

The Hydrogenation of Alkadienes

VII. 1,2-Butadiene Hydrogenation Catalyzed by Two Forms of Nickel

J. GRANT,¹ R. B. MOYES, R. G. OLIVER,² AND P. B. WELLS³

Department of Chemistry, The University, Hull HU6 7RX, England

Received June 13, 1975

The reaction of 1,2-butadiene with deuterium catalyzed by nickel has been examined in the range 46–115°C. Hydrogenation of 1,2-butadiene is accompanied by the formation of higher hydrocarbons and by slow isomerization to 1,3-butadiene. Hydrogenated C₄-products are almost entirely butenes. Type A nickel gives 1-butene and *cis*-2-butene as major products, the yield of *trans*-2-butene being only 2–5%, whereas type B nickel gives all three butenes as major products. Reaction mechanisms are proposed which involve the participation of π -allylic intermediates at the type B surface but not at the type A surface.

INTRODUCTION

Nickel has been prepared in two forms which are distinguished by their properties as catalysts for 1,3-butadiene hydrogenation (1). Type A nickel catalyzes the formation of 1-butene as the major product and the 2-butene formed simultaneously has a low *trans*:*cis* ratio (ca. 1–2). Type B nickel provides *trans*-2-butene as the major product the yields of *cis*-2-butene and 1-butene being comparable and the *trans*:*cis* ratio in the 2-butene being about 6. Cobalt can similarly be prepared in two distinguishable forms (1). A study of the mechanisms of these reactions (1) has suggested that 1,3-butadiene and the half-hydrogenated states derived from it are chemisorbed as π -allylic species at the type B surface, but as σ -bonded and π -olefin-bonded intermediates at the type A surface. The surface

structures of these types A and B catalysts have been discussed (2) and are being further investigated (3).

The object of the present investigation was to test the proposals mentioned above concerning the types of chemisorption bond between adsorbent and adsorbate at types A and B surfaces by examining the hydrogenation of 1,2-butadiene. The expectation was (see Discussion) that type A nickel would provide two major products, *cis*-2-butene and 1-butene, whereas type B nickel would provide all three *n*-butenes as major products. This expectation has been realized, and the use of deuterium as an isotopic tracer has provided detailed information concerning the reaction mechanism.

Nickel-catalyzed 1,2-butadiene hydrogenation has not been studied before. However, the nickel-catalyzed reaction of propadiene with hydrogen has been discussed briefly by Bond and Sheridan (4), and the palladium-catalyzed reaction of 1,2-butadiene with deuterium has been reported by Meyer and Burwell (5).

¹ Present address: Department of Chemistry, College of Technology, Hull HU1 3DG.

² Present address: Southwark College of Further Education, The Cut, London SE1.

³ To whom correspondence should be addressed.

EXPERIMENTAL METHODS

Catalysts

Type A nickel powder. Nickel oxide (B.D.H.) was heated to 1000°C for 16 hr in air and then reduced to metallic nickel in static hydrogen at 240°C over 10 hr, the hydrogen being changed frequently. The nickel powder weighed 0.04 g.

Type A nickel-silica. Aerosil was impregnated with nickel nitrate from neutral aqueous solution. The impregnated material was dried, calcined at 650°C for 7 hr and reduced in a stream of hydrogen at 250°C for 6 hr. The concentration of nickel in the catalyst was 10% by weight; the sample weighed 0.30 g.

Type B nickel-alumina. Alumina, 16-22 mesh (Peter Spence Type A), was impregnated with nickel nitrate and dried. The impregnated material was calcined at 650°C for 20 hr and reduced in flowing hydrogen at 450°C over 4 hr. The nickel concentration was 10% by weight; the sample weighed 0.50 g.

X-ray powder photography confirmed that complete reduction of nickel oxide to metallic nickel was achieved in each preparation.⁴

These catalysts were classified as being of type A or of type B by examination of their behavior in 1,3-butadiene hydrogenation. Products obtained from reactions of 100 Torr 1,3-butadiene with 100 Torr deuterium at 100°C after 10% conversion are shown in Table 1. Since the precise experimental conditions are in no way critical (1), the assignments of the powder and the nickel-silica as type A catalysts and of the nickel-alumina as type B (see Introduction) are clear.

⁴ A type A nickel-alumina was also prepared; however, reduction of NiO supported on alumina at 250°C does not proceed to completion, and supported NiO was found to catalyze the isomerization of 1,2-butadiene to 2-butyne rapidly. It was, therefore, an unsatisfactory catalyst for the present study.

TABLE 1

Assignment of Catalysts as Type A or Type B

Catalyst	Products of 1,3-butadiene hydrogenation ^a (%)			Behavior type
	1-b	t-2-b	c-2-b	
Nickel powder	65	22	13	A
Nickel-silica	60	27	13	A
Nickel-alumina	27	63	10	B

^a For conditions see text. Butane yield <1%.

Apparatus, Materials, and Methods

A grease-free high vacuum apparatus was used, capable of attaining vacuums of 10⁻⁵ Torr or better and having a 130-cm³ Pyrex reaction vessel. Reaction mixtures were separated into pure components by preparative glc. The conditions of operation of the mass spectrometer and the methods used to interpret the mass spectra have been described (6).

1,2-Butadiene (Kodak) was 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 ¹³C 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 deuterium and of protium atoms in the effective ratio *a*:*b*. For a discussion 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 (7) for the calculation of *N*-profiles has been used, together with the computational and manual procedures described in Part IV of this series (8). Thus Table 4 contains experi-

TABLE 2
Butenes Formed in the Nickel-Catalyzed
Hydrogenation of 1,2-Butadiene^a

	Catalyst		
	Type A Ni-powder ^b	Type A Ni-SiO ₂ ^c	Type B Ni-Al ₂ O ₃ ^d
<i>cis</i> -2-Butene (%)	57	62	44
1-Butene (%)	38	36	30
<i>trans</i> -2-Butene (%)	5	2	26

^a Initially, $P_{C_4H_6} = 50$ or 100 Torr; $P_{D_2} = 275$ - 300 Torr. Percentage of hydrogenation = 20%.

^b 75 and 110°C.

^c 115°C.

^d 46 and 75°C.

mentally determined distributions of deuterium in the butenes, 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 the mechanism of hydrogenation is based entirely on the interpretation of the *N*-profiles.

RESULTS

When 1,2-butadiene reacted with hydrogen over each of the nickel catalysts described above, about half of the alkadiene was converted to C₄-products, and half to

C₈- and higher hydrocarbons which were not analyzed in detail. Because of this extensive dimerization and polymerization, a detailed study of the kinetics was not undertaken. However, in conformity with nickel-catalyzed 1,3-butadiene hydrogenation (1) reactions were of zero order in hydrocarbon and of first order in hydrogen (by the initial rate method) and exhibited an activation energy of 55 ± 5 kJ mol⁻¹ over the range 46–100°C. This activation energy agrees exactly with that reported for the nickel-catalyzed hydrogenation of propadiene (4).

Hydrogenations over the three nickel catalysts gave the butene compositions shown in Table 2, where "percentage of hydrogenation" is defined as the instantaneous value of $10^2(P_{C_4H_8} + P_{C_4H_{10}})/(P_{C_4H_6} + P_{C_4H_8} + P_{C_4H_{10}})$. In addition, small quantities of 1,3-butadiene (~3%) and of butane (<1%) were formed; no other isomers of C₄H₆ were detected. The butene compositions shown in Table 2 were independent of conversion until the near-removal of alkadiene, were strictly independent of reactant pressures over a wide range, and were only weakly temperature dependent. They represent, therefore, the characteristic products of reactions over these catalysts. Although each catalyst provides *cis*-2-butene as the major product,

TABLE 3
Distributions of Deuterium in 1,2-Butadiene and in 1,3-Butadiene^a

Catalyst	Butadiene	Deuterium distribution (%)							D.N. ^b
		C ₄ H ₆	C ₄ H ₅ D	C ₄ H ₄ D ₂	C ₄ H ₃ D ₃	C ₄ H ₂ D ₄	C ₄ HD ₅	C ₄ D ₆	
Type A									
Ni-powder at 75°C	{ 1,2-Butadiene	98.5	0.5	0.2	0.1	0.6	0.1	0.0	0.04
	{ 1,3-Butadiene	71.5	17.0	1.8	2.7	6.0	0.7	0.2	0.58
Type B									
Ni-Al ₂ O ₃ at 46°C	{ 1,2-Butadiene	99.3	0.4	0.1	0.0	0.2	0.0	0.0	0.01
	{ 1,3-Butadiene	63.6	24.4	2.9	2.4	5.8	0.7	0.2	0.65

^a Reactant partial pressures and conversion as shown in Table 2.

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

TABLE 4
Observed and Calculated Distributions of Deuterium in Butenes^a and *N*-Profiles

Catalyst	Butene	<i>x</i>										D.N. ^b	<i>a</i> : <i>b</i>
		0	1	2	3	4	5	6	7	8			
Type A Ni-powder (75°C)	<i>cis</i> -2-Butene	obs C ₄ H _{8-x} D _x (%)	0.9	26.9	60.5	7.4	2.2	1.1	0.5	0.3	0.2	1.91	81:19
		<i>N_x</i>	0.0	0.0	82.5	11.1	2.7	1.8	1.0	0.0	0.9		
		calcd C ₄ H _{8-x} D _x (%)	3.1	26.4	58.8	7.4	2.2	1.1	0.5	0.3	0.2	1.87	
		<i>N_x</i>											
	1-Butene	obs C ₄ H _{8-x} D _x (%)	4.2	17.2	60.6	9.7	5.5	1.6	0.7	0.4	0.1	2.05	87:13
		<i>N_x</i>	0.0	0.0	77.8	10.2	8.0	2.2	0.8	0.7	0.3		
	calcd C ₄ H _{8-x} D _x (%)	1.3	18.1	62.6	9.7	5.5	1.6	0.7	0.4	0.1	2.10		
	<i>N_x</i>												
<i>trans</i> -2-Butene	obs C ₄ H _{8-x} D _x (%)	3.9	19.4	54.0	11.6	5.0	3.1	1.5	1.0	0.5	2.18	84:16	
	<i>N_x</i>	0.0	0.0	70.4	11.8	5.3	4.8	1.9	0.7	2.1			
	calcd C ₄ H _{8-x} D _x (%)	1.9	20.0	55.4	11.6	5.0	3.1	1.5	1.0	0.5	2.21		
	<i>N_x</i>												
Type B Ni-Al ₂ O ₃ (46°C)	<i>cis</i> -2-Butene	obs C ₄ H _{8-x} D _x (%)	1.9	11.9	81.3	3.5	0.8	0.3	0.1	0.1	0.1	1.92	93:7
		<i>N_x</i>	0.0	0.0	94.3	4.0	1.0	0.3	0.1	0.1	0.2		
		calcd C ₄ H _{8-x} D _x (%)	0.5	12.3	82.3	3.5	0.8	0.3	0.1	0.1	0.1	1.94	
		<i>N_x</i>											
	1-Butene	obs C ₄ H _{8-x} D _x (%)	1.6	10.6	80.3	5.3	1.6	0.3	0.2	0.1	0.1	1.97	94:6
		<i>N_x</i>	0.0	0.0	91.5	5.8	1.9	0.4	0.2	0.1	0.1		
	calcd C ₄ H _{8-x} D _x (%)	0.3	10.4	81.7	5.3	1.6	0.3	0.2	0.1	0.1	2.00		
	<i>N_x</i>												
<i>trans</i> -2-Butene	obs C ₄ H _{8-x} D _x (%)	2.3	13.4	76.8	4.8	1.4	0.6	0.3	0.2	0.2	1.95	92:8	
	<i>N_x</i>	0.0	0.0	91.1	5.6	1.7	0.8	0.3	0.1	0.4			
	calcd C ₄ H _{8-x} D _x (%)	0.6	13.5	78.4	4.8	1.4	0.6	0.3	0.2	0.2	1.98		
	<i>N_x</i>												

^a Reaction conditions and product compositions as shown in Table 2.

^b See footnote b, Table 3.

type A nickel gives only very small yields of *trans*-2-butene (*trans*:*cis* ratios of 11.4 and 31.0) whereas type B nickel provides a substantial yield of the *trans*-isomer (*trans*:*cis* ratio = 1.7).

A full isotopic analysis of two of the reactions described in Table 2 was carried out. The deuterium distributions in 1,2- and 1,3-butadiene are shown in Table 3, and those in the butenes, together with the best *N*-profiles and calculated deuterium distributions, are shown in Table 4. The rate of formation of HD and H₂ was negligible in both reactions.

DISCUSSION

1,2-Butadiene Chemisorption

There have been no reports of the use of direct methods to investigate the chemisorbed state of 1,2-butadiene or of the parent compound, propadiene, on nickel. Bond and Sheridan, in terms of the then-accepted conventions, postulated the di- σ -adsorption of propadiene on nickel (4), and Meyer and Burwell similarly described the chemisorption of 1,2-butadiene on palladium (5) (see A and B, Fig. 1). Alternative formulations of the adsorbed state,

involving π -interactions between metal atom sites and olefinic bonds, are C, D, and E. In such states, adsorption leaves the *sp*-hybridization of C_{ii} relatively unperturbed.⁵ Species C and D represent

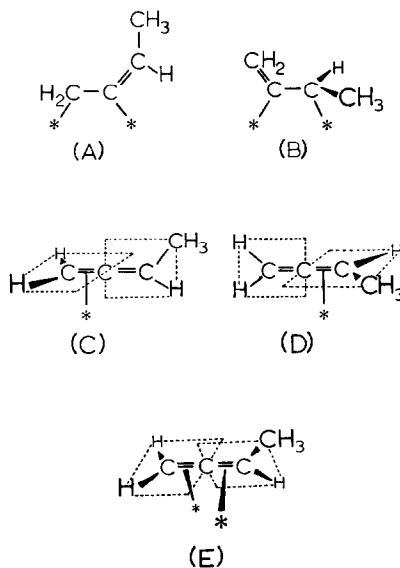


FIG. 1. Representations of chemisorbed 1,2-butadiene.

⁵ Carbon atoms in 1,2-butadiene are designated thus H₂C_i = C_{ii} = C_{iii}H — C_{iv}H₃.

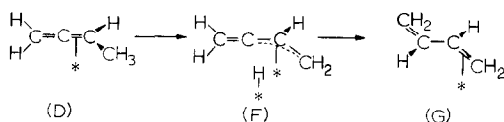


FIG. 2. Isomerization of 1,2-butadiene to 1,3-butadiene by intramolecular hydrogen atom transfer.

adsorption by the interaction of one double bond with the surface, whereas E involves the simultaneous interactions of both. We argue, with Meyer and Burwell (5), that an approach of a molecule of 1,2-butadiene to the surface with the methyl group directed towards the surface leads, on steric grounds, to no adsorption. Thus the *trans* form of A and the methyl-down forms of C and E are not considered.

Information concerning reactive forms of adsorbed 1,2-butadiene can be obtained from the distribution of deuterium in the reactant and in 1,3-butadiene formed by isomerization (Table 3). The 1,3-butadiene produced is largely C_4H_6 , which is unexpected, since the composition of the chemisorbed "hydrogen" that participates in butene production is very rich in deuterium (see values of $a:b$ in Table 4). The formation of 1,3-butadiene must therefore proceed by hydrogen atom transfer that is largely intramolecular (Fig. 2), and this in turn implies the participation of dissociatively chemisorbed 1,2-butadiene as species F. Hydrogen atom abstraction from a methyl group adjacent to a double bond in an adsorbed alkadiene, followed by 1,3-transfer of the hydrogen atom, has been observed previously in the *cis-trans* isomerization of deuterium-labeled 1,3-pentadiene catalyzed by type B cobalt (9).

The distributions of deuterium in 1,2-butadiene and in 1,3-butadiene each possess

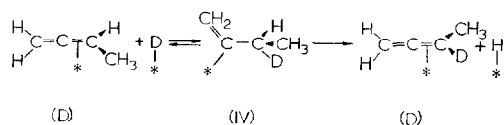


FIG. 3. Exchange of protium for deuterium at C_{iii} in chemisorbed 1,2-butadiene.

as a prominent feature a subsidiary maximum at $C_4H_2D_4$. Multiple interconversions of (D) and (F) (Fig. 2) at sites where $a:b$ is high would give adsorbed $CH_2=C=CHCD_3$ and this, accompanied by the exchange of protium bonded at C_{iii} (Fig. 3), provides $C_4H_2D_4$. The participation of (C) in an analogous process provides $DHC=C=CXCX_3$ and $D_2C=C=CXCX_3$ ($X = H$ or D) and this, with or without the process shown in Fig. 2, interprets the formation of 1,2- and 1,3-butadiene- d_3 , and $-d_6$, or $-d_1$ and $-d_2$ respectively. Although chemisorbed 1,3-butadiene (G, Fig. 2) may undergo exchange, such exchange does not provide a subsidiary maximum at $C_4H_2D_4$ when catalyzed by types A and B nickel (1).

Thus, exchange and isomerization of 1,2-butadiene provide evidence for the formation of both dissociative and associative adsorbed states of 1,2-butadiene. Remarkably, however, the subsidiary maximum in the deuterium distributions at $C_4H_2D_4$ in the butadienes is not accompanied by any subsidiary maximum at $C_4H_2D_6$ in the butenes (Table 4). Thus, 1,2-butadiene exchange and isomerization, on the one hand, and 1,2-butadiene hydrogenation, on the other, must involve different surface sites or different adsorbed states of the alkadiene (or both).

Mechanism of Hydrogenation. General

No distinction can be made on mechanistic grounds between the species shown in Fig. 1, and species E will be adopted for purposes of discussion.

The close similarity of the N -profiles of the three butenes formed in a given reaction (Table 4) shows that they were each formed as primary products. At the type B surface, over 90% of the product was butene- N_2 ; i.e., $C_4H_6X_2$ ($X = H$ or D); the remainder was more highly exchanged, the shape of the tail of the N -profile being the same for each product. At the type A surface, 70–82% of the molecules formed were

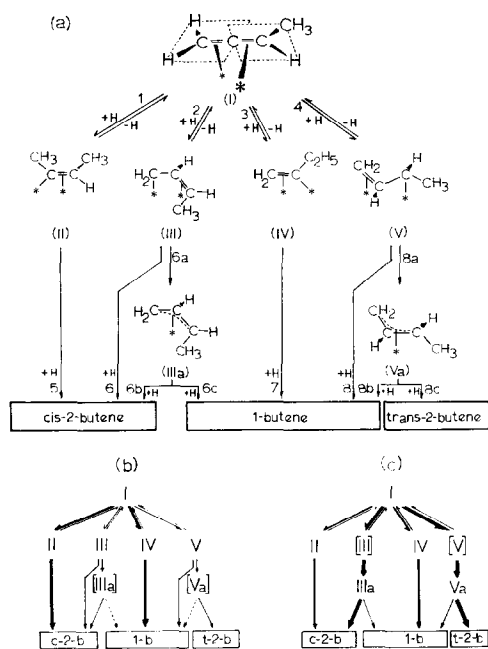
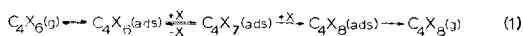


FIG. 4. Mechanisms of nickel-catalyzed 1,2-butadiene hydrogenation: (a) general; (b) at the type A surface; (c) at the type B surface.

butene- N_2 . Again, the tails of the N -profiles were similar, except that in 1-butene $N_3 \sim N_4$ whereas in the 2-butenes, $N_3 > N_4$. Also, a very small subsidiary maximum occurs at 2-butene- N_8 but not at 1-butene- N_8 . Notwithstanding these small differences, the similarities of the N -profiles of the products of a given reaction indicate that the major routes to the formation of each product are of formally identical type, differing only in the stereochemistry of the intermediates involved.

The N -profiles are in general similar to those reported for 1,3-butadiene hydrogenation catalyzed by types A and B nickel (1); the proposed mechanism is therefore based on a similar scheme [Eq. (1)] in which chemisorbed reactant interconverts with half-hydrogenated states, and the rate-determining step is the conversion of half-hydrogenated states to products. Figure 4 shows that molecules of chemisorbed



reactant (I) may be converted by hydrogen atom addition into six possible half-hydrogenated states (II), (III), (IIIa), (IV), (V), and (Va). [If adsorbed states A and B, or C and D, had been considered in place of E, species (III) and (V) would have been described as having one σ -bond and no π -bond to the surface at the moment of their formation. Meyer and Burwell (5) considered (II) and (IV) but neglected (III) and (V).]

Species (IIIa), (V), and (Va) feature in the published mechanisms of 1,3-butadiene hydrogenation (1) and we examine now the consequences of supposing that these intermediates behave similarly during 1,2-butadiene hydrogenation. Species (III), although not formed in 1,3-butadiene hydrogenation, is formally similar to (V) and is treated analogously.

Type A Behavior

Figure 4b presents the mechanism expected at the type A surface. Hydrogen atom addition to C_i and C_{iii} in (I) gives (II) and (IV) which, on further hydrogen atom addition yield *cis*-2-butene and 1-butene by steps 5 and 7 respectively. Hydrogen atom addition to C_{ii} in (I) gives CH₂CHCHCH₃(ads) which will be chemisorbed as (III) and (V) at the type A surface (1); a proportion gives *cis*-2-butene and 1-butene directly by steps 6 and 8, whereas a similar proportion is converted to olefin via the transient species (IIIa) and (Va) and subsequent hydrogenation (steps 6b, 6c, 8b, and 8c). The likely relative importance of the various steps (based on scheme 2 of Ref. (1)) is denoted by variations in the thickness of the arrows in Figure 4b. *cis*-2-Butene and 1-butene are thus expected to be major products and *trans*-2-butene a very minor product. The yield of *cis*-2-butene (Table 2) exceeds that of 1-butene, indicating that the surface concentration of (II) probably exceeds that of (IV) which, in turn, indicates that the

rate of hydrogen atom addition at C_i exceeds that at C_{iii} which is hindered by the methyl group. The very low yield of *trans*-2-butene shows that the whole of route 8 is of minor importance, and, by analogy, this will apply also to route 6. Thus, the rate of hydrogen atom attack at C_{ii} is lower than that at C_i and C_{iii} , and the likely relative concentrations of the half-hydrogenated states are $[(II)] > [(IV)] > [(III)] \sim [(V)]$.

Type B Behavior

Figure 4c presents the mechanism expected at the type B surface. Intermediates (II) and (IV) and steps 5 and 7 are present as before. $\text{CH}_2\text{CHCHCH}_3(\text{ads})$ is chemisorbed at the type B surface as a π -allylic intermediate having syn- and anti-conformations (Va) and (IIIa), respectively (1). Thus there is now a favorable route for the formation of *each* butene. The 26% yield of *trans*-2-butene (Table 2) shows that route 8 now accounts for about one-third of the product. If route 6 is similarly responsible for a further third, it follows that the hydrogen atom attack at C_{ii} in 1,2-butadiene is now more favored than that at C_i or C_{iii} . The product composition in Table 2 concurs with the ratios $[(II)]:[(IIIa)]:[(IV)]:[(Va)]$ being in the region 1:2:1:2 with $k_{6b}:k_{6c}$ and $k_{7b}:k_{7c}$ being about 9:2.

From the observation that 1,2-butadiene adsorbed at a type A site undergoes relatively slow hydrogen atom attack at C_{ii} , whereas at a type B site such attack is relatively fast, it is inferred that the sites themselves differ and that in consequence the nature of the adsorbed state of 1,2-butadiene differs. Thus the representation of the adsorbed state as E in Fig. 4 is an oversimplification, but no refinement can be introduced until the nature of the sites has been established.

The Formation of Highly Exchanged Butenes

The origin of the small yields of highly exchanged butenes is uncertain. Multiple interconversions of (I) and (II) cause exchange in the methylene group of (I) and hence the formation of $\text{C}_4\text{H}_5\text{D}_3$ and $\text{C}_4\text{H}_4\text{D}_4$. However, interconversions of (I) with (III), (IV), and (V) achieve no exchange in (I). Hydrogenation of 1,3-butadiene (formed by reactant isomerization) must be expected to contribute to the butene yield in small measure, and this reaction is known to provide small yields of highly exchanged butene (1) but not the small subsidiary maxima at $-N_8$ (Table 4). Processes which bring about complete exchange in butene have been observed in the 1,2-butadiene-deuterium reaction catalyzed by palladium (10) and will be reported in a later paper. These processes, which involve $\alpha\alpha$ -adsorbed intermediates of the type $\text{CH}_3\overset{*}{\text{C}}\overset{*}{\text{C}}\text{H}_2\text{CH}_3$, may have contributed to the nickel-catalyzed reaction to a very minor extent, and are likely also to be responsible for the observations that *trans*-2-butene formed in the type A reaction has a slightly higher deuterium number and lower value of $-N_2$ (Table 4) than the 1-butene and *cis*-2-butene formed simultaneously.

Polymerization

Dimerization and polymerization accompany the metal-catalyzed hydrogenation of acetylene and of simple mono-substituted alkynes but not that of di-substituted alkynes or conjugated alkadienes. The polymerization of 1,2-butadiene is related to the presence of the *sp*-hybridized carbon atom. In general, such polymerization occurs via the formation of free radical forms of adsorbed vinylic intermediates and, following Bond and Sheridan (4), 1,2-butadiene polymerization commences in the manner shown in Eq. (2). However, the

