JOURNAL OF CATALYSIS 51, 355–363 (1978)

Hydrogenation of Alkadienes

IX. 1,3-Butadiene Hydrogenation Catalyzed by Rhenium and by Sulfur-Contaminated Rhenium

JOHN GRANT,* RICHARD B. MOYES,† AND PETER B. WELLS†

*The College of Higher Education, Hull HU6 7LJ, and †Department of Chemistry, The University, Hull HU6 7RX, England

Received April 25, 1977

1,3-Butadiene hydrogenation has been catalyzed by rhenium film, rhenium wire, rhenium–silica, and rhenium supported on various aluminas. Products over uncontaminated catalysts were typically 1-butene, 54%; *trans*-2-butene, 30%; *cis*-2-butene, 13%; butane, 3%, this composition being fairly insensitive to reactant pressures and temperature. Such reaction at 150°C was first order in initial hydrogen pressure and negative order in initial butadiene pressure; the activation energy over the range 60–155°C was 35 ± 4 kJ mol^{-1}. The reaction of 1,3-butadiene with deuterium over rhenium–silica at 100°C is reported in detail. From the kinetics, the product composition, and the distribution of deuterium in the products it is concluded that the mechanism of hydrogenation is adequately described by that proposed for the nickel-catalyzed reaction in Part III of this series (J. J. Phillipson, P. B. Wells, and G. R. Wilson, *J. Chem. Soc. A*, 1351, 1969). The low butane yield, which is notable by comparison with the high yield obtained over the neighboring element osmium, is attributed to the measured low extent of hydrogen occlusion in rhenium. The distribution of deuterium in the butane shows that virtually no butene–butyl interconversions occur during butane formation and suggests that butane is formed at special sites. Contamination of rhenium by sulfur caused the 1:4 addition process to predominate and reduced the butane yield nearly to zero.

INTRODUCTION

The mechanism of 1,3-butadiene hydrogenation catalyzed by each of the Group 8 metals and copper has been described in previous parts of this series (*1–3*). Both butene and butane are formed as initial products. For reactions at low pressure (butadiene ~ hydrogen ~ 100 Torr typically) and moderate temperatures (0–150°C) the the butane yield is zero over copper (*3*) and gold (*4, 5*), small (0.5–5%) over iron, cobalt, nickel, and palladium (*1, 2*), and more extensive over the remaining Group 8 metals; butane may be the major product of iridium- and osmium-catalyzed reactions. The factors that determine the butane yield have been reviewed (*6, 7*).

All the isomeric normal butenes are always formed as initial products. The Group 8 metals usually provide 1-butene as the major product, the *trans*:*cis* ratio in the 2-butene being about 2. Deuterium tracer studies of reactions over cobalt and nickel (*3*) and over rhodium and platinum (*8*) have established that this butene composition is the primary product, and that butene isomerization before desorption is negligible.

Under certain conditions nickel and cobalt behave as preferential 1:4-addition catalysts; the mechanism operative under

0021-9517/78/0513-0355$02.00/0

these conditions has been established (*3*), and recently this behavior has been shown to be due to surface contamination by sulfur or certain other nonmetals (*9*).

Catalysis by rhenium has come into prominence in recent years since its incorporation in the platinum-reforming catalyst led to improvements in performance (*10–13*). However, there is still little information available concerning the mechanism of simple reactions catalyzed by this metal. In 1973 we described the reaction of ethylene with deuterium catalyzed by 17% rhenium–silica in the range of 25–150°C (*14*). The characteristics of the reaction, as regards the relative probabilities of the elementary steps, were similar to those previously reported for the neighboring cph metals ruthenium and osmium (*15*) but different from those reported for the fcc metals rhodium, palladium, iridium, and platinum (*16*). However, the specific activity of rhenium–silica was several orders of magnitude lower than that reported for silica-supported Group 8 metals by Schuit and van Reijen (*17*).

The purpose of the present work was to establish the mechanism of 1,3-butadiene hydrogenation over rhenium, to compare the selectivity of rhenium with that of the Group 8 metals, and to determine whether the product composition was influenced by sulfur contamination in the manner already established for cobalt and nickel (*9*).

EXPERIMENTAL METHODS

Catalyst Preparation

All supported catalysts contained 17% by weight of rhenium.

Rhenium supported on silica (Re-S). Aerosil 200 silica (Bush, Beach and Segner Bayley) was impregnated with the required amount of ammonium perrhenate from an aqueous solution at 100°C. Then 0.3 g of the impregnated material was placed in the reaction vessel at 25°C and reduced *in situ.* With hydrogen flowing through the vessel at 5 liters h^{-1}, the temperature was raised to 450°C over a period of about 2 h, maintained at 450°C for 18 h, and then allowed to fall to 100°C. The hydrogen flow was then stopped, the vessel was evacuated, and the catalyst was ready for use.

Rhenium supported on α-alumina (Re-A1). α-Alumina was prepared by heating Analar aluminium nitrate to 1320°C for 120 h; the oxide so formed was found to have the corundum structure (by *X*-ray powder photography) and a surface area of about 3 $m^2 g^{-1}$ (by the BET method). Impregnation was achieved as described above for Re-S; reduction was at 500°C in static hydrogen, the hydrogen being changed frequently.

Rhenium supported on $(\alpha + \kappa)$-alumina (Re-A2). Pelleted alumina (ICI, Billingham; surface area, 13.7 ± 0.9 $m^2 g^{-1}$) was used as support. Impregnation and reduction at 500°C were as described for Re-S.

Rhenium supported on high area alumina (Re-A3). Peter Spence Type A alumina ($Al_2O_3 \cdot H_2O$; surface area, 183 ± 4 $m^2 g^{-1}$) was used as support. Impregnation and reduction were as described for Re-S.

Rhenium supported on α-alumina intentionally contaminated by sulfate (Re-A4). α-Alumina (0.25 g) was impregnated at 100°C with an aqueous solution containing 0.060 g of ammonium perrhenate and 0.010 g of aluminium sulfate. The sample was reduced by the procedure described for Re-A1.

The preparation of Re-A5 is described in the text.

Rhenium wire (10 cm in length, 0.025 cm in diameter) was supplied by Engelhard Industries and had a certified purity of 99.99%. The wire catalyst was mounted and activated by electrical heating to incandescence in hydrogen as described previously (*2*).

Rhenium film was prepared by evaporation from a carefully degassed filament in ultrahigh vacuum (pressure not greater than 10^{-7} Torr during evaporation).

Catalysts Re-S, Re-A2, and Re-A3 were examined by X-ray powder photography. All photographs showed the expected diffraction pattern for metallic rhenium and no lines were attributable to any of the rhenium oxides, from which we conclude that reduction was complete. The rhenium particle size distribution obtained by electron microscopy for a 17% rhenium–silica catalyst reduced at 500°C is reported in Ref. (*14*); in that case 77% of the particles were below 50 Å in size.

Apparatus, Materials, and Methods

With the exception of the rhenium film, all catalysts were contained in static Pyrex reactors (130 cm^3) connected to high-vacuum apparatus. Catalysts Re-S, Re-A2, Re-A3, and rhenium wire were investigated using an apparatus fitted with greased taps; Re-A1, Re-A4, and Re-A5 were studied using a grease-free apparatus. In both sets of apparatus pressures and pressure changes were measured by means of a mercury manometer. Rhenium film was prepared in a 420-cm^3 Pyrex vessel attached to an ultrahigh vacuum apparatus; pressure measurement during reaction was achieved by use of a pressure transducer.

1,3-Butadiene, hydrogen, and deuterium were purified as previously described (*1*, *3*).

Reaction mixtures were analyzed and separated into pure components by glc. Positive ion mass spectra of hydrocarbons were obtained using an ionization energy of 12.0 eV. 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 (*18*) for the calculation of N-profiles has been used, together with the computational and manual procedures described in Part IV of this series (*8*). Table 2 contains experimentally determined deuterium distributions accompanied by the best calculated distributions and the N-profiles and values of $a:b$ used in the calculations. Since agreement between observed and calculated distributions is good, only deviating a little in respect of C_4H_8 and C_4H_7D, the discussion of mechanism is based on the interpretation of the N-profiles.

RESULTS AND DISCUSSION

Butene Formation

The initial rate of 1,3-butadiene hydrogenation over Re-S and over rhenium wire at 154°C, r, varied with initial reactant pressures according to Eq. (1):

$$r = kP_{C_4H_6}^{-0.5}P_{H_2}^{1.0}. \qquad (1)$$

The activation energy (Re-S, 60–155°C; Re-A3, 100–150°C) was 35 ± 4 kJ mol^{-1}. These orders and activation energies are typical of those reported for the Group 8 metals (*1*, *3*), and indicate that butadiene is strongly adsorbed and hydrogen is weakly adsorbed at the rhenium surface under these conditions.

Product compositions at low conversion, obtained using each catalyst at 150°C, are given in Table 1. The initial product compositions over Re-S, Re-A2, Re-A3, and Re wire varied only slightly with initial reactant pressures and temperature (e.g., Re-S: hydrogen = 50–300 Torr; butadiene = 18–68 Torr; temperature = 60–155°C). As reactions progressed the 1-butene yield diminished very slowly (except over Re wire, see below) and that of the 2-butenes correspondingly increased. When reaction mixtures contained an excess of hydrogen,

TABLE 1

Products of 1,3-Butadiene Hydrogenation Obtained Using Various Rhenium Catalysts[a]

Catalyst	Catalyst support[b]	Temperature (°C)	Butene composition (%)			Selectivity[c]
			1-Butene	*trans*-2-Butene	*cis*-2-Butene	
Re-Al	α-Al_2O_3	150	55	31	14	0.980
Re-A2	$(\alpha + \kappa)$-Al_2O_3	150	57	29	14	0.970
Re-S	Silica	150	55	32	13	0.960
		100	57	30	13	0.990
		100[d]	50	33	17	0.880
Re	None (film)[e]	150	54	34	12	0.910
Re	None (wire)	150	44	41	15	1.000
		150[d]	49	34	17	0.990
Re-A3	Commercial alumina	150	44	37	19	1.000
Re-A4	α-Al_2O_3[f]	150	42	45	13	0.999
Re-A5	α-Al_2O_3[f]	150	26	50	24	0.998

[a] Reaction conditions (except for Re film): initial pressures, C_4H_6 = 50 Torr, H_2 = 100 Torr; conversion ~15%.

[b] Metal loading of all supported catalysts = 17% by weight.

[c] Selectivity = [butenes]/([butenes] + [butane]).

[d] Conversion = 67%, other conditions as in Footnote *a*.

[e] Reaction conditions: initial pressures, C_4H_6 = 5 Torr, H_2 = 10 Torr; conversion = 5%.

[f] See text; rhenium intentionally contaminated by sulfur.

high selectivity for butene formation was retained until 90% or so of the butadiene had been removed, and no acceleration in rate occurred as butene hydrogenation became appreciable.

Table 1 shows that virtually identical butene compositions and selectivities were obtained using rhenium film, rhenium–silica, and the two rhenium–aluminas, Re-Al and Re-A2. The evaporated film, prepared as it was under ultrahigh vacuum conditions, was devoid of adventitious impurities, and the product composition thus characterizes the behavior of a surface that is clean except for carbon contamination. With this as a reference point, we infer that the surfaces of Re-Al, Re-A2, and Re-S were also devoid of adventitious impurities that modify the butene composition or selectivity. These product compositions resemble most closely those previously obtained over nickel–alumina (e.g., at 77°C 1-butene = 50%; *trans*-2-butene = 35%; *cis*-2-butene = 14%; selectivity = 0.99) reported in Part III (*3*).

The product compositions obtained over Re-A3 and over rhenium wire differed from those obtained over Re-Al, Re-A2, and Re-S; there was a slight preferential formation of 2-butene, and the butane yield was zero (limit of detection = 0.01%). Previous work with nickel and cobalt catalysts (*9*) has shown that these effects might be due to the presence of a nonmetal contaminant at the surface; sulfur is the most likely contaminant, but phosphorus, arsenic, antimony, and bromine exert a similar effect. Sulfur contamination of Re-A3 can reasonably be suspected because the support was found to contain 0.3% sulfate. To determine whether sulfur was responsible for this behavior catalyst Re-A4 containing sulfate, but otherwise identical to Re-Al, was prepared and examined. The butene composition and selectivity provided (Table 1) by this catalyst closely

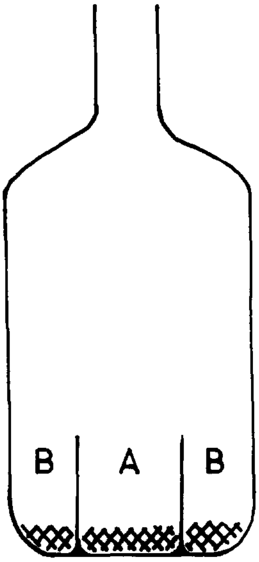

FIG. 1. A cross section through the Pyrex reaction vessel used for the preparation and evaluation of Re-A5. The material in the bucket (A) was initially α-alumina impregnated with aluminium sulfate; the material outside the bucket (B) was initially α-alumina impregnated with ammonium perrhenate.

resembled that of Re-A3, and hence sulfur contamination of the latter can reasonably be supposed.

We were curious to know whether the transfer of sulfur contaminant from the support to the metal occurred by surface transport or via the gas phase. Accordingly, catalyst Re-A5 was prepared in the vessel shown in Fig. 1. The inner glass compartment or bucket contained α-alumina impregnated with aluminium sulfate, and the outer compartment contained α-alumina impregnated with ammonium perrhenate. The standard reduction procedure (see Experimental Methods), which does not generate volatile rhenium oxide, provided catalyst Re-A5 which was a very good 1:4-addition catalyst of low activity (Table 1). Thus we conclude that surface contamination of metal by the transport of a sulfur compound through the gas phase can occur when catalyst supports containing sulfate are employed and that this contamination modifies the 1:2/1:4-addition properties of the resulting catalyst when it is used to achieve 1,3-butadiene hydrogenation. This is the first occasion on which we have been able to induce extensive 1:4-addition activity at the surface of a metal other than cobalt or nickel (*9*).

The product composition obtained using the rhenium wire suggests that this surface too was contaminated, but we have no evidence of the identity of the contaminant in this case. A remarkable effect was observed with this catalyst in the following sense. As a given reaction progressed, the butene composition changed as shown in Table 1 (the opposite of the trend with uncontaminated catalysts, see above), the reaction accelerated, and butane formation commenced. On the assumption that the mechanism proposed in Ref. (*9*) for the modification of cobalt and nickel by the action of sulfur and bromine applies to this contaminated rhenium surface, we interpret these observations to mean that the reaction of butadiene with hydrogen caused a progressive clustering of the adsorbed contaminant, thus creating a larger area of uncontaminated surface at which reaction typical of the uncontaminated surface could occur. If this conclusion is correct then evacuation of the reactant mixture and/or exposure to pure hydrogen between runs had the effect of dispersing the clustered contaminant, because the product composition at low conversion in each of a series of runs was as shown in Table 1. Such dispersal was also observed previously.

Reaction of 1,3-butadiene with deuterium over Re-S at 100°C was examined in detail. The distribution of deuterium in the hydrocarbon products is shown in Fig. 2 and Table 2. Deuterium appeared in the butadiene, indicating that the rate of desorption of the reactant was appreciable. The rate of appearance of HD was very slow, which is consistent with the proposed low surface coverage of hydrogen and deuterium atoms. The deuterium distributions in the butenes are similar to those observed in the nickel-catalyzed reaction

(*3*, *19*). N-Profiles for the butenes at all measured conversions were calculated (*20*). The calculated and observed distributions agree well (those for 11% conversion are shown in Table 2), the only disparities occurring at C_4H_8 and C_4H_7D. The N-profiles reveal that, at low conversions, 71–78% of the butene is formed by direct hydrogenation of butadiene [Eq. (2)]:

$$\begin{array}{l} \qquad\quad 2H(ads) \\ \qquad\qquad or \\ C_4H_6(ads) + H(ads) + D(ads) \longrightarrow \text{butene-}N_2. \\ \qquad\qquad or \\ \qquad\quad 2D(ads) \end{array} \qquad (2)$$

Smaller yields of products undergo exchange as well as hydrogenation (N_3–N_6), but no completely exchanged butene was formed.

The N-profiles for butenes obtained in the rhenium-catalyzed reaction are closely similar to those reported for the nickel-catalyzed reaction at 68°C (*3*); a comparison at comparable conversion is given in Table 3. The N-profiles have the same general shape; over each metal the N_2 contribution is largest in *cis*-2-butene, and a subsidiary maximum or discontinuity in the profile occurs at -N_6. In view of these similarities, we propose that the very detailed discussion of the mechanism of the nickel-catalyzed reaction applies *mutatis mutandis* to the rhenium-catalyzed reaction, and that Schemes 1A and 2 in Part III (*3*) adequately represent the processes involved and their relative importance.

The effective ratio of deuterium to hydrogen atoms at the surface, utilized in butene formation (see a:b values, in Table 2), was slightly higher at the rhenium surface than at the nickel surface at comparable conversion. This arises because the extent of exchange of H for D in the butenes was slightly higher in the nickel-catalyzed reaction.

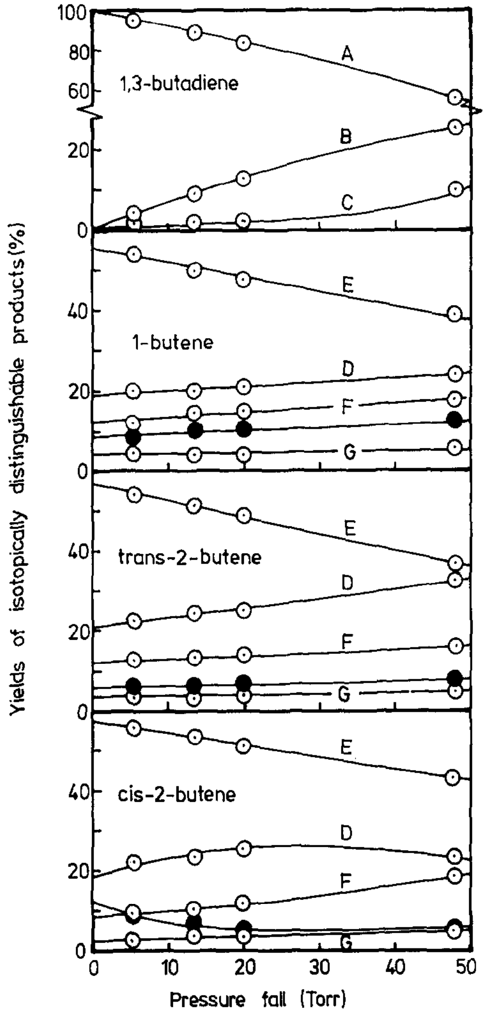

FIG. 2. The variation, with pressure fall, of the yields of isotopically distinguishable products in the reaction of 50 Torr of 1,3-butadiene with 100 Torr of deuterium over rhenium–silica at 100°C. (A) C_4H_6; (B) C_4H_5D; (C) $C_4H_4D_2$. Very small yields of all other deuteriated butadienes were obtained but are not shown. (Filled points) C_4H_8; (D) C_4H_7D; (E) $C_4H_6D_2$; (F) $C_4H_5D_3$; (G) $C_4H_4D_4$. Very small yields of $C_4H_3D_5$ and $C_4H_2D_6$ were obtained but are not shown. C_4HD_7 and C_4D_8 were not observed.

Butane Formation

A remarkable feature of the rhenium-catalyzed reaction is the high selectivity for alkene formation that was achieved. The butane yield was 5% at 70°C over rhenium–silica and over rhenium–alumina, which compares with 37% obtained over osmium–alumina under the same condi-

TABLE 2

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

Compound	Conversion[a] (%)		x										Deuterium number[b]	$a:b$
			0	1	2	3	4	5	6	7	8	9		
1-Butene	11	Obsd $C_4H_{8-x}D_x$ (%)	8.3	19.3	53.9	11.2	4.5	2.0	0.8	0.0	0.0		1.94	
		N_x	0.0	0.0	73.2	14.8	6.6	2.3	3.1	0.0	0.0			80:20
		Calcd $C_4H_{8-x}D_x$ (%)	3.1	24.6	53.9	11.1	4.5	2.0	0.8	0.0	0.0		1.98	
trans-2-Butene	11	Obsd $C_4H_{8-x}D_x$ (%)	5.2	22.3	54.2	12.6	3.6	1.3	0.8	0.0	0.0		1.94	
		N_x	0.0	0.0	71.5	18.5	6.6	0.3	3.1	0.0	0.0			80:20
		Calcd $C_4H_{8-x}D_x$ (%)	2.8	24.8	54.2	12.5	3.6	1.3	0.8	0.0	0.0		1.96	
cis-2-Butene	11	Obsd $C_4H_{8-x}D_x$ (%)	9.0	21.8	55.4	9.5	2.9	0.9	0.5	0.0	0.0		1.80	
		N_x	0.0	0.0	79.4	13.7	5.5	0.5	0.9	0.0	0.0			80:20
		Calcd $C_4H_{8-x}D_x$ (%)	3.3	26.5	56.4	9.5	2.9	0.9	0.5	0.0	0.0		1.87	
Butane	27	Obsd $C_4H_{10-x}D_x$ (%)	0.5	0.0	4.0	20.8	52.7	14.6	4.5	1.5	1.0	0.4[c]	4.03	
		N_x	0.0	0.0	0.0	0.0	68.9	20.1	6.9	1.7	1.3	1.1[c]		90:10
		Calcd $C_4H_{10-x}D_x$ (%)	0.0	0.3	3.6	21.6	52.5	14.6	4.5	1.5	1.0	0.4	4.04	
trans-2-Butene	27	N_x	0.0	0.0	69.3	21.2	5.9	1.8	1.8	0.0	0.0			78:22

[a] Other experimental conditions as given in Fig. 1.

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

[c] Observed C_4D_{10} = zero; N_{10}-butane = zero.

tions (*1*). The butane yield early in reaction may depend on several factors (*6*), including (i) the relative specific activities of the metal for butadiene hydrogenation and for butene hydrogenation, (ii) the difference between the free energies of adsorption of butadiene and butene (if this difference is considerable butadiene may rapidly displace adsorbed butene), and (iii) the existence of regions in the metal in which hydrogen occlusion occurs (*6, 7*). The absence of a marked acceleration or deceleration in the rate when the conversion of butadiene to butene gave way to butene hydrogenation, over both rhenium and osmium, shows that the situation with respect to factor (i) above was similar for these two metals. The proportion of butane in the products increased only slowly with increasing conversion (0–50%) over both rhenium and osmium, which suggests that the situation with respect to factor (ii) was similar also. This led us to compare the extents of hydrogen occlusion in rhenium and osmium.

We have demonstrated (*6, 7, 21*) that the extent of butane formation in butadiene hydrogenation over Ru, Rh, Os, Ir, and Pt

TABLE 3

Comparison of N-Profiles of Butenes Formed in 1,3-Butadiene Hydrogenation over Rhenium–Silica at 100°C and over Nickel–Alumina at 68°C[a]

Catalyst	Conversion	Product	N_2	N_3	N_4	N_5	N_6	N_7	N_8	$a:b$
Re[b]	40	1-Butene	61.7	26.0	7.4	2.1	2.8	0.0	0.0	75:25
		trans-2-Butene	65.5	22.0	7.7	2.2	2.6	0.0	0.0	76:24
		cis-2-Butene	70.5	18.8	7.1	0.2	3.4	0.0	0.0	77:23
Ni[c]	54	1-Butene	57.0	15.0	11.0	10.0	5.0	1.0	1.0	66:34
		trans-2-Butene	63.0	15.5	9.0	2.5	10.0	0.0	0.0	67:33
		cis-2-Butene	65.7	18.8	5.3	4.7	4.5	1.0	0.0	63:37

[a] Initial pressures: butadiene = 50 Torr; deuterium = 100 Torr.

[b] This work.

[c] Reference (*3*).

increased with the extent to which these metals occlude hydrogen (as measured by butene titration or by exchange of occluded hydrogen for deuterium). Rhenium powder was prepared in like manner to the catalysts, and the extent of hydrogen occlusion was measured. Butene titration at 100°C indicated an empirical formula of $ReH_{0.01}$; this extent of occlusion is lower than that recorded for Rh (x in $MH_x = 0.02$), Ru ($x = 0.04$), Os ($x = 0.07$), or Ir ($x = 0.13$–0.20). The observation that rhenium provides a lower yield of butane in butadiene hydrogenation than do Rh, Ru, Os, or Ir under comparable conditions provides a useful extension of our correlation (*7*) and demonstrates that this factor probably determines the high selectivity of rhenium for butene formation.

The deuterium distribution in the butane (Table 2) provides information concerning the mechanism of butane formation from butene. The N-profile of the butane is almost identical to that of butenes formed simultaneously (Table 2). This shows that the consecutive addition of two hydrogen or deuterium atoms [Eq. (3)], is the major process, and that the chance of adsorbed butyl reverting to adsorbed butene is very slight:

$$\underset{*}{C_4X_8} \xrightarrow{+X} \underset{*}{C_4X_9} \xrightarrow{+X} C_4X_{10}(g) \qquad (X = \text{H or D}). \qquad (3)$$

This is the first occasion on which we have observed such direct formation of butane from butene in butadiene hydrogenation. Over rhodium and platinum the extent of butyl–butene interconversion was considerable (*8*); other metals have not been examined in this respect. This trend mirrors that observed in the ethylene–deuterium reaction at 25°C, where the chance of ethyl conversion to ethane, relative to its chance of conversion to ethylene, is highest over rhenium (up to 81%) and lowest over rhodium and platinum (up to 16%) (*14*).

The value of $a{:}b$ associated with the N-profile of butane, 90:10, differs from that associated with the N-profile of the butene, 78:12 (Table 2). Again this was so for the rhodium- and platinum-catalyzed reactions (*8*). This is further evidence that butane was formed at special sites at the surface, possibly cognate to regions of hydrogen occlusion in the metal (*7*).

CONCLUSION

Rhenium catalyzes 1,3-butadiene hydrogenation to give a butene distribution and selectivity not dissimilar to those obtained over nickel. Use of deuterium as a tracer reveals that the mechanisms at the two surfaces bear a fundamental similarity, despite the fact that rhenium is a metal of high melting point and cph structure, whereas nickel has a relatively low melting point and an fcc structure. The slight preference of the uncontaminated rhenium surface to catalyze 1:2-addition of hydrogen to butadiene can be converted to a preference for 1:4-addition, at the expense of some activity, by the action of sulfur; this property is also possessed by nickel and cobalt. The low yield of butane obtained by direct hydrogenation of butadiene over uncontaminated rhenium is attributed to the low extent of hydrogen occlusion in this metal.

ACKNOWLEDGMENTS

The assistance of M. Eyre and D. P. Murphy with some aspects of the experimental work is acknowledged.

REFERENCES

1. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Chem. Soc.*, 3218 (1965).
2. Wells, P. B., and Bates, A. J., *J. Chem. Soc. A*, 3064 (1968).
3. Phillipson, J. J., Wells, P. B., and Wilson, G. R., *J. Chem. Soc. A*, 1351 (1969).
4. Bond, G. C., Sermon, P. A., Webb, G., Buchanan, D. A., and Wells, P. B., *J. Chem. Soc. Chem. Commun.*, 444 (1973).
5. Buchanan, D. A., and Webb, G., *J. Chem. Soc. Faraday Trans. 1* 71, 134 (1975).

6. Wells, P. B., *in* "Surface and Defect Properties of Solids" (M. W. Roberts and J. M. Thomas, Eds.), Vol. 1, p. 236. Chemical Society, London, 1972.
7. Wells, P. B., *J. Catal.*, in press.
8. Bates, A. J., Leszczynski, Z. K., Phillipson, J. J., Wells, P. B., and Wilson, G. R., *J. Chem. Soc. A*, 2435 (1970).
9. George, M., Moyes, R. B., Ramanarao, D., and Wells, P. B., *J. Catal.*, in press.
10. Kluksdahl, H. E., U. S. Patent 3,415,737 (1968).
11. Sterba, M. J., Wienert, P. C., Lickus, A. G., Pollitzer, E. L., and Hayes, J. C., *Oil Gas J.* **66**, 140 (1968).
12. Jacobson, R. L., Kluksdahl, H. E., McCoy, C. S., and Davis, R. W., *Proc. Amer. Petrol. Inst.*, 504 (1969).
13. Ciapetta, F. G., and Wallace, D. N., *Catal. Rev.* **5**, 67 (1972).
14. Grant, J., Moyes, R. B., and Wells, P. B., *J. Chem. Soc. Faraday Trans. 1* **69**, 1779 (1973).
15. Bond, G. C., Webb, G., and Wells, P. B., *Trans. Faraday Soc.* **61**, 999 (1965).
16. Bond, G. C., Phillipson, J. J., Wells, P. B., and Winterbottom, J. M., *Trans. Faraday Soc.* **60**, 1847 (1964).
17. Schuit, G. C. A., and van Reijen, L. L., *Advan. Catal.* **10**, 242 (1958).
18. Smith, G. V., and Burwell, R. L., *J. Amer. Chem. Soc.* **84**, 925 (1962).
19. Phillipson, J. J., Ph.D. Thesis, University of Hull, Hull, England, 1964.
20. Grant, J., M.Sc. Thesis, University of Hull, Hull, England, 1971.
21. Wells, P. B., *in* "Proceedings of the Symposium on Electrocatalysis" (M. Breiter, Ed.), p. 1. The Electrochemical Society, Princeton, N.J., 1974.