587. *The Hydrogenation of Alkadienes. Part I. The Hydrogenation of Buta-*1,3-*diene Catalysed by the Noble Group VIII Metals*

By G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom

The gas-phase hydrogenation of buta-1,3-diene has been studied in a static system using alumina-supported ruthenium (0—50°), rhodium (15—80°), palladium (0—45°), osmium (25—70°), iridium (−20—75°), and platinum (0—150°). Orders of reaction and activation energies were measured. But-1-ene and *cis*- and *trans*-but-2-ene were initial products under all conditions. Palladium is completely selective for olefin formation but the other metals provide n-butane as an initial product, and it is the major product of the iridium-catalysed reaction. The dependence of the product composition on conversion, hydrogen pressure, and temperature is reported.

1 : 2-Addition of hydrogen to the diene is responsible for but-1-ene formation on all of the metals. Formation of but-2-ene by a 1 : 4-addition process occurs on palladium and probably on the other metals; the relative yields of *trans*- and *cis*-but-2-ene formed by this process depend on the conformational characteristics of adsorbed precursors. Where n-butane formation takes place, simultaneous olefin isomerisation modifies the olefin distribution produced by 1 : 2- and 1 : 4-addition.

The proportion of n-butane produced depends on the inherent activities of the metals for butene hydrogenation relative to desorption, and on the difference between the free energies of adsorption of buta-1,3-diene and the butenes.

Reaction characteristics were not dependent on the crystal structure of the metal.

Much interest currently centres on the selective behaviour of heterogeneous catalysts. The hydrogenation of conjugated diolefins is a relatively untouched field which is particularly well suited to studies of selectivity because catalysts may show (i) a preference for the production of mono-olefin rather than paraffin or *vice-versa* and (ii) preferential production of one isomer of the olefin rather than another. We believe that the elucidation of such reaction mechanisms will not only advance our understanding of catalytic phenomena and provide useful information for the preparative chemist but, more important, will ultimately allow variations in catalytic behaviour to be related to the chemistry of the metals themselves.

Little fundamental work has been carried out on the metal-catalysed hydrogenation of buta-1,3-diene. Its gas-phase deuteration using palladium–alumina has been reported by Meyer and Burwell[1] who propose that 1 : 2- and 1 : 4-addition of hydrogen to the diolefin takes place at room temperature. Hydrogenation in the liquid phase, using Group VIII metals and ethanol as solvent has been studied[2–5] but the only mechanistic discussion is that of Rieche, Grimm, and Albrecht[4] who assumed an ionic mechanism. Previous reports of product distributions by Young *et al.*[5] contained no mechanistic proposals since their object was to demonstrate that butenes were formed as initial products, thus refuting an earlier report by Paal.[2]

The object of the present work was to compare the characteristics of alumina-supported ruthenium, rhodium, palladium, osmium, iridium, and platinum, as catalysts for hydrogenation of gaseous buta-1,3-diene in order to gain an understanding of the factors governing the two types of selective behaviour mentioned above.

[1] E. F. Meyer and R. L. Burwell, *J. Amer. Chem. Soc.*, 1963, **85**, 2881.

[2] C. Paal, *Berichte*, 1912, **45**, 2221.

[3] S. V. Lebed'ev and A. O. Yabubchik, *J.*, 1928, 2190.

[4] V. A. Reiche, A. Grimm, and H. Albrecht, *Brennstoff-Chemie*, 1961, **42**, 5.

[5] W. G. Young, R. L. Meier, J. Vinograd, H. Bollinger, L. Kaplan, and S. L. Linden, *J. Amer. Chem. Soc.*, 1947, **69**, 2046.

EXPERIMENTAL

Catalysts.—The catalysts consisted of 5 molar percent (Rh, Pd; Ir, Pt) or 1 molar percent (Ru, Os) metal supported on 8–16 mesh α-alumina (American classification); preparations of the stocks have been described elsewhere.[6,7] Weights of catalyst were typically 0·3 g. and samples were reduced a second time in hydrogen, *in situ*, for an hour at 200° before use.

Apparatus, Materials, and Experimental Methods.—Cylindrical 100-ml. Pyrex reaction vessels were connected to a conventional high vacuum system, and each catalyst sample rested on the bottom of the vessel. Buta-1,3-diene and hydrogen were admitted to the vessel in that order and pressure changes were measured by either (i) a spiral glass gauge and spot galvanometer (Rh, Pd, Ir, and Pt studies) or (ii) a mercury manometer (Ru and Os). Catalysts were kept under 150 mm. of hydrogen when not in use and reproducible activities were observed throughout the study.

Buta-1,3-diene (Distillers Company Limited) was completely freed from a high-boiling impurity by successive bulb-to-bulb distillations. Hydrogen (British Oxygen Company) was either dried and used without further treatment (Rh, Pd, Ir, Pt) or was purified by passage over palladised asbestos and then dried (Ru, Os).

Gas-liquid chromatography was used to estimate the proportions of hydrocarbons in gas samples removed from the vessel. A 22 ft. column of 40% w/w hexane-2,5-dione supported on 30—60 mesh firebrick was operated at ambient temperatures using hydrogen or nitrogen as carrier gas. The detector was a hot-wire katharometer. Hydrocarbons were eluted in the order: n-butane, but-1-ene, *trans*-but-2-ene, *cis*-but-2-ene, buta-1,3-diene. Complete separation was achieved.

RESULTS

Kinetics.—Table 1 contains the orders of reaction and activation energies derived from initial rate measurements. The uncertainty in the orders is ±0·1 and the activation energies are uncertain to ±1·0 kcal. mole^{-1} in each case.

The pressure fall against time curves were accurately of first-order with respect to the instantaneous hydrogen pressure for rhodium, palladium, iridium, and platinum (other metals not studied) when the initial pressures of hydrogen and buta-1,3-diene were each 100 mm. When initial hydrogen : buta-1,3-diene ratios were two or greater the pressure fall against time curves were of the forms shown in Figure 1. When rhodium and osmium were used the rate was proportional to the first power of the instantaneous hydrogen pressure throughout the reaction. Over the remaining metals, the reactions accelerated after about 80% (Pd, Ir, Pt) or 100% (Ru) removal of buta-1,3-diene. The rate of reaction, before acceleration was either of first order in instantaneous hydrogen pressure (Ru, Ir) or of zero order (Pd, Pt).

TABLE 1

Orders of reaction and activation energies for buta-1,3-diene hydrogenation

Metal	Order in hydrogen	Order in buta-1,3-diene	Temp.	Activation energy (kcal. mole^{-1})	Temp. range
Ru	1·0	0·0	14°	12·5	0—48°
Rh	1·0	0·1	0	11·1	16—82
Pd	1·7	−0·7	16	16·7	20—42
Os	1·0	0·0	70	10·2	24—70
Ir	0·8	0·0	0	4·5	0—62
Pt	1·3	−0·5	16	19·5	0—152

Selectivity.—The selectivity for butene formation exhibited by a metal M, is denoted by S_M, and is defined as:

$$S_M = P_{C_4H_8}/(P_{C_4H_8} + P_{C_4H_{10}})$$

where $P_{C_4H_8}$ is the total butene pressure irrespective of its isomeric composition.

When the initial pressure of each reactant was 50 mm. the selectivities and butene distributions were always independent of hydrogen uptake throughout the reaction (Rh, 18 and 56°; Pd, 14°; Ir, −20°; Pt, 15 and 107°; Ru and Os were not studied.

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[6] G. C. Bond, D. A. Dowden, and N. Mackenzie, *Trans. Faraday Soc.*, 1958, **54**, 1537.

[7] G. C. Bond and G. Webb, in the press.

Figure 2 shows the variations of selectivity with hydrogen uptake observed when an excess of hydrogen was used. n-Butane always appeared as an initial product except when palladium was used; it was the major product of the iridium-catalysed reaction. S_{Pd} was initially independent of conversion but the selectivities shown by the other metals decreased slowly at first. S_{Pd}, S_{Rh}, S_{Pt}, and S_{Ir} decreased rapidly to zero after about eighty percent removal of the diene; this point corresponds with the acceleration points observed in the pressure against time curves II, III, and IV shown in Figure 1 and denotes conditions under which re-adsorption and hydrogenation of butene become appreciable. The position of the acceleration point in the ruthenium-catalysed reaction suggests that hydrogenation of butene did not become appreciable until almost complete removal of the buta-1,3-diene.

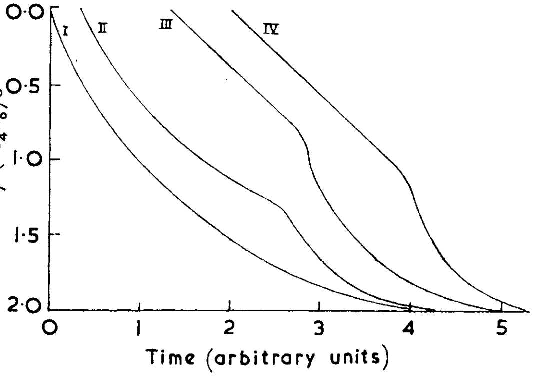


FIGURE 1. Pressure fall, $-\Delta p$, against time curves. Curve I, Rh at 18° and Os at 115°; II, Ir at $-20°$ and Ru at 75°; III, Pd at 0°; IV, Pt at 15°. Initial buta-1,3-diene pressure, $(P_{C_4H_6})_0 = 35$ mm. (Ru, Os) or 50 mm. (Rh, Pd, Ir, Pt); initial hydrogen pressure = 150 mm.

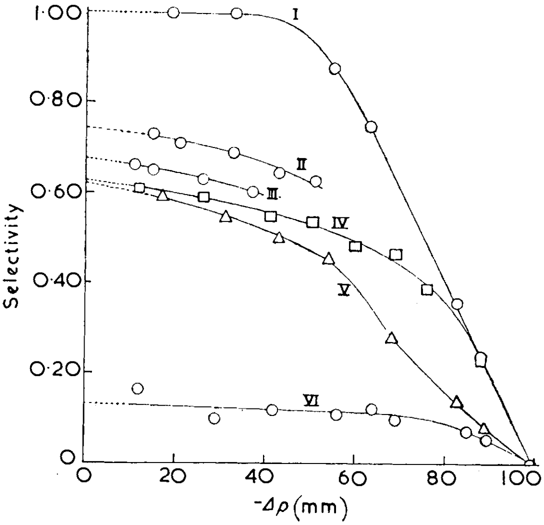


FIGURE 2. Variation of selectivity with pressure fall, $-\Delta p$. Initial buta-1,3-diene pressure = 50 mm. Initial hydrogen pressure = 100 mm. (Ru), 150 mm. (Rh, Pd, Ir, Pt), 250 mm. (Os). Curve I, Pd at 0°; II, Ru at 0°; III, Os at 67°; IV, Rh at 18°; V, Pt at 15°; VI, Ir at $-20°$

The dependence of selectivity upon hydrogen pressure is shown in Figure 3. S_{Pd} was unity and independent of hydrogen pressure, whereas the selectivities exhibited by the other metals decreased with increasing initial hydrogen pressure. All curves were convex with respect to the origin.

Excepting palladium, all catalysts became increasingly selective for butene formation as the temperature was raised (see Table 2).

The Distribution of Butenes.—The butene produced during the initial stages of the reaction contained but-1-ene as the major component, except when iridium was used above 70° (see Table 2 and Figure 4). The *trans* : *cis* ratio in the but-2-ene varied widely: its value was about 16 for Pd at 0°; 1·6 for Ru at 0°; 1·9 for Rh at 16°; 1·2 for Pt at 15°; and Os at 24°; and 0·8 for Ir at $-20°$.

TABLE 2

The dependence of butene distribution and selectivity upon temperature

Initial $P_{C_4H_6}$ = 50 mm. throughout. Initial P_{H_2} = 155 mm. (Ru, Rh, Pd, Ir, Pt) and 250 mm. (Os).

Metal	Pressure fall before analysis (mm.)	Temp.	Butene distribution (%) b-1 *	*t*-b-2 *	*c*-b-2 *	$\frac{t\text{-b-2}}{c\text{-b-2}}$	Selectivity
Ru	12	0°	69	19	12	1·6	0·736
		25	64	21	15	1·4	0·820
		49	61	23	16	1·4	0·835
Rh	20	16	51	32	17	1·9	0·743
		36	52	31	17	1·8	0·834
		70	51	31	18	1·7	0·867
		82	48	32	20	1·6	0·906
Pd	25	0	64·4	33·2	2·4	13·8	1·000
		21	60·2	37·0	2·8	13·2	1·000
		43	59·4	36·8	3·8	9·7	1·000
Os	15	24	65	19	16	1·2	0·431
		46	60	21	19	1·1	0·570
		70	57	21	22	0·9	0·630
Ir-I	12	−20	75	11	14	0·8	0·167
Ir-II.........	16	24	59	19	22	0·9	0·251
		43	51	22	27	0·8	0·278
		75	32	34	34	1·0	0·384
Pt-I	25	0	72	18	10	1·8	0·501
		15	65	18	17	1·1	0·563
		45	64	17	19	0·9	0·625
Pt-II	25	107	61	22	17	1·3	0·800
		134	47	32	21	1·5	0·910
		152	38	36	26	1·4	0·920

* b-1 = but-1-ene; *t*-b-2 = *trans*-but-2-ene; *c*-b-2 = *cis*-but-2-ene.

The dependence of the butene distribution upon conversion was measured using each metal in turn (see Figure 4). The ruthenium and osmium reactions were studied [Figures 4(a) and (d)] during the first half of the hydrogen uptake only, during which the butene distributions altered a little, the change being towards the thermodynamic equilibrium proportions which are shown as dotted horizontal lines. (At all temperatures used in this work the equilibrium proportions have the relative magnitudes: *trans*-but-2-ene > *cis*-but-2-ene > but-1-ene.)

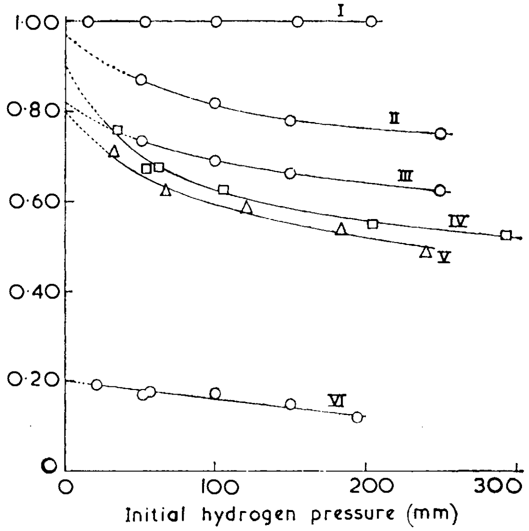


FIGURE 3. Dependence of selectivity upon initial hydrogen pressure. Initial buta-1,3-diene pressure = 50 mm. (Ru, Pd, Os, Ir, Pt) or 100 mm. (Rh). Percentage removal of diene before analysis = 10% (Ru) or 20—25% (other metals). Curve I, Pd at 18°; II, Ru at 13°; III, Os at 70°; IV, Rh at 18°; V, Pt at 15°; VI, Ir at −20°

The complete course of reaction was studied with the other metals. Using Rh at 18°, Pd at 0°, and Pt at 104° [Figures 4(b), (c), and (g), respectively] the butene composition changed rapidly during the second half of the reaction and attained thermodynamic equilibrium proportions. Over palladium, the *cis*-but-2-ene concentration passed through a maximum before equilibrium was achieved. Ir at −20° and Pt at 16° [Figures 4(e), (f)] differed in that rapid changes of butene composition did not occur and, in consequence, equilibrium proportions were not achieved. It is notable that for metals other than palladium the initial proportion of *cis*-but-2-ene does not differ greatly from the thermodynamic equilibrium proportion and that this isomer reaches its equilibrium concentration before *trans*-but-2-ene and but-1-ene.

In six series of reactions, the buta-1,3-diene pressure was maintained constant at 50 mm. (Ru, Pd, Os, Ir, Pt) or 100 mm. (Rh) and the hydrogen pressure varied from about 25 to 250 mm. Ruthenium at 0°, rhodium at 16°, palladium at 0°, osmium at 67°, and iridium at −20° all gave butene distributions which were independent of the initial hydrogen pressure. However, with platinum at 15°, the butene distribution varied linearly with initial hydrogen pressure between the following extreme values:

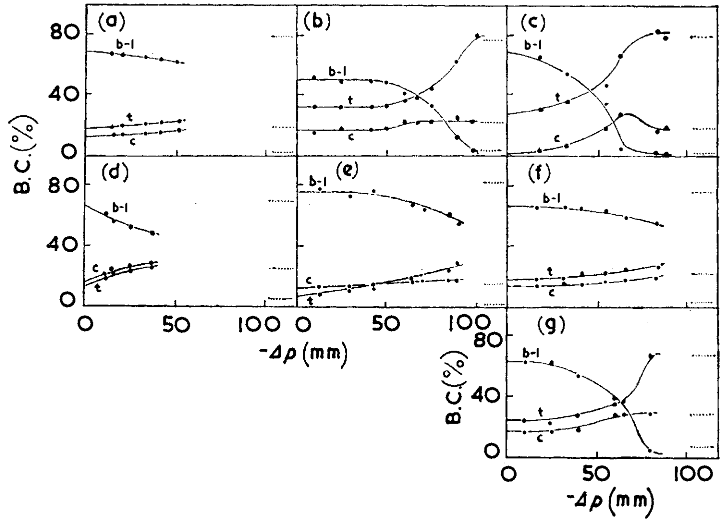


FIGURE 4. Variation of butene composition, B.C., with pressure fall, $-\Delta p$, observed using (a) Ru at 0°, (b) Rh at 18°, (c) Pd at 0°, (d) Os at 70°, (e) Ir at −20°, (f) Pt at 15°, and (g) Pt at 104°. Initial buta-1,3-diene pressure = 50 mm.; initial hydrogen pressure = 100 mm. (Ru), 155 mm. (Rh, Pd, Ir, Pt), or 250 mm. (Os). Abbreviations: b-l = but-l-ene, t = *trans*-but-2-ene, c = *cis*-but-2-ene

initial P_{H_2} = 25 mm., but-l-ene = 76%, *trans*-but-2-ene = 13%, *cis*-but-2-ene = 11%,
initial P_{H_2} = 200 mm., but-l-ene = 63%, *trans*-but-2-ene = 22%, *cis*-but-2-ene = 15%.

The butene distribution showed no definite trend with increasing temperature for the rhodium-catalysed reaction, but over each of the other metals the fraction of but-l-ene produced decreased with increasing temperature (see Table 2). The *trans* : *cis* ratio (in but-2-ene) decreased with increasing temperature when using all catalysts except Ir-II and Pt-II for which an increase was observed. However, the opposite behaviours of Pt-I and Pt-II suggest that these variations in the *trans* : *cis* ratio are not of prime importance.

DISCUSSION

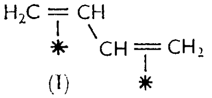
The distribution of products from buta-1,3-diene hydrogenation varies widely depending on the metal employed as catalyst and on the experimental conditions used. However, over each of the six metals, all three n-butenes were formed as initial products under all conditions and n-butane was also produced initially in all but the palladium-catalysed reaction. This discussion examines those aspects of the mechanism which govern the product distributions.

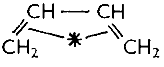
Negative or zero orders in buta-1,3-diene and positive orders in hydrogen (see Table 1) indicate that the diene was the more strongly adsorbed reactant and consequently the surface coverage of diene was high relative to that of hydrogen. The very slow or negligible re-adsorption of butene before about eighty percent removal of diene shows that butene was less strongly adsorbed than buta-1,3-diene. Studies of butene hydrogenation by the present authors, using catalyst samples from the same stocks, have shown that butene is more strongly adsorbed than hydrogen on these metals.[7,8] Consequently, the strengths of adsorption of reactants and products in buta-1,3-diene hydrogenation decrease in the sequence:

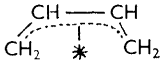
buta-1,3-diene $>$ butenes $>$ hydrogen $>$ n-butane

The stronger adsorption of buta-1,3-diene relative to butene shows that the diene adsorbs by the interaction of both olefinic linkages with the surface. The adsorbed state may contain four carbon–metal σ-bonds, one from each of four carbon atoms which exhibit sp^3 hybridisation; or alternatively, two π-bonds may be formed between the olefinic linkages of the diene and appropriate sites on the catalyst surface, in which case the sp^2 hybridisation of the carbon skeleton will be little disturbed. Adsorbed buta-1,3-diene will be formulated as the di-π-adsorbed species, as shown below. The degree of internal strain inherent in this structure is much lower than in the tetra-σ-adsorbed species.

When di-adsorbed, a given buta-1,3-diene molecule must adopt one of two conformations. Geometrical considerations require conformation (I) to be adsorbed to two metal atoms. However, in the alternative conformation the double bonds appear more likely to interact with one metal atom, and where this occurs the double bonds may retain their individuality (structure II) or the π-electrons may become delocalised over all four carbon atoms (structure III). If the adsorbed states are correctly represented by (I) and (II), then conformational interconversion may take place *via* a mono-π-adsorbed species.

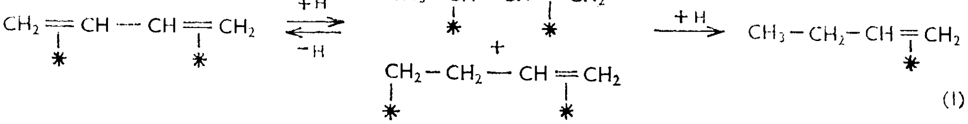

(I)


(II)


(III)

It is widely accepted that hydrogenation reactions proceed by the following elementary steps: (i) the adsorption of one or both reactants, (ii) the formation of one or more " half-hydrogenated states " and (iii) the reaction of the half-hydrogenated state with hydrogen to give the product. In buta-1,3-diene hydrogenation, where both butenes and butane are produced, this sequence occurs twice. Studies of both olefin and acetylene hydrogenation using deuterium as an isotopic tracer, have shown that the formation of half-hydrogenated states is usually a readily reversible step.[8,9] This characteristic will be assumed to be true of buta-1,3-diene hydrogenation.

Butene Distributions.—(1) *General.* But-1-ene is formed by 1 : 2-addition of two hydrogen atoms to the diene as shown in equation (1); the conformations of the adsorbed diene are irrelevant to this process.


(1)

But-2-ene may be formed as an initial product (i) by 1 : 4-addition of two hydrogen atoms

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[8] G. C. Bond, J. J. Phillipson, P. B. Wells, and J. M. Winterbottom, *Trans. Faraday Soc.*, 1964, **60**, 1847.

[9] G. C. Bond and J. Turkevitch, *Trans. Faraday Soc.*, 1953, **49**, 281; G. C. Bond, *ibid.*, 1956, **52**, 1235; J. Addy and G. C. Bond, *ibid.*, 1957, **53**, 377.

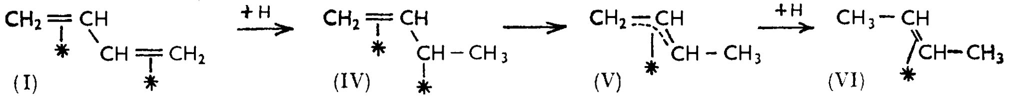
to the diene, or (ii) by the isomerisation of but-1-ene formed in equation (1) by alkyl reversal:

$$\text{but-1-ene (ads)} \underset{-\mathrm{H}}{\overset{+\mathrm{H}}{\rightleftharpoons}} \mathrm{C_4H_9}\ \text{(ads)} \underset{+\mathrm{H}}{\overset{-\mathrm{H}}{\rightleftharpoons}} \textit{cis-}\text{ and }\textit{trans-}\text{but-2-ene (ads)} \qquad (2)$$

or (iii) by a combination of both processes (i) and (ii).

Two important deductions can be made immediately concerning the mechanisms of but-2-ene formation on our catalysts. First, since the palladium catalyst was extremely active for the hydrogenation of the butenes, we attribute the absence of n-butane formation during buta-1,3-diene hydrogenation to an absence of adsorbed-C_4H_9 on the surface. Consequently, but-2-ene must have been formed in this reaction by 1 : 4 addition of hydrogen to the diene. This conclusion is in agreement with that of Meyer and Burwell.[1] Secondly, the other metals studied all give n-butane as an initial product and its precursor, adsorbed-C_4H_9, must have been formed in these reactions. Consequently butene isomerisation by equation (2) will almost certainly complicate the butene distribution obtained by direct diene hydrogenation to olefin.

(2) *The geometrical characteristic of the but-2-ene.* In the 1 : 4-addition process the conformation of adsorbed-C_4H_7 determines the configuration of the but-2-ene produced. Equation (3) shows how the addition of the second hydrogen atom is envisaged, the 1-methyl-π-allylic species (V) may be a true intermediate or it may represent a transition state between (IV) and (VI). Thus, *cis*-but-2-ene derives from adsorbed *anti*-1-methyl-π-allyl and *trans*-but-2-ene (VI) from adsorbed *syn*-1-methyl-π-allyl (V) (designations of *syn*- and *anti*-C_4H_7 follow current practice [10]).



(3)

The palladium-catalysed reaction always provided a high proportion of the but-2-ene in the *trans*-configuration (typically, *trans*/*cis* ~10). We suggest that the conformations of adsorbed buta-1,3-diene (I) and (II) do not readily interconvert, and that the conformations of adsorbed-C_4H_7 do not readily interconvert. Thus the relative proportions of *cis*- and *trans*-but-2-ene are similar to the proportions of cissoid and transoid buta-1,3-diene in the gas phase,[11] *i.e.*, 1 : 10 to 1 : 20. The increasing yield of but-2-ene as temperature is increased necessitates that 1 : 4-addition has a higher activation energy than 1 : 2-addition; the additional energy increment may be associated with the transformation of adsorbed-C_4H_7 from the σ-π-di-adsorbed form (IV) to the adsorbed 1-methyl-π-allylic species (V) [see equation (3)].

If 1 : 4-addition of hydrogen to the diene is important at the ruthenium, rhodium, osmium, iridium, and platinum surfaces it does not provide a high *trans* : *cis* ratio in the but-2-ene as was the case over palladium, from which it is concluded that the various conformations of adsorbed diene and/or C_4H_7 may be readily interconvertible.

Interesting correlations exist between the characteristics of buta-1,3-diene hydrogenation and but-1-ene hydroisomerisation. Table 3 shows that, with the exception of palladium and perhaps also iridium, the metals provide similar *trans*-but-2-ene : *cis*-but-2-ene ratios in both reactions under similar experimental conditions. The isomerisation results were obtained by the present authors, using catalysts from the same stocks.[7,8,12] Secondly, the activities of each of the noble metals for but-1-ene hydroisomerisation increases with increasing temperature, and the yield of but-2-ene obtained from buta-1,3-diene hydrogenation also increased with increasing temperature (see Table 2). These

[10] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

[11] L. B. Smith and J. L. Massingil, *J. Amer. Chem. Soc.*, 1961, **83**, 4301.

[12] P. B. Wells and P. C. Taylor, unpublished work.

TABLE 3

trans-But-2-ene : *cis*-but-2-ene ratios (t/c) observed in but-1-ene hydroisomerisation and buta-1,3-diene hydrogenation under similar conditions. (Ratios measured after 10% removal of hydrocarbon)

Metal	Hydrocarbon	Initial pressures (mm.) P_{hc}	P_{H_2}	Temp.	t/c	Ref.
Ru	But-1-ene	50	50	13°	1·4	7
	Buta-1,3-diene	50	50	13	1·6	
Rh	But-1-ene	50	150	80	1·8	8
	Buta-1,3-diene	50	150	80	1·6	
Pd	But-1-ene	50	50	0	1·4	8
	Buta-1,3-diene	50	150	14	15·0	
Os	But-1-ene	50	50	70	1·1	7
	Buta-1,3-diene	50	50	78	0·9	
Ir	But-1-ene	100	50	40	0·1	12
	Buta-1,3-diene	50	150	40	0·7	
Pt	But-1-ene	60	155	15	1·0—1·5	8
	Buta-1,3-diene	50	200	15	1·1	

correlations suggest that common intermediates are involved in but-2-ene formation in both reactions on all of the metals studied except palladium.

(3) *Dependence of the butene distribution on initial hydrogen pressure.* The independence of the butene distribution on initial hydrogen pressure obtained by using ruthenium, rhodium, palladium, osmium, and iridium, shows that the routes to each isomer were equally effected by changes in the availability of adsorbed hydrogen. This is understandable where the butenes are formed by 1 : 4-addition of hydrogen to the diene, as is the case with palladium, and thus this route to but-2-ene may be important at Ru, Rh, Os, and Ir surfaces. An increase in the yield of but-2-ene was observed as the initial hydrogen pressure was increased when using platinum and this is consistent with the operation of a butyl reversal mechanism. However, the magnitude of the effect was small, suggesting that the contribution of olefin isomerisation to the formation of but-2-ene was also small. Thus, the results obtained by varying this parameter support 1 : 4-addition as an important route to but-2-ene.

(4) *Dependence of butene distribution on conversion.* A variety of effects was observed. The butene distribution obtained by using palladium moved slowly towards equilibrium throughout the first stage of the reaction, but this change in distribution was not accompanied by butane formation. Therefore we infer that butyl reversal was not responsible for the change in the distribution, but that interconversion of diene conformations (I) and (II) or of the C_4H_7 conformations or of both together became increasingly easy as the reaction proceeded.

When ruthenium, osmium, and iridium were used the olefin composition again changed slowly throughout the first stage of the reaction when $(P_{H_2})_0/(P_{C_4H_6})_0 \geqslant 2$, but this behaviour was accompanied by a gradual decrease in the selectivity. These observations are consistent with there being a continually increasing chance that olefins undergo hydrogenation to adsorbed-C_4H_9 as the reaction proceeds; the butyl group may then give n-butane by hydrogenation or butene by hydrogen atom explusion.

Over platinum (at 16°) and rhodium the butene distribution was initially independent of conversion, but became dependent during the first stage of the reaction, whereas the selectivity decreased slowly throughout the first stage. Thus, under these conditions only a small degree of butene isomerisation accompanies the formation of n-butane.

During the second stage of the reaction (*i.e.*, after 80—100% removal of diene) butene re-adsorption and hydrogenation took place; this was accompanied by rapid isomerisation over palladium, rhodium, and platinum (at 104°) which are efficient isomerisation catalysts, but little isomerisation occurred using platinum at 16° and iridium which are poor isomerisation catalysts. The second stage was not examined with ruthenium and osmium.

Summary. It appears certain that 1 : 2-addition of hydrogen to diene is responsible for but-1-ene production on all metals and that 1 : 4-addition is responsible for but-2-ene production on palladium. The mechanism of but-2-ene formation using the other noble metals is less clear; the formation of n-butane implies that olefin isomerisation may occur, whereas the insensitivity of the butene distribution to hydrogen pressure suggests that such a secondary process requiring initiation by hydrogen is relatively unimportant and that all three butenes are produced mostly by the direct hydrogenation of buta-1,3-diene to butene.

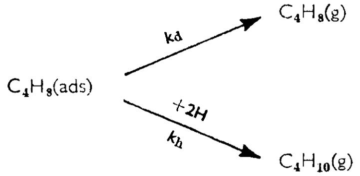
Comparisons with Previous Work.—The initial butene distributions and selectivities obtained by using palladium and platinum in the present work are compared with results from other studies in Table 4. Strict comparisons of one study with another cannot be made because of differences of phase and effective hydrogen pressure at the various catalyst surfaces. However, all reports agree that the *trans*-but-2-ene : *cis*-but-2-ene ratio obtained from palladium is higher than that from platinum. The relative yields of but-1-ene and but-2-ene are also fairly consistent. It is also agreed that palladium is much more selective for butene formation than platinum.

TABLE 4

Comparison of selectivities and butene distributions in the hydrogenation of buta-1,3-diene in the liquid phase (*L*) and the gas phase (*G*)

Catalyst	Phase	Temp.	Selectivity	But-1-ene (%)	*trans*-But-2-ene (%)	*cis*-But-2-ene (%)	Ref.
Pd-suspension	L	−12°	0·940	49	40	11	5
Pd–$BaSO_4$	L	20	1·000	64	31	5	4
Pd–Al_2O_3	G (flow system)	40	0·999	53	42	5	1
Pd–Al_2O_3	G (static system)	19	1·000	68	29	3	This work
Pt-suspension	L	−12	0·61	72	18	10	5
Pt–Al_2O_3	G (static system)	0	0·50	72	18	10	This work

Initial Selectivities.—The sequence $1{\cdot}00 = S_{\text{Pd}} > S_{\text{Ru}} \sim S_{\text{Rh}} > S_{\text{Pt}} > S_{\text{Os}} > S_{\text{Ir}}$ is always obtained under comparable experimental conditions. This pattern of behaviour is the same as that reported for the hydrogenation of acetylene, allene, and other di-unsaturated hydrocarbons.[13,14] Consider equation (4) where k_{d} and k_{h} are rate constants for butene desorption and overall hydrogenation, respectively. Studies of the reaction of butenes with deuterium and of butene hydroisomerisation, using catalysts from the same stock,[7,8] provide approximate values of (desorption rate)/(hydrogenation rate) for these reactions. At a given temperature and hydrogen pressure the value of this ratio decreases in the sequence Pd > Ru > Os > Ir ~ Pt. Pd is a more efficient olefin isomerisation and exchange catalyst than Rh at room temperature but the reverse is the case above about 80°. Extreme values of this ratio at 20°, for example, are ~2 for palladium and <0·05 for iridium and platinum. Thus, if the formation of butene in buta-1,3-diene hydrogenation was determined by this factor alone, the sequence at, say, 20° would be $1{\cdot}00 > S_{\text{Pd}} > S_{\text{RH}} \sim S_{\text{Ru}} > S_{\text{Os}} > S_{\text{Ir}} \sim S_{\text{Pt}} \sim 0{\cdot}0$. However, the presence of diene has two effects which are both thermodynamic in origin. First, the diene has a higher free energy of adsorption than the butenes and thereby tends to displace them from the surface. Secondly, strong adsorption of diene, relative to mono-olefin, causes the hydrogen surface



(4)

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[13] G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom, *J. Catalysis*, **1962**, **1**, 74.

[14] P. B. Wells, *Platinum Metals Review*, **1963**, **7**, 18.

coverage to be lower during buta-1,3-diene hydrogenation than during butene hydrogenation and hence butene desorption is again favoured relative to butane formation in the former reaction. The combined magnitude of these effects clearly varies from metal to metal; it is considerable for palladium, where the hydrogenation rate is initially depressed to zero, and for platinum where selectivities in the region of 0·7 were recorded at 20°, but it is less marked in the cases of the other metals.

Variations of Selectivity with Experimental Variables.—The initial selectivities afforded by all metals except palladium decreased with increasing initial hydrogen pressure (see Figure 3) and the extrapolated values, as initial hydrogen pressure approaches zero, are $(S_{\text{Pd}})_0 = 1{\cdot}00$ at 18°; $(S_{\text{Ru}})_0 = 0{\cdot}97$ at 13°; $(S_{\text{Rh}})_0 = 0{\cdot}90$ at 18°; $(S_{\text{Os}})_0 = 0{\cdot}82$ at 70°; $(S_{\text{Pt}})_0 = 0{\cdot}80$ at 15°; and $(S_{\text{Ir}})_0 = 0{\cdot}20$ at $-20°$. Since $k_{\text{h}}/k_{\text{d}} = (1\text{-}S_0)/S_0$, it follows that, at these temperatures, the values of $k_{\text{h}}/k_{\text{d}}$ were: Pd, 0·00; Ru, 0·03; Rh, 0·11; Os, 0·22; Pt, 0·25; and Ir, 4·00. The decrease in selectivity as the initial hydrogen pressure was increased is simply attributed to an increase in the rate of butene hydrogenation relative to the rate of butene desorption as the availability of adsorbed hydrogen is increased. Selectivities observed during the first stage of reaction are similarly interpreted. When initially $P_{\text{H}_2}/P_{\text{C}_4\text{H}_6} \geqslant 2$ (see Figure 2) the instantaneous value of this ratio increased continuously as the progressed reaction and the selectivity afforded by ruthenium, rhodium, osmium, and iridium fell because increasing hydrogen availability favoured n-butane formation at the expense of butene desorption. No variation of selectivity with conversion was observed when $P_{\text{H}_2}/P_{\text{C}_4\text{H}_6}$ was initially unity; this is expected since the instantaneous value of the pressure ratio remained constant (Pd) or diminished during reaction (other metals) and under these conditions the hydrogen availability is expected to remain fairly constant. Over all metals under conditions shown in Figure 2, competition of butene for the surface became appreciable when about 100% (Ru) or 80% (other metals) of the buta-1,3-diene had been removed, and with the subsequent onset of butene hydrogenation the selectivity dropped to zero.

The increase in selectivity observed as the temperature was increased (see Table 2) may indicate that the activation energy for butene desorption was greater than that for its hydrogenation. Alternatively, the availability of adsorbed hydrogen may have decreased as the temperature was raised.

Note on Metallic Structure.—Although the crystal structure of ruthenium and osmium (close-packed hexagonal) differs from that of rhodium, palladium, iridium, and platinum (face-centred cubic), there is no evidence from our results to suggest that a geometric factor was operative in determining reaction characteristics.

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