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The Hydrogenation of Alkadienes

VIII. Deuterium Tracer Study of Alkane Formation in the Palladium-Catalyzed Hydrogenation of Propadiene and of 1,2-Butadiene and Its Implications Concerning the Breakdown of Selectivity in Ethyne Hydrogenation

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Reactions of propadiene (allene) and of 1,2-butadiene (methylallene) with deuterium catalyzed at 293°K by palladium–alumina are reported. Reactions are selective for alkene formation at low conversions and low deuterium pressures, but at higher conversions and deuterium pressures considerable alkane yields are observed. Selective hydrogenation of 1,2-butadiene gives *cis*-2-butene ($\sim$60%) and 1-butene ($\sim$40%), each having a deuterium number (D.N.) of 2.0, by a mechanism identical to that described in Part VII [Grant, J., Moyes, R. B., Oliver, R. G., and Wells, P. B., *J. Catal.* **42**, 213 (1976)] for reactions catalyzed by nickel. The appearance of butane (D.N. = 5.0) is accompanied by *trans*-2-butene (D.N. = 3.0); both products are highly exchanged. A mechanism for their formation is proposed which involves the participation of an $\alpha\alpha$-diadsorbed intermediate. This mechanism has implications regarding the mode of ethane formation from ethyne (acetylene) under conditions in which palladium behaves unselectively.

INTRODUCTION

Palladium is well-known as a selective catalyst for the hydrogenation of alkynes and alkadienes to alkenes (*1*). However, there is an aspect of its behavior which has remained obscure, which concerns the observation that the selectivity of palladium in 1,3-alkadiene hydrogenations is high over a very wide range of conditions (*2*) whereas in alkyne hydrogenations, especially ethyne hydrogenation, high selectivity may be observed in the early stages of reaction, but a sudden and catastrophic collapse of selectivity occurs when the $H_2:C_2H_2$ pressure ratio exceeds a critical temperature-dependent value (*3*). Why should 1,3-alkadiene and alkyne hydrogenations show different features in this respect? In this study, propadiene and 1,2-butadiene hydrogenations have been examined in an attempt to resolve this problem.

1,2-Alkadiene hydrogenation is intermediate in character between alkyne hydrogenation and 1,3-alkadiene hydrogenation. The center carbon atom of the C=C=C unit is acetylenic in character with the result that, in 1,2-butadiene hydrogenation, two of the four half-hydrogenated states are identical with species formed in butyne hydrogenation, whereas the other two are identical with species formed in 1,3-butadiene hydrogenation (*4*). It was, therefore, of interest to determine whether or not the hydrogenation of 1,2-alkadienes over palladium proceeds selectively and, if not, to utilize the greater molecular com-

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plexity of these reactions to learn more about the mechanism of alkane formation.

Metal-catalyzed hydrogenation of simple 1,2-alkadienes has been little studied. Yields of C_3-products in the hydrogenation of propadiene over supported Ni, Ru, Rh, Pd, Os, Ir, and Pt (*5*, *6*) have been reported for very restricted ranges of conditions, and kinetic measurements have been made using supported Ni, Pd, and Pt (*5*). Reaction of propadiene with deuterium has not been described. With respect to 1,2-butadiene hydrogenation, a detailed study of reaction with deuterium catalyzed by palladium–alumina at 8 and 40°C under selective conditions has been described (*7*), but otherwise the reaction has been examined only over nickel (*4*).

EXPERIMENTAL METHODS

A grease-free high-vacuum apparatus (*4*) was used, capable of attaining a vacuum of 10^{-5} Torr or better, and having a 130-cm^3 Pyrex reaction vessel. Reaction mixtures were separated into pure components by preparative glc. Positive ion mass spectra of hydrocarbons were obtained using an ionization energy of 12.0 eV.

The catalyst (prepared by the Johnson Matthey Company) consisted of palladium supported at a concentration of 0.5% (wt/wt) on high-area alumina. Separate samples, each weighing 0.01 g, were used for propadiene hydrogenation and 1,2-butadiene hydrogenation. Before each investigation, protium atoms associated with the alumina support, present at a concentration of 10^{21}/g of catalyst, were exchanged for deuterium by treatment of the catalyst with successive doses of molecular deuterium at 293°K.

Propadiene (Matheson) and 1,2-butadiene (Kodak) were purified by preparative glc. Deuterium (Air Products) was purified by diffusion through a heated palladium–silver alloy thimble.

The correction of the mass spectra for the natural abundance of ^{13}C and for ion fragmentation provides the deuterium distribution in the product, i.e., the proportions of molecules containing 0, 1, 2, 3, ... n deuterium atoms. The "hydrogen" adsorbed at the catalyst surface consists of D and H atoms in the effective ratio $a:b$. For discussions of mechanism we require the quantities N_0, N_1, N_2, N_3, ... N_n (the N-profile) which describes the proportions of the product containing 0, 1, 2, 3, ... n "hydrogen" atoms which have come from the surface pool of H and D atoms. The method described by Smith and Burwell (*8*) for the calculation of N-profiles has been used, together with the computational and manual procedures described in Part IV of this series (*2c*). Table 1 contains experimentally determined deuterium distributions accompanied by the best calculated distributions and the N-profiles and values of $a:b$ used in the calculations. Agreement between observation and calculation is good, and hence the discussion of mechanism is based entirely on the interpretation of the N-profiles.

RESULTS

The reaction of propadiene with deuterium over palladium at 293°K gave propene, propane, hexenes, hexane, and branched C_6-hydrocarbons. Rates of hydrogenation and hydrodimerization were similar over fresh catalysts, but the latter diminished as the catalyst was used. The expression,

$$\text{Initial rate of pressure fall} = kP_{C_3H_4}{}^{-0.4}P_{D_2}{}^{1.1},$$

was obtained at 293°K over pressure ranges of 50–175 Torr in each reactant. The apparent activation energy over the range 273–320°K was 28.8 ± 2.0 kJ mol^{-1}. In the reaction of 1,2-butadiene with deuterium at 293°K only 5% of the pressure fall was attributable to hydrodimerization.

Product compositions at 293°K were measured as a function of conversion and deuterium pressure. Figure 1a shows the variation of the C_3-product composition

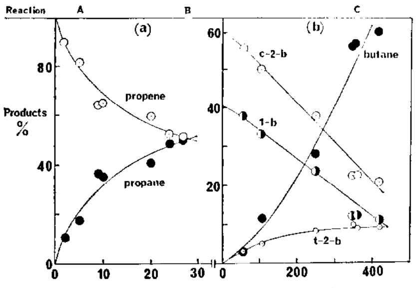


FIG. 1. (a) Variation of the C_3-product composition with conversion during 1,2-propadiene hydrogenation at 293°K. (b) Variation of the C_4-product composition with initial deuterium pressure during 1,2-butadiene hydrogenation at 293°K. Conditions: (a) initial pressures, $C_3H_4 = 100$ Torr, $D_2 = 200$ Torr; (b) initial C_4H_6 pressure = 50 Torr, conversion = 15 ± 2%.

with conversion, and Fig. 1b shows how the C_4-products varied with increasing initial deuterium pressure at constant conversion. Each reaction was highly selective for alkene formation at low conversion and low deuterium pressure, but appreciable alkane yields were evident as conversion increased and deuterium pressure was raised. In 1,2-butadiene hydrogenation, the production of butane was accompanied by the appearance of *trans*-2-butene. Unlike the situation in ethyne hydrogenation (*3*), alkane formation was not accompanied by a rapid increase in rate.

Products of all reactions were analyzed by mass spectrometry; deuterium distributions in products for reactions labeled A, B, and C in Fig. 1 are shown in Table 1, together with the *N*-profiles and calculated distributions. Deuterium did not appear in propadiene or in 1,2-butadiene, and no isomers of these substances were detected in the products. The rate of formation of HD was slow. 1-Butene and *cis*-2-butene formed in reaction C contained, on the average, two deuterium atoms per mole-

TABLE 1

Observed and Calculated Distributions of Deuterium in Products and *N*-Profiles

Reaction[a]	Compound		*x*											D.N.[b]	*a*:*b*
			0	1	2	3	4	5	6	7	8	9	10		
		Obs. $C_3H_{6-x}D_x$ (%)	1.8	22.9	64.0	6.5	3.1	1.1	0.6					1.92	
A	Propene	N_x	0.0	0.0	85.3	7.5	4.6	1.0	1.6						85:15
		Calc. $C_3H_{6-x}D_x$ (%)	2.0	22.2	64.5	6.5	3.1	1.1	0.6					1.92	
		Obs. $C_3H_{6-x}D_x$ (%)	2.7	26.6	56.9	8.0	3.7	1.4	0.7					1.90	
B	Propene	N_x	0.0	0.0	80.4	9.7	6.1	1.2	2.6						81:19
		Calc. $C_3H_{6-x}D_x$ (%)	3.0	25.8	57.4	8.0	3.7	1.4	0.7					1.91	
		Obs. $C_3H_{8-x}D_x$ (%)	1.6	4.4	10.7	18.7	22.3	16.1	12.9	8.9	4.4			4.27	
B	Propane	N_x	0.0	0.0	0.0	0.0	37.5	15.2	17.3	0.0	30.0				77:23
		Calc. $C_3H_{8-x}D_x$ (%)	0.1	1.6	8.6	21.8	26.3	16.1	12.9	8.9	3.7			4.39	
		Obs. $C_4H_{8-x}D_x$ (%)	4.7	22.3	53.3	10.2	4.9	2.2	1.2	0.8	0.4			2.06	
C	1-Butene	N_x	0.0	0.0	73.1	12.3	7.2	3.1	1.8	0.2	2.3				81:19
		Calc. $C_4H_{8-x}D_x$ (%)	2.7	23.8	53.8	10.2	4.9	2.2	1.2	0.8	0.4			2.09	
		Obs. $C_4H_{8-x}D_x$ (%)	5.8	24.6	53.3	6.6	4.0	2.7	1.5	1.1	0.4			2.00	
C	*cis*-2-Butene	N_x	0.0	0.0	79.3	7.6	3.8	4.6	1.0	1.5	2.2				81:19
		Calc. $C_4H_{8-x}D_x$ (%)	2.9	25.2	55.6	6.6	4.0	2.7	1.5	1.1	0.4			2.06	
		Obs. $C_4H_{8-x}D_x$ (%)	4.0	14.7	28.1	19.5	13.1	9.5	5.5	3.8	1.8			3.03	
C	*trans*-2-Butene	N_x	0.0	0.0	25.6	26.7	7.8	19.6	5.4	0.0	14.9				74:26
		Calc. $C_4H_{8-x}D_x$ (%)	2.3	14.6	29.3	20.6	13.1	9.5	5.5	3.8	1.3			3.05	
		Obs. $C_4H_{10-x}D_x$ (%)	1.4	2.9	8.6	15.5	18.3	15.4	12.5	9.8	7.6	5.5	2.5	4.96	
C	Butane	N_x	0.0	0.0	0.0	0.0	26.5	17.0	7.2	23.3	0.0	0.0	26.0		77:23
		Calc. $C_4H_{10-x}D_x$ (%)	0.1	1.2	6.6	17.1	22.0	15.5	12.5	9.8	7.6	5.7	1.9	5.06	

[a] Reaction conditions and product compositions as shown in Fig. 1.

[b] D.N. = deuterium number = mean number of deuterium atoms present per molecule.

cule, whereas *trans*-2-butene contained three, and butane five. Similarly, propene formed in reactions A and B had a deuterium number of 1.9, but propane contained than twice this amount of deuterium (D.N. = 4.3).

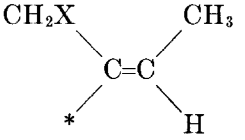
A check on the $a{:}b$ values that accompany the N profiles was obtained as follows. Six reactions of 100 Torr propadiene with 200 Torr deuterium were permitted to proceed to 25% conversion at 293°K. The propene fractions were combined and analyzed by mass and NMR spectrometry. The deuterium distribution was closely similar to that shown in Table 1 for reaction B; the deuterium number was 1.87, and the average distribution of deuterium within the molecules was: $CH_{2.11}D_{0.89}$–$CH_{0.18}D_{0.82}$=$CH_{1.84}D_{0.16}$. The "hydrogen" bonded to the center carbon atom has the isotopic composition of the pool. The observed value of $D = 0.82 \pm 0.02$, $H = 0.18 \pm 0.02$ agrees with the value of $a{:}b$ that accompanies the computed *N*-profile of 81:19 (see Table 1).

DISCUSSION

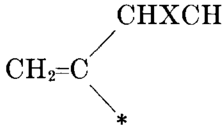
The negative order in alkadiene, the positive order in deuterium, the absence of exchange of H for D in the alkadiene, and the slow formation of HD demonstrate that these reactions adhere to the general pattern established hitherto (*1*) for ethyne and 1,3-butadiene hydrogenations in which the diunsaturated hydrocarbon is strongly chemisorbed and occupies much of the catalytically active surface, and deuterium is weakly chemisorbed and establishes only a small surface coverage.

The products of the selective hydrogenation of 1,2-butadiene over palladium at 293°K (lowest P_{D_2}, Fig. 1) agree closely with those reported by Meyer and Burwell (*7*) for reaction at 281–313°K: *cis*-2-butene, 53%; 1-butene, 40%; *trans*-2-butene, 7%; butane, trace. These authors also observed traces of 1,3-butadiene and 1-butyne which were not evident in this study.

The products of the palladium-catalyzed reaction are also closely similar to those obtained over Type A nickel at 348°K (*4*) (*e.g.*, *cis*-2-butene = 57%; 1-butene, 38%; *trans*-2-butene, 5%; butane, 0%). Moreover, the *N*-profiles of the *cis*-2-butene and 1-butene formed in the nickel-catalyzed reaction [see Table 4 of Ref. (*4*)] are very similar to those quoted for these hydrocarbons in Table 1 of this paper. Thus, the mechanism presented in Part VII (*4*) for 1,2-butadiene hydrogenation catalyzed by Type A nickel applies equally to reaction over palladium, insofar as the formation of the majority of the *cis*-2-butene and 1-butene and a proportion of the *trans*-2-butene (see ahead) is concerned. This mechanism envisages (II) and (IV) to be the most important half-hydrogenated states (the numbering used in the previous paper is retained), and



(II)



(IV)

(X = H or D)

these species give *cis*-2-butene and 1-butene, respectively, on further hydrogen atom addition. The mechanism proposed by Meyer and Burwell (*7*) is a simplified version of that given in Ref. (*4*).

A mechanism is now required to supplement that presented in Part VII (*4*) which interprets the coupled formation of butane and *trans*-2-butene such as was observed in Expt C (Fig. 1). The mechanism must accommodate the observations (i) that the butane had a deuterium number of 5.0 and the *trans*-2-butene a deuterium number of 3.0 (Table 1), and (ii) that the *N*-profiles of butane and *trans*-2-butene are similar (although, of course, one is displaced with respect to the other by two units) and are very different from those of *cis*-2-butene and 1-butene. These observations are interpreted by the mechanism shown in Fig. 2.

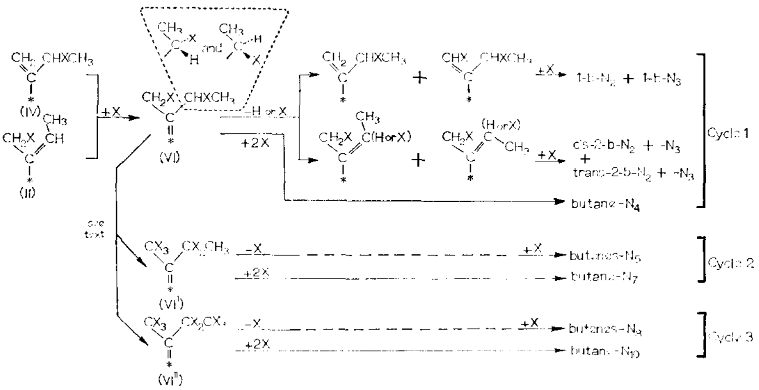


FIG. 2. Mechanism for the formation of products via the participation of species (VI). X = H or D. The interaction of the carbon–carbon double bond with a further surface site, which most probably precedes hydrogen atom addition to the =CH_2 group or follows hydrogen atom abstraction from –CH_3 or –CH_2–, is not shown.

The mechanism in Part VII (*4*) envisages that the addition of an X atom (X = H or D) to (II) and (IV) gives *cis*-2-butene-N_2 and 1-butene-N_2, respectively; we now propose that, at the palladium surface, (VI) is a further product. Species (VI) is a form of adsorbed-C_4X_8 which, by its nature, cannot undergo desorption to give gaseous butene. However, it may be converted directly to butane by addition of two further X atoms, or to butene by X-atom abstraction followed by X-atom addition. Figure 2 shows that these processes, in a single cycle (Cycle 1), give 1:2 yields of 1-butene-N_2 and -N_3, 1:1 yields of *cis*-2-butene-N_2 and -N_3, 1:1 yields of *trans*-2-butene-N_2 and -N_3, and butane-N_4. The results in Table 1 confirm the equal yields of *trans*-2-butene-N_2 and -N_3; the profiles for the other butenes are not informative at this point because 1-butene-N_2 and *cis*-2-butene-N_2 are formed in greater quantity by direct hydrogen atom addition to (II) and (IV) (*4*).

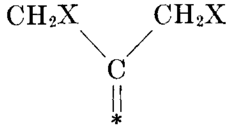
With regard to (VI), there is no direct evidence regarding the nature of the double bond, nor of the geometry or the number of surface metal atoms that constitute the site denoted by the asterisk.

Much of the *trans*-2-butene and butane was extensively exchanged, the former having large contributions at -N_5 and -N_8, and the latter at -N_7 and -N_{10}. By contrast, *cis*-2-butene exhibited weak subsidiary maxima at -N_5 and -N_8, and 1-butene showed a weak subsidiary maximum at -N_8 only. This pattern shows that (VI) undergoes rapid multiple exchange of H for X at carbon atoms 1 and 3 to give (VI'), and that further multiple exchange at carbon atom 4 gives (VI''). Conversion of (VI') and (VI'') to products in Cycles 2 and 3 of Fig. 2 provides the observed products. The intermediates involved in the formation of (VI') and (VII'') are unknown; they may be $\alpha\alpha\beta$- and $\alpha\alpha\gamma$-adsorbed intermediates or certain π-bonded species. [The interconversion of (VI) with (II) and (IV) might account for the formation of (VI'), but could not interpret the formation of (VI'')].

Figure 2 accounts for all products except butane-N_5 and -N_6. These most probably arise by the interposition of some butyl/butene interconversion into the sequence (VI) → butyl(ads) → butane(g).

It is now clear (in answer to the question raised in the Introduction) that alkyne hydrogenations may become nonselective, whereas 1,3-alkadiene hydrogenations do not, because only the former generate appreciable concentrations of (II) and (IV), which are the necessary precursors of both (VI) and the route to alkane shown in Fig. 2.

The N-profile of propane formed in propadiene hydrogenation is interpreted by a mechanism analogous to that shown in Fig. 2. The small subsidiary maximum at propane-N_6 shows that the methyl groups of (VII) [the analogue of (VI) in Fig. 2] may undergo exchange one at a time.



(VII)

It is clear from the values of $a:b$ in Table 1 that the H:D pool involved in the formation of propane, butane, or *trans*-2-butene was richer in protium and poorer in deuterium than that operative in propene, *cis*-2-butene, or 1-butene formation. The additional protium arises as a result of the multiple exchange of (VI) discussed before. That the H:D pool varies in composition from one location on the surface to another suggests (i) that hydrogen and deuterium atoms are not highly mobile in the chemisorbed layer under reaction conditions, and (iii) that specific regions of the surface may be involved in alkane formation.

Implications for Ethyne Hydrogenation

The identification of (VI) and (VII) as crucial intermediates in butane and propane formation, when palladium behaves nonselectively in 1,2-alkadiene hydrogenation, leads us to consider whether an analogous process (Fig. 3) is responsible for ethane formation from ethyne. The rapid increase in rate that occurs (*3*) when palladium-catalyzed ethyne hydrogenation is diverted from selective ethene formation to ethane formation has features in common with the rapid rise of the butane yield with increasing deuterium pressure shown in Fig. 1. Clearly, in each case, and increase in the surface concentration of hydrogen provides conditions for the formation of (X) or (VI). It is difficult to see why this should be unless, in its normal state, the vinylic intermediate (VIII) is chemisorbed only by a σ-bond, and chemisorbed hydrogen, when it achieves a critical coverage, so modifies the electronic structure of palladium that the metal–alkene bond is formed in addition (to give (IX)). The establishment of the metal–alkene bond in (IX) would activate the methylene group, making it more vulnerable to hydrogen atom attack producing (X). The pathway to alkane formation (Fig. 3), and hence to a breakdown in selectivity, is then open. Unfortunately, there is little chance of detecting the participation of (X) by deuterium tracer methods because adsorbed C_2HD and C_2D_2 are formed during the ethyne–deuterium reaction over palladium (*9*), and, hence, a proportion of the ethane produced will be -N_6, even in the absence of the process shown in Fig. 3.

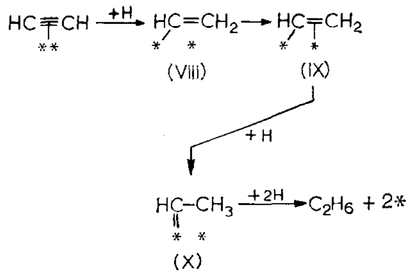


FIG. 3. Mechanism proposed for the palladium-catalyzed conversion of ethyne to ethane under nonselective hydrogenation conditions.

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