# Nature and Reactivity of Intermediates in Hydrogenation of Buta-1,3-Diene Catalyzed by Cobalt and Palladium-Gold Alloys

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The gas-phase hydrogenation of buta-1,3-diene has been studied in a static system using aluminasupported cobalt, a series of cobalt powders, and pumice-supported palladium-gold alloys as catalysts. But-1-ene and but-2-enes, which were formed by 1,2- and 1,4-addition of hydrogen respectively to adsorbed diene, were initial products under all conditions, and yields of n-butane were either very low or zero. The distributions of butenes were very dependent on the physical nature of the cobalt catalysts. Well-sintered metal, consisting of large particles, gave selective formation of trans-but-2ene, whereas, cobalt prepared in a finely divided state at lower temperatures was more active per unit surface area, but gave high yields of but-1-ene and much lower trans to cis ratios in the but-2-enes. These variations are attributed to differences in the catalytic properties of different crystal faces and the change in reaction mechanism is believed to be mainly due to a change in the ease of formation and stability of 1-methyl- $\pi$ -allyl intermediates.

Stable  $\pi$ -allylic complexes are formed readily on the surface of palladium and various amounts of gold in the alloys have a small effect on the mechanism of buta-1,3-diene hydrogenation. The but-1-ene yields and activation energies exhibited sharp maxima which coincided in the 60-75 % gold range and an explanation in terms of variations in the nature of the palladium *d*-orbitals is attempted. The temperature dependencies of the product distributions were influenced between 80 and 130°C by the  $\beta$ - to  $\alpha$ -phase change of the hydrides of palladium and palladium-rich alloys and the effect is discussed.

The concept that the chemisorption bond may, in appropriate cases, have  $\pi$ character has been introduced in recent years to interpret several features of hydrocarbon reactions with hydrogen or deuterium on transition metal catalysts. The major distinction between this and previous theories is that multi-centred bonding between hydrocarbon species and individual metal atoms in the surface is considered. Thus, reactions such as dehydrogenation and hydrogenation of paraffins, olefins, diolefins, acetylenes, aromatic hydrocarbons, etc., may occur by the interconversion of a variety of  $\sigma$ - and  $\pi$ -bonded complexes.<sup>1-4</sup> The  $\pi$ -complexes may include both the metal-olefin and metal-arene types.

Besides providing mechanistic insights, this theory leads to important general conclusions about surface reactions. First, catalytic activity and selectivity are considered to be functions of the chemical properties of individual surface atoms rather than functions of the bulk properties of the metals. Secondly, there may be a correlation between metal-adsorbate bonding on the one hand, and metal-ligand bonding in organometallic compounds on the other; a preliminary attempt at such a correlation has shown some success.<sup>4</sup> Thirdly, the role of the geometric factor in catalysis is given a new significance. Because of metal-metal bonding the arrangement and number of atoms which are nearest neighbours to a given surface atom influence the energy levels and electron occupation of the valency-shell atomic orbitals of the latter, and thus its bonding properties, as well as determining the number of coordinating positions available for the intermediates in a catalytic reaction. A view,

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previously held, that metal-metal spacings and thus the type of crystal face exposed play a vital role because only some of these match the geometrical requirements for multiple  $\sigma$ -bonding of adsorbates may be of limited validity.

The present theory also proposes that interpretation of catalytic behaviour must ultimately take into account, as does co-ordination chemistry, fundamental electronic properties which influence the nature and strength of metal-ligand bonds. These properties include, among others, the number of electrons in the valency shell of the isolated atom, the effective nuclear charge,  $d \rightarrow s$  and  $d \rightarrow p$  promotion energies and ionization potentials. Such properties distinguish the co-ordination chemistry, and possibly to some extent, the catalytic behaviour of one metal from that of another.

Progress in heterogeneous catalysis is limited by uncertainties concerning the nature of metal-metal bonds in solids and by ignorance of the precise arrangements of atoms which constitute active centres in catalysts. Therefore, a fruitful approach in this field at the present time may be one in which comparisons are made of the formation, stability and reactivity of the same ligands in organometallic complexes and in homogeneously and heterogeneously catalyzed reactions, the comparisons being made for as wide a range of metals as possible. By using co-ordination chemistry as a guide, a clearer picture of some of the fundamental factors governing heterogeneous reactions should emerge.

The hydrogenation of buta-1,3-diene (subsequently referred to as butadiene) is a particularly suitable reaction to test the validity of this approach. This is the simplest conjugated diene and it has been used to prepare a variety of organometallic compounds which exhibit several types of  $\sigma$ - and  $\pi$ -bonds. Furthermore, something is already known of the properties of all the group 8 metals as catalysts for the heterogeneous hydrogenation of this compound,<sup>5</sup> and homogeneous hydrogenation of butadiene and other dienes, catalyzed by some transition metal complexes is being studied by several workers.<sup>6</sup>, <sup>7</sup>

There are several reports of the liquid phase hydrogenation of butadiene,<sup>8-11</sup> with nickel, palladium and platinum as catalysts and ethanol as solvent, but only one report <sup>11</sup> contained a discussion of mechanism which was based on an ionic model.

In 1963, Meyer and Burwell reported details of the gas-phase reaction of butadiene with deuterium using a palladium-alumina catalyst. This was followed by a more detailed study by Bond, Wells *et al.*<sup>4, 5, 13-15</sup> of the catalytic activities of each of the group 8 metals and copper for the gas-phase reaction of butadiene with hydrogen; deuterium was also used when examining cobalt, nickel, copper, palladium and platinum.<sup>14, 15</sup>

Iron, cobalt, nickel, copper and palladium are the only metals which selectively hydrogenate butadiene to butenes.<sup>5, 14</sup> The yield of n-butane in the initial products is zero for iron, cobalt and copper, 0-3 % for nickel and palladium, and considerable for all the other group 8 metals.<sup>4, 5, 13</sup> The butene distributions obtained by selective hydrogenation are far removed from the thermodynamic equilibrium compositions and they remain constant, or nearly so, until the near removal of butadiene. They are also independent of the initial hydrogen pressure. These features suggest that butene desorption occurs in preference to isomerization, i.e., the butenes are formed entirely by 1,2- and 1,4-addition of hydrogen, a conclusion which is supported by isotopic studies. The reaction of butadiene with deuterium using cobalt, nickel and copper,<sup>15</sup> and palladium <sup>14</sup> has revealed a close similarity in the deuterium contents and distributions in each of the three n-butenes.

Some typical butene distributions for alumina-supported cobalt, nickel, copper and palladium catalysts are given in table 1, which shows two important features. First, the importance of 1,4-addition varies widely (from 15 % over copper to 70 % over cobalt), and secondly, the trans/cis ratio in the but-2-enes is much higher for cobalt and palladium (>equilibrium) than for nickel and copper (<equilibrium).

In the adsorbed state a butadiene molecule must take up one of two possible conformations.



Conformational interconversion may or may not occur and the same is true of the half-hydrogenated state, i.e., adsorbed  $C_4H_7$  species. For butadiene molecules in the gas phase, rotation about the central carbon-carbon bond occurs but is hindered by steric repulsion of the vinyl groups in conformation II. Smith and Massingill <sup>16</sup> have estimated the ratio I: II to be 95:5 approximately at ambient temperatures. Thus, at the instant that adsorption occurs the population of I is expected to exceed that of II on the surface.

TABLE 1.—TYPICAL INITIAL BUTENE DISTRIBUTIONS OBTAINED FROM BUTADIENE HYDROGENATION IN A STATIC SYSTEM USING ALUMINA-SUPPORTED COBALT, NICKEL, COPPER AND PALLADIUM CATALYSTS

Initial butadiene pressure = 50 mm; initial hydrogen pressure = 150 mm; initial butane yield = zero.

metal	temp. (°C)	B-1	butene composition (%) t-B-2	ition (%) c-B-2	
Co	125	29	65	6	
Ni	77	49	34	17	
Cu	100	85	6	9	
Pd	21	60.2	37.0	2.8	
Pd	18	68.4	30.1	1.7	

Co and Ni reduced at 400° and 250° respectively.

When 1,4- addition produces a high yield of trans-but-2-ene compared to cis-but-2ene we propose that the nature of chemisorption is such that (i) the conformations of adsorbed  $C_4H_7$  do not interconvert and (ii) for adsorbed diene either the conformations are non-interconvertible, or they interconvert but maintain an equilibrium similar to that which is operative in the gas phase. The notation for the adsorbed species is shown in fig. 1. Table 1 shows some results for palladium, obtained by



FIG. 1.—Notation suggested for the adsorbed species in butadiene hydrogenation when conformational interconversion of the half-hydrogenated state does not occur.

Leszczynski and Wells where trans/cis ratios in the but-2-enes approach closely the value of 19, which would signify virtually complete non-interconvertibility of the conformations on this metal at room temperature.

At the other extreme a trans/cis ratio of about unity signifies that conformational interconversion of adsorbed  $C_4H_7$  and perhaps  $C_4H_6$  occurs readily. The mechanism shown in fig. 2 allows this possibility to the extent that the key  $\sigma$ -bonded  $C_4H_7$  species,  $CH_3$ —CH—CH= $CH_2$ , is formed during reaction. The two 1-methyl- $\pi$ -allyl com-

plexes are believed to be less stable in this case and are either true intermediates or represent a more transient state attained by  $C_4H_7$  species before the addition of the second hydrogen atom.



FIG. 2.—Notation suggested for the adsorbed species in butadiene hydrogenation when conformational interconversion of the half-hydrogenated state occurs.

Two points are noted. Addition of the first hydrogen atom to adsorbed butadiene is believed to occur exclusively at a terminal carbon atom in agreement with the general behaviour of this compound in addition reactions. Secondly, for those butenyl species other than  $\pi$ -allylic complexes, addition of the second hydrogen atom takes place to the carbon atom which is  $\sigma$ -bonded to the surface. It follows that if 1-methyl- $\pi$ -allylic complexes are not formed during hydrogenation only 1,2-addition of hydrogen can occur.

Comparisons of fig. 1 and 2 with table 1 suggest strongly that  $\pi$ -allylic complexes are formed readily on cobalt and palladium surfaces but not on those of nickel and copper. This concurs with the organometallic properties of these metals <sup>17</sup> and with the previous finding that palladium has outstanding ability to form  $\pi$ -allylic complexes during the catalyzed exchange of cycloalkanes with deuterium.<sup>1, 2</sup> Our contention is therefore that the compositions of the product butenes yield information about the mode of chemisorption of their precursors.

We have successfully modified cobalt and palladium catalysts in that their stereoselectivity for the formation of trans-but-2-ene has been diminished. Modification has been achieved (i) by varying the conditions of preparation of the cobalt catalysts and (ii) by alloying palladium with gold. These features and other accompanying features are discussed in terms of the mechanisms described above.

# EXPERIMENTAL

#### CATALYSTS

A stock of alumina-supported cobalt catalysts containing 10 % (wt/wt) metal was prepared by depositing the required amount of A.R. cobalt nitrate by evaporation of an aqueous solution in which the support (Peter Spence type A alumina) was immersed. The dry material was then calcined, followed by reduction of metal oxide under 300 mm of hydrogen in a static system at 329°C. The hydrogen was changed after 6 h and the reduction continued for a further 14 h. Samples from the stock were reduced again at 200°C under 100 mm of hydrogen for 2 h before being used.

Cobalt powder P1 was prepared by the reduction of an aqueous solution of cobalt sulphate

by hypophosporous acid. The procedure, developed by Holbrook and Marsh,<sup>18</sup> consisted of adding hypophosphorous acid to the metal ions in a boric acid+sodium hydroxide buffer solution at pH 9.0. Hydrogen was evolved after heating to 90°C for 20 min and a black precipitate of cobalt deposited. Spectrophotometric analysis showed a phosporus content of 2 %.

Cobalt powders  $P_2$ - $P_8$  were prepared by reduction of grey cobalt oxide (B.D.H. Ltd.) in a stream of hydrogen for 24 h at elevated temperatures. X-ray powder photographs were obtained for all the powders, surface areas of  $P_2$ ,  $P_4$  and  $P_8$  were measured by the B.E.T. method, and  $P_2$  and  $P_8$  were examined by electron microscopy.

Stocks of pumice-supported palladium, gold, and palladium-gold alloys were prepared by deposition of palladium and gold chlorides (Johnson, Matthey and Co. Ltd.) from acid solution on 18-30 B.S.S. mesh pumice (Hopkin and Williams Ltd.). After evaporation to dryness, the salts were reduced to metal in a stream of hydrogen for 24 h at room temperature, then at 200°C for 2 h, followed by further reduction for 3 h under 100 mm of hydrogen at 300°C in a static system. Finally, the preparations were heated *in vacuo* for 3 h at 450°C. Samples from the stock were reduced again at 200°C under 100 mm of hydrogen for 2 h before being used. These catalysts contained 5 % (wt/wt) metal.

#### APPARATUS, MATERIALS AND EXPERIMENTAL METHODS

The apparatus consisted of a conventional high vacuum system. Each catalyst sample rested on the bottom of a cylindrical 100 ml Pyrex reaction vessel and pressure changes during reaction were measured manometrically.

Butadiene (Distillers Company Ltd.) contained no detectable impurities either by G.L.C. or mass-spectrometric analysis.

Hydrogen was purified by passage over a Pt-silica catalyst at  $300^{\circ}$ C and then dried, or by diffusion through a palladium thimble.

Gas samples withdrawn from the reaction vessel were analyzed using a G.L.C. unit containing a 25 ft column of 40 % (wt/wt) hexane-2,5-dione supported on 30-60 B.S.S. mesh firebrick. The column was operated at room temperature with nitrogen as carrier gas, and the detector was a katharometer.

Mass-spectrometric analyses were obtained using a modified A.E.I. M.S.3 spectrometer, with an electron beam energy of 12.0 eV.

#### RESULTS

#### COBALT CATALYSTS

The distributions of isomeric n-butenes obtained from butadiene hydrogenation were dependent on the previous temperature treatment of the catalyst. For example, when cobalt-alumina was prepared by reduction of the supported oxide by deuterium at 329°C, subsequent hydrogenation of diene at 144°C gave but-1-ene as the most abundant isomer, whereas, a catalyst sample which had received further treatment at 414°C under 200 mm deuterium for 20 h, gave trans-but-2-ene as the major product. The following results are typical (reaction temp. = 144°C; initial  $P_{D_2}/P_{C_4H_6} = 2/1$ ; analyses after 20 % removal of diene).

	reduction temp. (°C)	products (%)					
		B-1	t-B_2	c-B_2	n-butane		
reaction A	329	51	31	17	1		
reaction B	414	28	56	16	0		

The yields of cis-but-2-ene and n-butane were only slightly influenced by the more drastic treatment. Both types of butene distribution were independent of conversion up to 60 % removal of butadiene. In reaction A the average number of deuterium atoms present in each butene was  $2.00 \pm 0.01$ ; it was also observed that the "hydrogen

exchange "reaction  $[D_2+H (ads) \rightarrow HD+D (ads)]$  and the butadiene exchange reaction  $[C_4H_6+D (ads) \rightarrow C_4H_5D+H (ads)]$  occurred at similar rates. In reaction B the average deuterium content of each butene was  $1.39\pm0.01$  but here the rate of butadiene exchange exceeded the rate of "hydrogen" exchange.

Orders of reaction measured before and after the treatment at 414°C were similar, being zero or slightly negative in butadiene and 1.0-1.5 in hydrogen. Apparent activation energies were  $12.2 \pm 1.2$  kcal mole<sup>-1</sup> (94-153°C) and  $8.9 \pm 1.0$  kcal mole<sup>-1</sup> (100-187°C) before and after this treatment respectively.

These results suggest either that a change in the physical structure of the cobalt particles accompanied the treatment at 414°C or that a change in the support had occurred which altered the properties of the metal. To decide between these alternatives the catalytic activity of unsupported cobalt, in powder form, was investigated as a function of preparation temperature.



FIG. 3.—Butene distributions and selectivities ( $S = C_4H_8/(C_4H_8+C_4H_{10})$ ) for the hydrogenation of butadiene at 110°C over a series of cobalt powders P<sub>1</sub>-P<sub>8</sub>, prepared at various reduction temperatures. Initial butadiene pressure = 50 mm; initial hydrogen pressure = 100 mm; analyses after  $12\pm1$  % removal of butadiene.

S,  $\bigcirc$ ; but-1-ene,  $\bigcirc$ ; trans-but-2-ene,  $\triangle$ ; cis-but-2-ene,  $\Box$ .

The effect of reduction temperature on the physical characteristics of a series of cobalt powders is shown in table 2 and in plate 1, the products obtained from butadiene hydrogenation at 110°C are shown in fig. 3. The powders produced at lower temperatures were also more active per unit weight or per unit surface area than those produced at higher temperatures.

Powders  $P_1$ - $P_3$ , which catalyzed the preferential formation of but-1-ene (type A behaviour), had relatively high surface areas and consisted of small particles of metal which were mostly or completely in the  $\alpha$ -phase (c.p.h.); micrograph (a) in plate 1 shows the presence of large numbers of particles below 50 Å in size.

Powders  $P_5$ - $P_8$ , which catalyzed the preferential formation of trans-but-2-ene (type B behaviour), were sintered; their surface areas were relatively low and electron micrographs revealed an almost complete absence of small particles (micrograph (b) is typical). The metal was mostly or completely in the  $\beta$ -phase (f.c.c.). Powder  $P_4$ ,



(a)



PLATE 1.—Typical electron micrographs of the edges of cobalt particle clusters: (a) powder P2 prepared at 298°C; (b) powder P8 prepared at 580°C; width of micrographs =  $0.75 \ \mu$ .

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reduced at intermediate temperatures, exhibited intermediate physical characteristics and catalytic behaviour. Fig. 3 shows, as for cobalt-alumina, that the yields of cisbut-2-ene and n-butane are not greatly influenced by the reduction temperature.

Behaviour similar to that shown in fig. 3 has also been observed using nickel powders where there is no change of phase as the reduction temperature is increased.

# TABLE 2.—PHYSICAL CHARACTERISTICS OF COBALT POWDERS

	P1	$\mathbf{P_2}$	$\mathbf{P}_3$	P4	$P_5$	$P_6$	$\mathbf{P}_7$	$P_8$
reduction temperature (°C)	97	298	324	415	443	467	514	580
weight used (g)	0.263	0.034	0.021	<b>0</b> ·183	0.202	0.176	0·277	0.303
surface area $(m^2 g^{-1})$		14•4		4·8				0.9
phase of cobalt	pure $\alpha$	pure $\alpha$	pure *α	mixture	β	β	pure $\beta$	pure $\beta$
				α+β (	$(trace \alpha)$	(trace	x)	

\* some cobalt oxide present.

# PALLADIUM-GOLD ALLOYS

The initial mixture of reactants used throughout this work consisted of 100 mm of hydrogen and 50 mm of butadiene unless otherwise stated. Although freshly prepared catalysts were highly active they were somewhat unstable but after about 5 runs at room temperature the rate of reaction had declined to a steady value and the product distributions became reproducible and virtually independent of conversion up to some 80 % removal of butadiene. The selectivity for butene formation was very high on all the catalysts and only decreased slightly with conversion. Some butene distributions and selectivity values for low and high conversions on three catalysts of widely different gold content are given in table 3.

TABLE 3.—DEPENDENCE OF BUTENE DISTRIBUTIONS AND SELECTIVES ON CONVERSION ON PALLADIUM-GOLD ALLOYS

temp.	Pd	conversion	butenes (%)					
(°C)	(%)	(%)	B-1	t-B-2	c-B-2	S		
19	100	22.4	<b>48</b> ·1	47.5	4∙4	1.000		
19	100	76.4	48.8	46.2	5.3	0.967		
20	50	17.9	47.6	46.9	6.3	1.000		
20	50	85.8	<b>4</b> 8·1	44.9	7.0	0.981		
19	25	20.5	49.4	43.5	7.2	0·991		
19	25	74·0	<b>49</b> ∙0	43-3	7.6	0.989		

Orders of reaction were determined from initial rates, the initial pressure of one reactant being held constant at 50 mm while the pressure of the other was varied between 50 and 200 mm. Orders in hydrogen were between 0.7 and 0.9 while the order in butadiene was zero in all cases. During these estimations of order in hydrogen the products were analyzed at 50 % conversion and found to be virtually independent of hydrogen pressure.

Activation energies were evaluated from initial rates in the range 0-88°C but, because of its low activity, the value for the 95 % gold alloy (all compositions are expressed as atomic percentages) was obtained for a slightly higher, though overlapping temperature range. A 100 % gold catalyst was almost completely inactive at 200°C. The activation energies and corresponding initial yields of but-1-ene in the total butenes are given in table 4.

While the activation energies did not vary within experimental error between 0 and 60 % gold a sharp increase of  $\sim 4.5$  kcal mole<sup>-1</sup> was noted when the gold content

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reached 65 %. At 70 % gold the value was still high but on increasing to 75 % a sharp drop of  $\sim 5.0$  kcal mole<sup>-1</sup> was found and the lowest activation energy was that for the 95 % alloy. A corresponding maximum in the yields of but-1-ene was also observed in the 60-70 % gold range.

TABLE 4.	Orders of reaction	ON, ACTIVATION E	NERGIES, AND BUT-1-	ENE YIELDS
	AT ROOM TEMPERA	TURE FOR PALLA	DIUM-GOLD ALLOYS	
Pd (%)	order (H <sub>2</sub> )	order (C <sub>4</sub> H <sub>6</sub> )	E (kcal mole <sup>-1</sup> )	B-1 (%)
100	0.9	0.0	10.5	48.5
80	0.8	0.0	10.2	55.0
50	0.9	0.0	11.0	50.0
40			10.3	59.5
35	0.9	0.0	14.9	61·0
30			14.6	60·0
25	0.7	-0.1	9.4	50.0
5	0.7	0.0	8.9	51.0

The temperature dependencies of the product distributions were then examined by analyzing reaction mixtures after 50 % conversion at several temperatures between 18 and 200°C. Yields of the individual butenes are plotted against temperature for three catalysts in fig. 4. The major effect of increasing the reaction temperature,



FIG. 4.—Temperature dependence of butene distributions in the hydrogenation of butadiene on palladium-gold alloys.

0 % gold, A; 65 % gold, B; 75 % gold, C. but-1-ene,  $\bigcirc$ ; trans-but-2-ene,  $\oplus$ ; cis-but-2-ene,  $\Box$ .

using pure palladium, was an increase in the yield of cis-but-2-ene at the expense of the trans-isomer, while the yield of but-1-ene remained almost constant. A feature of these results was the sharp dip through a minimum and corresponding rise through a maximum in the yields of but-1-ene and trans-but-2-ene respectively between 100 and 130°C. Similar results were also obtained with the alloys but as the gold content increased the dip and rise in the yields of but-1-ene and trans-but-2-ene became less

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sharply defined and broadened over a much wider temperature range. The minimum and maximum in the appropriate curves also shifted to slightly lower temperatures, especially with alloys of higher gold content. The only alloy which did not exhibit these features was that containing 95 % gold where the yields of but-1-ene and cis-but-2-ene fell and rose in a linear fashion respectively, while the yield of trans-but-2-ene remained virtually constant, as the temperature was raised. Yields of cis-but-2-ene often rose more steeply in the same temperature range where the dip and rise in the percentages of the other isomers occurred than at higher or lower temperatures. The yields of but-1-ene were also about 10 % higher over the whole temperature range for the 60-70 % gold alloys than for those of higher or lower gold content.

Maxima in the yields of n-butane were also found between 90 and  $130^{\circ}$ C and these are shown for some of the catalysts in fig. 5. While the maximum was highest for 100 % palladium it decreased steadily and broadened as the gold content increased until it was barely perceptable, within experimental error, at 75 % gold.



FIG. 5.—Temperature dependence of n-butane yields in the hydrogenation of butadiene on palladiumgold alloys.

0 % gold,  $\bigcirc$ ; 20 % gold,  $\triangle$ ; 50 % gold,  $\bigcirc$ ; 65 % gold,  $\square$ .

Isothermal plots of the ratios of trans-but-2-ene to cis-but-2-ene as a function of alloy composition are shown in fig. 6. An increase in gold content at a fixed temperature resulted in a continuous decline in this ratio over the whole range of composition. When the temperature was raised at a given composition there was also a decrease in the ratios, the effect being most marked for 100 % palladium, and becoming less as the alloys became richer in gold.

We believe that the peculiar changes in product yields in the temperature range 80 to 130°C might be associated with the  $\beta$ - to  $\alpha$ -phase change in palladium and palladium-gold hydrides so hydrogen solubility in these catalysts was briefly studied. A weighed quantity of each catalyst (~2.5 g) was maintained at 200°C in 150 mm of hydrogen for 2 h, cooled at room temperature, and allowed to equilibrate with fresh hydrogen at a pressure of 75 mm. The temperature was then raised by 1°C every 2-3 min and the pressures recorded up to 160°C; the sample was then cooled at the same rate and again the pressures noted. Since the system was effectively one of constant volume these pressures, when corrected to s.t.p., were a measure of the hydrogen evolved or absorbed by the catalysts. A slight evolution of hydrogen from 100 % palladium, 0.016 atoms per palladium atom, was found up to 89°C, but at this temperature rapid evolution commenced and finally ceased at 109°C; the total hydrogen

evolved in this range was 0.38 atoms per palladium atom. The alloys behaved similarly with slow evolution of a comparable quantity of hydrogen, but in the critical temperature range the amount of hydrogen released decreased continuously with increasing gold content and at 70 % gold or more evolution could not be detected. The temperature range for rapid evolution of hydrogen from the alloys was between 72 and 97°C and therefore slightly below that for 100 % palladium. The usual hysteresis effect in the evolution and absorption of hydrogen by palladium and the alloys was also observed.



FIG. 6.—Dependence of isothermal ratios of trans-but-2-ene to cis-but-2-ene on composition in the hydrogenation of butadiene on palladium-gold alloys. 40°C, ○; 80°C, △; 100°C, ●; 160°C, □.

#### DISCUSSION

# COBALT CATALYSTS

Cobalt-alumina reduced at 414°C behaved exactly as reported previously.<sup>15</sup> The present results again show that butenes are formed on this catalyst solely by 1,2and 1,4- addition of hydrogen to butadiene and that the syn- and anti- conformations of the C<sub>4</sub>H<sub>7</sub> intermediates do not interconvert. However, the product distributions obtained using cobalt-alumina reduced at 329°C are similar to those obtained using nickel-alumina <sup>15</sup> (table 1) and we conclude that although the same modes of hydrogen addition are operative conformational interconversion of the C<sub>4</sub>H<sub>7</sub> intermediates occurs readily. These conclusions are supported by two further observations (i) that the kinetics before and after the treatment at 414°C are similar and (ii) that each butene from reaction A had the same deuterium content (D.N. = 2.00), as did each butene from reaction B (D.N. = 1.39). Had the but-2-enes produced in either reaction been formed in two stages, i.e., by the primary formation of but-1-ene followed by its isomerization to but-2-ene before desorption, the deuterium number of the but-2-enes would have differed from that of but-1-ene. Powdered cobalt prepared at temperatures in the range 90-330°C behaved like cobalt-alumina prepared at 329°C (type A behaviour in fig. 3), whereas, powders prepared at temperatures in the range 440-580°C behaved like cobalt-alumina prepared at 414°C (type B behaviour in fig. 3). Thus conformational interconversion of the C<sub>4</sub>H<sub>7</sub> intermediates occurs readily on powders P<sub>1</sub>-P<sub>3</sub> which were mostly or completely  $\alpha$ -cobalt in a finely divided state (micrograph (*a*)). On the other hand, conformational interconversion did not take place readily at the surfaces of powders P<sub>5</sub>-P<sub>8</sub> which were mostly or completely  $\beta$ -cobalt in a sintered state of relatively low surface area (table 2 and micrograph (*b*)).

The change of mechanism provided a change in product distributions that is in the sense expected. According to the mechanism in fig. 1, the predominant  $C_4H_7$ intermediate is syn-1-methyl- $\pi$ -allyl which on addition of a hydrogen atom gives but-1ene and trans-but-2-ene, although the latter will be somewhat favoured if the methyl group sterically hinders hydrogen addition. However, if  $\pi$ -allylic complexes are not formed readily, as provided by the mechanism in fig. 2, addition of hydrogen to  $C_4H_7$ intermediates is expected to give mainly but-1-ene. Consequently, a gross change in the butene distributions as the mode of chemisorption changes is both expected and observed.

The present results (fig. 3) also closely resemble those which have been obtained from the homogeneous hydrogenation of butadiene by pentacyano-cobalt catalysts.<sup>6</sup> Here but-1-ene amounted to 80 % of the total butenes when the CN/Co ratio was high but as this ratio decreased below a critical value of ~6 trans-but-2-ene became the predominant product. Yields of cis-but-2-ene were also low in all cases and independent of variations in the nature of the catalyst. The mechanisms suggested for these homogeneous hydrogenations <sup>19</sup> have also many features in common with those which we have postulated.

The change from type A to type B behaviour (fig. 3) is not a consequence of the  $\alpha$ - to  $\beta$ -phase change in cobalt because a similar change in catalytic behaviour has been observed for a series of nickel powders which show no phase change. Thus, the product distribution is apparently a function of the particle size of the metal, i.e.,  $\pi$ -allylic bonded intermediates are more important at the surface of well-sintered cobalt than on cobalt prepared below 330°C. This marked distinction in behaviour may be due to considerable differences in the catalytic properties of different crystal planes, which might also explain why the activities per unit surface area, activation energies, and the results using deuterium also differed widely, as the physical charac-Well-sintered cobalt particles may expose low-index teristics of the metal altered. planes, whereas, the smaller particles formed below 330°C probably expose both high and low-index planes and may also possess a greater number of structural defects. There is therefore the possibility that the type of bonding of the intermediates varies from one plane to that of another and an examination of butadiene hydrogenation at particular planes of single crystals is being undertaken at present to test this.

# PALLADIUM-GOLD ALLOYS

The present results for pure palladium agree well with those previously reported <sup>5</sup>, <sup>12</sup>, <sup>14</sup> and again demonstrate the marked ability of this metal for forming  $\pi$ -allylic complexes in heterogeneous reactions of hydrocarbons. Thus the mechanism of butadiene hydrogenation is mainly that shown in fig. 1 and it is significant that such ready conversion of dienes to  $\pi$ -allylic complexes is also an important feature of the homogeneous organometallic chemistry of palladium.<sup>20</sup>

Since pumice-supported gold was virtually inactive, even at 200°C, the palladium atoms are the active centres in the alloys and the results are a measure of the change

in catalytic properties of this metal with progressive modification by gold. In the region 0-60 % gold there was very little variation in the major features of the product distributions and apart from the 65 and 70 % gold alloys the yields of but-1-ene did not alter significantly over the whole range of composition. Although the trans/cisratio in the but-2-enes decreased at lower temperatures by a factor of ~2 from 0 to 95 % gold (fig. 6) this was due to a relatively minor increase in the yield of cis-but-2-ene at the expense of the trans-isomer. Thus, the relative proportions of 1,2- and 1,4- addition of hydrogen were virtually constant so that the presence of gold has no major effect on the ability of palladium to form  $\pi$ -allylic complexes. The slight decrease in stereoselectivity for trans-but-2-ene formation indicates that the stability of the  $\pi$ -allylic complexes was not greatly diminished by increasing gold content so that the fraction of the C<sub>4</sub>H<sub>7</sub> intermediates which undergo conformational interconversion at room temperature is small. The stereoselectivity also decreases with temperature at a given composition but this could also be partly due to a decrease in the relative proportions of anti- and syn-butadiene in the gas-phase and on the surfaces.

The activation energies (table 4) show several features which are similar to those obtained by Couper and Eley<sup>21</sup> for parahydrogen conversion on palladium-gold alloy wires. Thus, the activation energies for both reactions are independent of gold content up to 60 % and the average value of  $10.5\pm0.5$  kcal mole<sup>-1</sup> for butadiene hydrogenation in this range, obtained under conditions where both palladium and the alloys form the  $\beta$ -phase hydride (see later), is close to the value of ~11 kcal mole<sup>-1</sup> for parahydrogen conversion on a palladium wire, which had been charged with hydrogen. Couper and Eley also noted a sharp increase in activation energy of some 5 kcal mole<sup>-1</sup> as the gold content increased from 60 to 70 % and we have found an increase of the same magnitude from the 60 to 65 % gold alloy. In this region, 60-70 % gold, both the paramagnetism and solubility of hydrogen drop to zero. The major difference between the two investigations is that while the activation energies for parahydrogen conversion remained high for alloys of gold content above 70 %, those for butadiene hydrogenation decreased sharply between the 70 and 75 % alloys. Consequently, the activation energies for butadiene hydrogenation exhibit a peak of some 5 kcal mole<sup>-1</sup> in height in a narrow range of composition.

Couper and Eley suggested that the slow step in parahydrogen conversion is the formation of an activated complex between an adatom of hydrogen and a hydrogen molecule. The above similarities indicate that the slow step in butadiene hydrogenation may also be activation of molecular hydrogen on surfaces which are covered by adsorbed diene, and that the same orbitals of the palladium atoms are responsible in both systems. These authors argued that the increase in activation energy, as the paramagnetism of the alloys decreased to zero at ~60 % gold, showed that *d*-orbital vacancies help to lower the energy of the activated complex. The present results support this view since the maximum in but-1-ene yields, which paralleled the maximum in activation energies in the 60-75 % gold range, reveals that 1,4-addition of hydrogen and thus  $\pi$ -allylic bonding also occurs with maximum difficulty in this composition region. Now  $\pi$ -allylic bonding should occur more readily if the palladium atoms have appropriate  $d\pi$ -orbitals which are not fully occupied and the same orbitals may also participate in activating molecular hydrogen.

The sharp drop in both but-1-ene yields and in activation energies between 70 and 75 % gold (table 4) is interesting because the palladium atoms at the latter composition are apparently behaving like those in the 0-60 % range, in contrast with those of the 65 and 70 % gold alloys, in spite of the fact that the gold-rich alloys are no longer paramagnetic. The simple electronic theory of catalysis based on the presence or absence of holes in the *d*-band is not completely adequate to account for these results

because the theory makes no distinction between palladium and gold atoms when there is 65 % or more of the latter. Also, a strongly adsorbing species such as butadiene may have as much influence on the *d*-orbitals of the surface palladium atoms as neighbouring gold atoms. Although the surface atoms in alloys containing 75 % or more gold may have no *d*-vacancies some of the palladium atoms seem to be sufficiently modified by adsorbed diene to behave in much the same way as atoms in alloys of less than 65 % gold. Apparently chemisorbed hydrogen cannot exert this influence, as the activation energies for parahydrogen conversion remain high in the gold-rich region, which might suggest that donor bonding between  $d\pi$ -orbitals on the metal and empty anti-bonding  $\pi$ -orbitals on butadiene has an important influence.

In order to account for the behaviour of the 65 and 70 % gold alloys we suggest that there may be a tendency towards phase-separation in this narrow range where the composition is given by the formula PdAu<sub>2</sub>, or very close to it. Since gold can behave as a quasi-halogen the palladium atoms may tend to adopt an ordered environment and have essentially the electronic configuration associated with a square-planar arrangement as in PdCl<sub>2</sub>. If this were so the  $d\pi$ -orbitals would be fully occupied and perhaps less readily influenced by adsorbed diene in a direction which would favour easier activation of hydrogen or  $\pi$ -allylic bonding.

The product distributions, especially with palladium and palladium-rich alloys, are apparently influenced by the nature of dissolved hydrogen. Thus the minima in but-1-ene and maxima in trans-but-2-ene yields (fig. 4) and the maxima in n-butane percentages (fig. 5) occurred in the same temperature range where the  $\beta$ - to  $\alpha$ -phase change of palladium and palladium-gold hydrides was found at roughly the same hydrogen pressures used in the hydrogenation experiments. Moreover, the decrease in size of the maximum in n-butane yields with increasing gold content of the alloys paralleled the smooth decrease in the quantity of hydrogen rapidly evolved when the  $\beta$ -phase hydrides became unstable. These changes in product distributions are understood if the surface concentration of hydrogen atoms goes through a maximum in the region where the  $\beta$ - and  $\alpha$ -phase hydrides co-exist. Such an increase in hydrogen concentration would favour the chance of adsorbed butene hydrogenating to but ne via the formation of adsorbed  $C_4H_9$  species before desorption occurred. The surface concentration of butyl groups must also have been at a maximum in the same temperature region so adsorbed butenes would also have the highest chance of isomerizing by the mechanism of alkyl reversal before leaving the surface. However, this may not be the complete explanation because these changes in product distributions were observed over too broad a temperature range with alloys of higher gold content, and were still present with the 75 % alloy, even though rapid evolution of hydrogen was not detected with alloys containing more than 65 % gold.

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# NOTE ADDED IN PROOF

The following are the weights of the pumice-supported palladium-gold alloys required to maintain an initial rate of hydrogenation of butadiene of 2 % per minute at 20°C ( $P_{C_4H_6} = 50 \text{ mm}$ ;  $P_{H_2} = 100 \text{ mm}$ ).

Pd (%)	100	80	50	40	35	30	25	5
weight (g)	0.14	0.8	3.3	3.0	2.0	4.0	2.8	50

If these weights are assumed to be a measure of surface areas the activation energies (table 4) show that the frequency factors for the 35 and 30 % alloys must be larger than those of the 40 and 25 % palladium alloys by a factor of  $\sim 10^3$ .

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