteriogenation was the most prevalent reaction. Results support a mechanistic sequence involving addition of Pd–D species. Reversal of addition appears most likely with monoolefins while deuteriogenolysis of alkyls is favored in reaction of conjugated dienes.

INTRODUCTION

Hydrogenation of mono- and diolefins catalyzed by various palladium complexes has been explored (1). Results were rationalized on the basis of mechanistic schemes involving the addition and abstraction of palladium hydride species. However, questions such as the origin of such hydrides (interaction of palladium with gas phase hydrogen, solvent or ligands), whether gas phase hydrogen is complexed associatively or dissociatively, whether and to what extent the addition of hydrides to substrates is reversible, the types of complexes formed with mono- and diolefinic substrates, and the effect of oxygen pretreatment of catalysts on various steps in reaction sequences were not resolved. Therefore, a brief study of the reaction of deuterium with several substrates catalyzed by $(\phi_2PCH_2P\phi_2)_3Pd_2$ (I) was undertaken.

METHODS

Complex preparation and general experimental procedures were those employed

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earlier (1). Deuterium (99.5%) was used without further purification. Deuterium contents of various reaction products were determined by MS after gas chromatographic separation.

RESULTS AND DISCUSSION

Only minor amounts of HD were formed when (I) in toluene solution was exposed to D_2 (Table 1). This extremely slow exchange can be accounted for by formation of monodeuterotoluene which was detected in trace amounts after 1 mo. No deuterium was found in the reisolated catalyst indicating that the type of interaction with ortho hydrogens in the ligand phenyl groups which has been found in the case of similar iridium and ruthenium complexes (2) is absent in this case. Thus, neither the catalyst itself nor the solvent are sources of hydride.

Oxygen pretreated (I) catalyzed the equilibration of D_2 and H_2. Therefore, at least under these conditions, hydrogen can be considered to be complexed dissociatively and reversibly. Based on the formation of gas phase HD in deuteriogenation of olefins with unpretreated catalyst (*vide infra*), similar processes may be assumed under anaerobic conditions.

Formation of all possible species from

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TABLE 1

HYDROGEN–DEUTERIUM EXCHANGE[a]

Reagents (atm)	Time (hr)	Gas phase composition (%)			
		D_2	HD	H_2	Ar
D_2 (6.7)	42	86.6	1.1	—	12.3
	144	84.9	1.85	—	13.2
	720[b]	81.7	6.3	—	11.9
D_2 (2.5), H_2 (2.8)	48[c]	17.4	41.1	30.2	11.2

[a] 50 ml toluene solution, 2.0×10^{-3} M in $(\phi_2PCH_2P\phi_2)_3Pd_2$, room temperature, 1 atm argon.

[b] $C_7H_7D = 0.39\%$ max.

[c] Catalyst pretreated with O_2.

C_2H_4 to C_2D_6 in the deuteriogenation of ethylene catalyzed by oxygen pretreated (I) (Table 2) supports the assumption of completely reversible 1,2 addition of palladium hydride species to monoolefins. As indicated by the low average deuterium content of ethane, exchange of palladium hydrido or deuterio species with each other or with the gas phase is slow relative to addition to olefins (3).

Formation of mono-, di-, and triexchanged species from 3-methyl-1-butene and a maximum deuterium content of d_4 for 2-methyl-2-butene (Table 3) is again compatible with the assumption of reversible hydride addi-

TABLE 2

PRODUCTS FROM ADDITION OF DEUTERIUM TO ETHYLENE[a]

m/e	Species	Mole %
28	C_2H_4	30.0
29	C_2H_3D	27.5
30	$C_2H_2D_2$, C_2H_6	19.6
31	C_2HD_3, C_2H_5D	12.1
32	C_2D_4, $C_2H_4D_2$	6.4
33	$C_2H_3D_3$	2.1
34	$C_2H_2D_4$	1.2
35	C_2HD_5	0.7
36	C_2D_6	0.4
	d_{av} ethane = 0.98[b]	

[a] 50 ml toluene solution, 2.0×10^{-3} M in $(\phi_2PCH_2P\phi_2)_3Pd_2$, pretreated with O_2 (1 hr), sat. with C_2H_4, 1 atm argon, 2.7 atm D_2, room temp, 48 hr.

[b] Assuming all species m/e 30–36 are ethane.

tion to the double bond i.e., Pd–D addition, Pd–H elimination in either the same or opposite directions (Fig. 1). In a separate experiment, it was found that 2-methyl-2-butene was not deuteriogenated in 282 hr and also remained essentially unexchanged during this time (maximum 2-methyl-2-butene-d_1 found was 0.21%). It may, therefore, be assumed that 2-methyl-2-butene, once formed, is not recomplexed and multiply exchanged species can be formed only from starting material. The large amount of unexchanged 3-methyl-1-butene present while some material is undergoing multiple exchange, therefore, indicates that some 3-methyl-1-butene remains more closely associated with the catalyst than the bulk of substrate, either as a π-complex, or trapped in the outer coordination sphere or in a solvent cage. Another possibility is rapid olefin exchange and isotopic discrimination favoring Pd–H addition (4).

Based on assumption of a 1,2 Pd–D addition, Pd–H abstraction mechanism, it was expected that 2-methyl-2-butene-d_1 would be the most prevalent isomerized species. The much larger amount of 2-methyl-2-d_0 found is, therefore, surprising. Formation of this species could be explained readily by dissociative addition of 3-methyl-1-butene to Pd(0) (π-allyl hydride formation). While this path would be less likely to lead to observed exchange maxima and is inconsistent with the finding that 3-methyl-1-butene was not isomerized in the absence of D_2 when the catalyst was pretreated with air, it cannot be dismissed out of hand. There is also the possibility that isomerization proceeds by addition and re-abstraction of the π-allyl hydride—a plausible mechanism for olefin isomerization catalyzed by Pd(II) (5). A more likely route would involve addition–elimination of palladium hydrido species formed in prior exchange with starting material. This requires that exchange with gas phase deuterium be slower than readdition of Pd–H as expected from results of ethylene deuteriogenation and indicated in this case as well by the average deuterium content of isopentane which is less than two (3).

TABLE 3

PRODUCTS FROM ADDITION OF DEUTERIUM TO 3-METHYL-1-BUTENE[a]

% d	Hydrogen	3-Methyl-1-butene (90.2%)		2-Methyl-2-butene (4.5%)		Isopentane (5.3%)	
		Found	Random[b]	Found	Random[b]	Found	Random[b]
d_0	—	85.9	79.2	64.3	54.1	14.9	14.6
d_1	24.6	11.4	18.7	18.1	34.2	28.5	30.6
d_2	75.4	2.5	1.97	12.3	9.35	38.8	29.0
d_3		0.22	0.12	4.3	1.67	8.4	16.1
d_4				1.0	0.19	3.7	6.59
d_5						2.3	1.84
d_6						3.4	0.37
d_{av}/molecule	1.75	0.17		0.60		1.78	

[a] 50 ml toluene solution, $2.0 \times 10^{-3} M$ in $(\phi_2PCH_2P\phi_2)_3Pd_2$, $6 \times 10^{-1} M$ in 3-methyl-1-butene, no pretreatment, 1 atm argon, initial D_2 pressure = 100 psig, room temp, 138 hr.

[b] Values expected for random distribution of deuterium at found d_{av}/molecule.

Catalysis of 3-methyl-1-butene deuteriogenation by oxygen pretreated (I) also was examined (Table 4). This experiment continued for a period equivalent with the anaerobic case, i.e., well past complete conversion of 3-methyl-1-butene. Under these conditions, some isomerization and more extensive exchange of 2-methyl-2-butene occurred. Also, the approach to random distribution of deuterium in isopentane is closer than under anaerobic conditions indicating more complete deuterium redis-
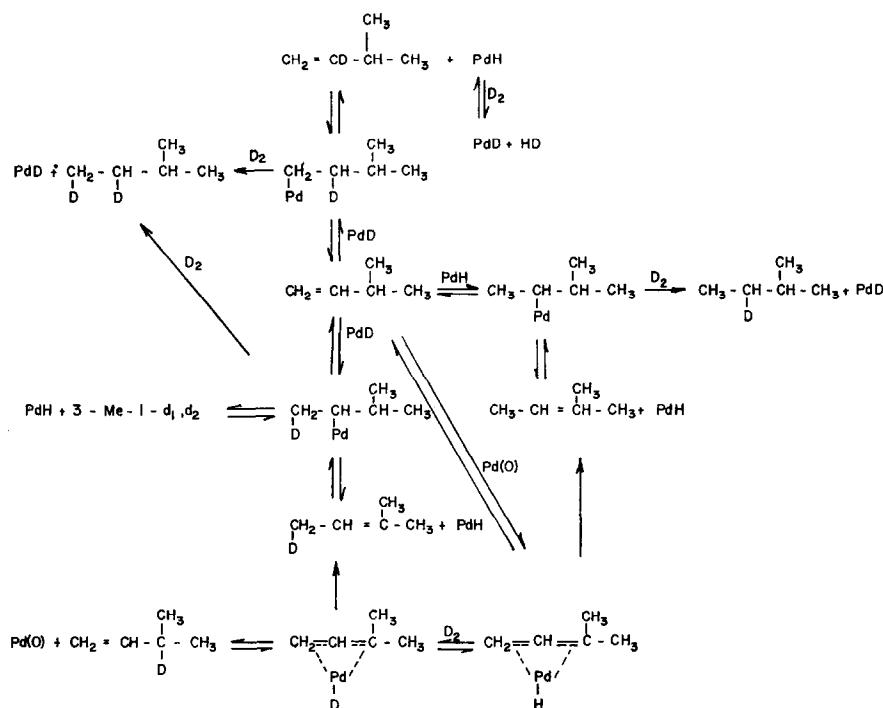

FIG. 1. Deuteriogenation of 3-methyl-1-butene.

TABLE 4

PRODUCTS FROM ADDITION OF DEUTERIUM TO 3-METHYL-1-BUTENE[a]

% d	Hydrogen	2-Methyl-2-butene (31.0%)		2-Methyl-1-butene (1.3%)		Isopentane (67.7%)	
		Found	Random[b]	Found	Random[b]	Found	Random[b]
d_0	—	19.5	12.8			15.7	14.8
d_1	37.2	29.0	29.2			29.4	30.6
d_2	62.8	25.3	30.1			30.5	29.1
d_3		14.2	18.4			15.0	15.9
d_4		5.4	7.31			6.6	6.45
d_5		2.4	2.02			1.7	1.79
d_6		1.7	0.38			1.1	0.36
d_7		1.1	0.05				
d_8		1.0	0.004				
d_9		0.5	0.002				
d_{av}/molecule	1.63	1.86				1.77	

[a] 50 ml toluene solution, $2.0 \times 10^{-3} M$ in $(\phi_2PCH_2P\phi_2)_3Pd_2$, $2 \times 10^{-1} M$ in 3-methyl-1-butene, catalyst pretreated with O_2 (1 hr) then flushed with Ar; 1 atm Ar, initial D_2 pressure = 90 psig, room temp, 136 hr (basis pressure drop—addition complete in ca. 1.25 hr).

[b] Values expected from random distribution of deuterium at found d_{av}/molecule.

tribution between exchanging species (6) or by internal rearrangement of complexed olefins. The most abundant 2-methyl-2-butene species in this case was d_1 rather than d_0 due, possibly to an increase in the rate of exchange of Pd–H species or more likely, in view of an average deuterium content of isopentane, which is the same as under anaerobic conditions, of an increase in the

rate of deuteriogenolysis of Pd–C bonds (deuteriogenation) relative to reelimination (exchange and isomerization).

The relative abundance of species formed in deuteriogenation of 3-methyl-1-butene catalyzed both by untreated and oxygen pretreated (I) is shown in Table 5 and a mechanistic scheme consistent with observations in Fig. 1.

TABLE 5

ORDER OF RELATIVE ABUNDANCE OF SPECIES FROM ADDITION OF DEUTERIUM TO 3-METHYL-1-BUTENE[a]

No catalyst pretreatment[b]

3-Me-1-d_0 > 3-Me-1-d_1 > 2-Me-2-d_0 > 3-Me-1-d_2 > isopentane-d_2 > isopentane-d_1
(77.5)   (10.3)   (2.9)   (2.3)   (2.0)   (1.5)
> 2-Me-2-d_1 = isopentane-d_0 > 2-Me-2-d_2 > isopentane-d_3 > 3-Me-1-d_3 = 2-Me-2-d_3
(0.8)   (0.8)   (0.6)   (0.4)   (0.2)   (0.2)

Catalyst pretreated with O_2[c]:

isopentane-d_2 isopentane-d_1 > isopentane-d_0 > isopentane-d_3 > 2-Me-2-d_1 > 2-Me-2-d_2
(20.6)   (19.9)   (10.6)   (10.2)   (9.0)   (7.8)
> 2-Me-2-d_0 > isopentane-d_4 > 2-Me-2-d_3 > 2-Me-2-d_4 > isopentane-d_5 > 2-Me-2-d_5
(6.0)   (4.5)   (4.4)   (1.7)   (1.2)   (0.8)
$\sim$ isopentane-d_6
(0.7)

[a] Numbers in parentheses are percentage of total C_5 fraction.
[b] 99.5% of product accounted for.
[c] 97.4% of product accounted for.

TABLE 6

PRODUCTS FROM ADDITION OF DEUTERIUM TO ISOPRENE[a]

% d	Hydrogen	Isoprene (83.4%)		3-Methyl-1-butene (3.4%)		2-Methyl-1-butene (5.0%)		2-Methyl-2-butene (8.2%)	
		Found	Random[b]	Found	Random[b]	Found	Random[b]	Found	Random[b]
d_0	2.9	96.6	96.0	2.9	9.6	3.8	11.2	6.6	11.9
d_1	24.8	2.8	3.86	20.9	25.3	22.7	27.4	22.3	28.2
d_2	72.3	0.3	0.068	52.9	30.3	53.9	30.2	52.2	30.2
d_3		0.1	0.007	13.3	21.2	12.1	19.7	11.5	19.1
d_4		0.1		7.9	9.8	6.8	8.5	5.9	7.9
d_5				2.1	3.1	0.6	2.5	1.4	2.3
d_{av}/molecule 1.69	0.04			2.09		1.97		1.92	

[a] 50 ml toluene solution, 7.4×10^{-3} M in $(\phi_2PCH_2P\phi_2)_3Pd_2$, 1 M in isoprene, no pretreatment; 1 atm Ar, initial D_2 pressure = 100 psig, room temp, 72 hr.

[b] Values expected from random distribution of deuterium at found d_{av}/molecule.

It is evident that in catalysis by (I) under anaerobic conditions monoexchange, most likely by reversible addition of Pd to the terminal carbon, is the fastest reaction followed by isomerization, diexchange and deuteriogenation all of which occur at similar rates. When the catalyst has been pretreated with oxygen, the rates of all processes increase. However, hydrogenation becomes faster than exchange which appears to proceed at roughly the same rate as isomerization.

Deuteriogenation of isoprene was investigated only under anaerobic conditions. Results at low conversion are shown in Table 6 and those at high conversion in Table 7. At low conversion, it is evident, once again, that deuterium is adding to some isoprene which has already undergone exchange although the bulk of isoprene remains unexchanged. Therefore, as in the case of monoolefins, it appears that isoprene does not diffuse away rapidly from the reaction site or that isotopic discrimination favors Pd–H addition.

Exchange at low conversion is not extensive although (as seen in results at high conversion) all hydrogens on isoprene are exchangeable. Deuterium contents of various species again are not randomly distributed.

In contrast to results obtained with 3-methyl-1-butene, the average deuterium content of products is very nearly two (low conversion) or greater than two (high conversion) is very nearly two (low

version). Since it is doubtful that the rate of exchange of palladium hydride species with gas phase deuterium would depend on substrate and since isoprene is deuteriogenated faster than 3-methyl-1-butene, this must be due to a relatively lower abundance of Pd–H species in this case, consistent with the observation that exchange is slow relative to deuterium addition. The finding that at low conversion the average deuterium content of reduced species is inversely proportional to yield is in line with the expectation of the highest deuterium content in those compounds with the slowest deuteriogenation rate relative to Pd–H exchange with the gas phase (3). A change in this order at high conversion (i.e., lowest d_{av} for 2-methyl-1-butene) likely is due to some further reaction of monoolefins having taken place, in which case reversible Pd addition to the terminal double bond carbon in 2-methyl-1-butene could not lead to exchange. Addition in the opposite direction would be less favored than addition to 3-methyl-1-butene. The order of prevalence of species formed at both low and high conversions is shown in Table 8. The most prevalent 2-methyl-2-butene species in both cases is d_2 in agreement with conclusions drawn previously (1) that this species is formed directly from isoprene rather than by isomerization of terminal olefinic products. Thus, as shown in the mechanistic scheme (Fig. 2), the most likely event is

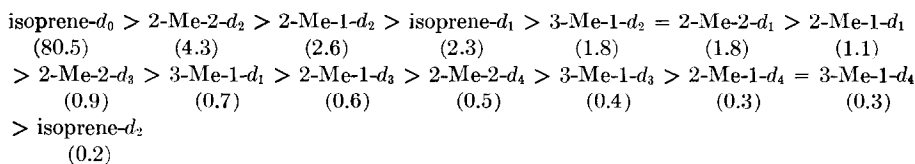TABLE 7

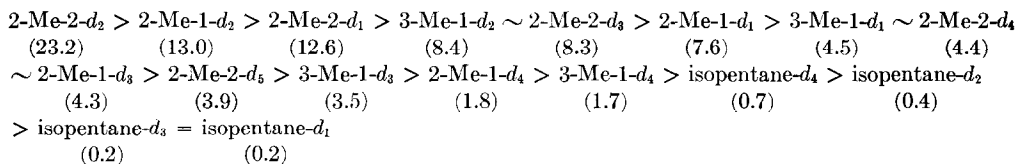PRODUCTS FROM ADDITION OF DEUTERIUM TO ISOPRENE[a]

% d	Hydrogen[b]	Isoprene (0.5%)	3-Methyl-1-butene (19.0%)		2-Methyl-1-butene (27.2%)		2-Methyl-2-butene (50.5%)		Isopentane (2.8%)	
			Found	Random[c]	Found	Random[c]	Found	Random[c]	Found	Random[c]
d_0	2.6		—	7.3	—	9.8	—	8.0	—	0.6
d_1	24.0		23.7	21.9	27.8	25.6	24.9	25.2	6.3	3.4
d_2	73.4		44.3	29.5	47.8	30.2	45.7	29.5	13.1	10.9
d_3			18.7	24.0	15.7	21.0	16.7	22.7	17.3	19.5
d_4			8.8	12.2	6.7	9.6	8.8	11.4	25.2	23.6
d_5			2.3	4.4	1.2	3.0	2.2	3.9	15.1	20.3
d_6			0.9	1.1	0.4	0.7	0.9	0.9	10.2	12.8
d_7			0.5	0.2	0.1	0.1	0.3	0.2	5.9	5.9
d_8			0.2	0.02	0.06	0.01	0.2	0.02	1.6	2.0
d_9			0.3	0.001	0.06		0.1		1.0	0.5
d_{10}			0.2		0.03		0.05		1.8	0.08
d_{11}									1.5	
d_{av}/molecule	1.71		2.30		2.07		2.23		4.20	

[a] 50 ml toluene solution, 7.4×10^{-3} M in $(\phi PCH_2P\phi_2)_3Pd_2$, 1 M in isoprene, no pretreatment, 1 atm Ar, initial D_2 pressure = 100 psig, room temp, 240 hr.

[b] After several additions of D_2 to restore pressure.

[c] Values expected from random distribution of deuterium at found d_{av}/molecule.

ORDER OF RELATIVE ABUNDANCE OF SPECIES FROM ADDITION OF DEUTERIUM TO ISOPRENE[a]

72 hr[b]

isoprene-d_0 > 2-Me-2-d_2 > 2-Me-1-d_2 > isoprene-d_1 > 3-Me-1-d_2 = 2-Me-2-d_1 > 2-Me-1-d_1
     (80.5)   (4.3)   (2.6)   (2.3)   (1.8)   (1.8)   (1.1)
> 2-Me-2-d_3 > 3-Me-1-d_1 > 2-Me-1-d_3 > 2-Me-2-d_4 > 3-Me-1-d_3 > 2-Me-1-d_4 = 3-Me-1-d_4
     (0.9)   (0.7)   (0.6)   (0.5)   (0.4)   (0.3)   (0.3)
> isoprene-d_2
     (0.2)

240 hr[c]

2-Me-2-d_2 > 2-Me-1-d_2 > 2-Me-2-d_1 > 3-Me-1-d_2 ∼ 2-Me-2-d_3 > 2-Me-1-d_1 > 3-Me-1-d_1 ∼ 2-Me-2-d_4
   (23.2)   (13.0)   (12.6)   (8.4)   (8.3)   (7.6)   (4.5)   (4.4)
∼ 2-Me-1-d_3 > 2-Me-2-d_5 > 3-Me-1-d_3 > 2-Me-1-d_4 > 3-Me-1-d_4 > isopentane-d_4 > isopentane-d_2
   (4.3)   (3.9)   (3.5)   (1.8)   (1.7)   (0.7)   (0.4)
> isopentane-d_3 = isopentane-d_1
     (0.2)   (0.2)

[a] Numbers in parentheses are percentage of total C_5 fraction.
[b] 99.1% of product accounted for.
[c] 98.7% of product accounted for.

addition of Pd–D to either double in such a manner as to lead to σ and π-allyl formation followed by deuteriogenolysis to yield 2-methyl-2-butene-d_2. Direct 1,4 addition of D_2 would seem a less likely possibility as discussed earlier (1). Moreover, the observation that the most prevalent 2-methyl-1-butene and 3-methyl-1-butene species are also d_2 is consistent with this path. The driving force for π-allyl formation apparently is sufficiently great to overcome steric effects which otherwise would be expected
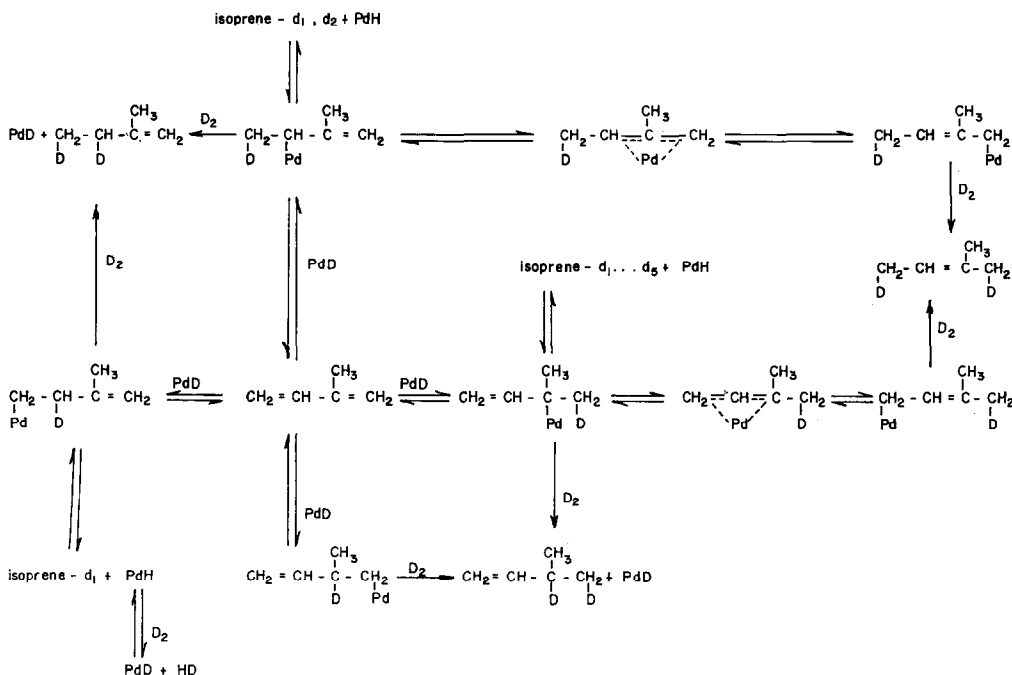

FIG. 2. Deuteriogenation of isoprene.

to favor attack by Pd on terminal carbons, and more extensive exchange; i.e., as expected, π-allyl formation is less reversible than 1,2 addition. However, either type of attack appears to take place preferably on the less hindered end of the molecule.

In summary, hydrogenation of olefins catalyzed by Pd complexes appears to involve the following steps: Dissociation of the complex, dissociative complexing of hydrogen and complex formation with substrate—likely formation of a π-complex, followed by insertion to form a σ-complex in the case of monoolefins and σ- and π-allyl complexes in the case of conjugated diolefins. Reversal of insertion results in exchange and isomerization. Hydrogenolysis of Pd–C or π-allyl bonds leads to hydrogenation.

Reversal seems to be favored in the case of monoolefins while with conjugated diolefins the most likely event is hydrogenolysis.

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