Catalytic hydrogenation in the liquid phase. Part 1. Hydrogenation of isoprene catalysed by palladium, palladium–gold and palladium–silver catalysts

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Abstract

The hydrogenation of isoprene (2-methyl-1,3-butadiene) proceeds at 273 K in EtOH solvent in the presence of Pd catalysts to give the three possible methylbutene isomers with high selectivity ($\geq 98\%$): their proportions, which remain constant until all the isoprene has reacted, are approximately 2-methyl-2-butene, 50%; 3-methyl-1-butene and 2-methyl-1-butene, each 25%. However especially with $Pd/CaCO_3$, $Pd/BaSO_4$ and Pd/C the proportion of the 2-methyl-2-butene is significantly less than 50% and those of the others correspondingly greater; with $Pd–Au/SiO_2$ made by reduction with N_2H_4, the proportion of 2-methyl-2-butene decreases with increasing concentration of the Group 11 element. Monoalkene selectivities are described by a simple reaction model based on two isomeric half-hydrogenated π-allylic radicals; the terminal carbon atoms of the delocalised π-bond carry charges which depend on the number of CH_3-substituents, and the relative chances of adding an H atom at each position, which determine product composition, are affected by the charge on the H atom. Increasing Au or Ag concentration is the bimetallic series increases its negative charge.

Keywords: Hydrogenation; Liquid phase; Isoprene; Palladium; Gold; Silver

1. Introduction

The selective hydrogenation of alkynes and of alkadienes to monoalkenes continues to attract attention by reason both of the practical importance [1] and the theoretical interest of this reaction system. With Rh [2], Pd [3] and Pt [4] catalysts these reactions often exhibit structure-sensitivity, but reviews [5,6] of recent research on the catalytic properties of small metal particles have revealed a number of fundamental questions that still require answers. What, for example, is the origin of particle size effects? How stable is the surface during catalysis [7]? How should one explain the apparent structure *insensitivity* of certain types of reaction? These and many related questions will continue to stimulate research in this field and the questions will be further refined as the knowledge base grows. As an example of this progressive refinement of concepts, we can cite the view [5] that no clear dividing-line should exist between reactions that are structure-sensitive and those that are structure-insensitive: even reactions such as alkene hydrogenation, that are often deemed

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to be in the latter category, show a mild degree of structure-sensitivity [8], and it is therefore preferable, and more in keeping with the spirit of H.S. Taylor's concept of active centres [9], to regard structure-sensitivity as a continuously-variable parameter.

Surface structure is usually altered either by diluting the catalytically active element with another that is inactive, or by altering the mean particle size [5]. The former approach is predicated on the assumption that the addition, say, of Au to Pd would lower the mean size of the Pd ensembles; indeed, such often appears to be the case, and evidence for electronic effects is generally lacking. There are however several complicating factors: (i) the element of lower surface energy will tend to segregate to the surface; but (ii) its distribution may not be random and it may prefer sites of low coordination number [10]; and (iii) these effects may be counteracted by the chemisorptive interaction of the reactants with the active atoms, which will thereby by drawn to the surface [11]. Conceptual difficulties such as these do not however prevent useful practical advantages being obtained from the use of bimetallic catalysts [1,12].

If working with bimetallic catalysts is not without its problems, it is no easier to change the particle size without altering a host of other parameters, especially the extent of metal–support interaction. In any event the correlation between particle size and surface geometry depends on the applicability of structural models,

such as those due to Hartog and Van Hardeveld [13], and the implied assumption that all particles of metal have perfect crystal forms is unlikely to be correct (see however Ref. [14]). The interpretation of the experimental observations deriving from both the use of bimetallic systems and from alteration of particle size is therefore unresolved, and in particular the cause of structure-*insensitivity* has been considered a more challenging question than that of structure-*sensitivity* [5]. Resolution of these issues will require not only the use of more refined techniques for examining supported metals, but also more precise and informative measures of catalytic properties.

The use of turnover frequencies (TOFs) as the basis for discussing correlations between structure and catalytic activity is fraught with difficulties: there is no certain way of estimating the number of active centres, and even evaluating the number of surface atoms by selective gas chemisorption usually involves some guesswork. The concept that reactions capable of exhibiting some selectivity features are more useful and have a greater information content than those for which only a single rate can be measured is a very old one [15]. The reactions of alkynes and alkadienes with H_2, and a fortiori with D_2, provide a wealth of mechanistic information from which principal pathways and adsorbed intermediates can be confidently identified.

With Pd however selectivity to the mono-al-
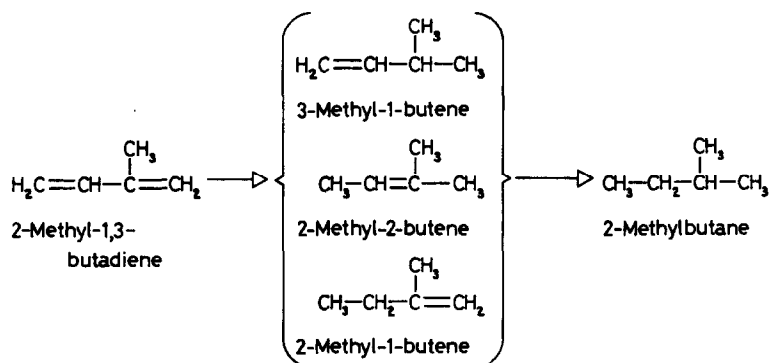
Scheme 1.

kene is invariably high [15], and this is not therefore a useful quantity with which to discriminate between catalysts. Study of the reactions of 1,3-butadiene [2–4,16] has been particularly rewarding because three distinguishable isomeric butenes are formed; on Pd catalysts the half-hydrogenated state comprises two non-interconvertible π-allylic radicals, the proportions of which depend on the conformation of the reactant as it adsorbs [16]. In this paper we examine the liquid-phase hydrogenation of isoprene (2-methyl-1,3-butadiene) which also forms three distinguishable mono-alkenes (see Scheme 1), but although this molecule also can adsorb in two different conformations they react in the same way and give the same products. We have used a number of supported Pd catalysts in order to establish the extent to which particle size and metal–support interactions affect product selectivities, and a number of Pd–Au and Pd–Ag bimetallic catalysts [17] to explore the ensemble size parameter (with the reservations mentioned above).

2. Experimental

2.1. Preparation and characterisation of catalysts

Samples of Pd catalysts supported on carbon, $CaCO_3$ and $BaSO_4$, and Pd black, were generously supplied by the Johnson Matthey Technology Centre, having been taken from production batches. Those that were supplied unreduced were first reduced in H_2 at room temperature for 1 h. 5% Pd/SiO_2 catalysts were prepared in the laboratory by impregnating Davison 70 SiO_2 gel with aqueous solutions of either H_2PdCl_4 or $Pd(NO_3)_2$ or $[Pd(NH_3)_4](NO_3)_2$, followed by reduction in aqueous N_2H_4 [17]. Series of Pd–Au and Pd–Ag bimetallic catalysts, also supported on Davison 70 SiO_2, were prepared by co-impregnation with (i) H_2PdCl_4 and $HAuCl_4$ solutions of (ii) $[Pd(NH_3)_4](NO_3)_2$ and $[Ag(NH_3)_2]NO_3$, fol-

lowed in each case by reduction with N_2H_4 [17]. Their compositions are expressed on a molar basis, as for example $Pd_{50}Au_{50}$. These catalysts have been examined thoroughly by a number of chemical and physical techniques [17], and essential conclusions will be mentioned in the Discussion. Total metal content obtained by analysis was 4–5 wt.%, and the ratios of the two metals were always close to nominal values. CO chemisorption isotherms measured volumetrically at ambient temperature after reduction (393 K, 1 h) and outgassing (670 K, 2 h) provide estimates of the number of surface Pd atoms, but values for monolayer coverage obtained by extrapolating isotherms to zero pressure are expressed as a molar CO/Pd ratio to avoid uncertainty concerning CO/Pd_s stoichiometry. The loan by the Johnson Matthey Technology Centre of the salts used in this work is also gratefully acknowledged.

2.2. Reaction conditions

Reactions were conducted at 273 K in an 80 ml spherical glass vessel, having a side-arm sealed by a serum cap, and attached to a volumetric apparatus in which the pressure was automatically maintained close to atmospheric. Action of the motor controlling the level of the reservoir provided a plot of volume change vs. time, from which the rate could be estimated. The vessel was charged with catalyst and the air swept from the apparatus by purified H_2. Precautions against ignition by the catalyst of explosive H_2–air mixtures were only taken when Pd black was used; here the catalyst was protected by N_2 during purging. No untoward incidents occurred. Ethanol (11.4 ml) and isoprene (1 ml) were then injected through the serum cap, and the reaction initiated by shaking the vessel (1000–1200 min^{-1}). Catalyst weights were selected to give rates not exceeding 5 cm^3 H_2 min^{-1} to avoid mass-transport limitation (see below): they were typically 50–150 mg. Samples (20 μl) for analysis were withdrawn via the side-arm periodically: usually 6–8 such

samples were taken during the first mol H_2 uptake. Analysis was performed on a benzyl cellosolve/Chromsorb P column, operating at 373 K; for further details, see [17].

Rates are expressed as TOFs (mol H_2 consumed (mol CO adsorbed)$^{-1}$ min^{-1}), product selectivities were derived from slopes of a plot of composition vs. conversion (Fig. 1). Alkene selectivity S is the percentage of all three butene isomers in the products; the methylbutene isomer composition is expressed on a percentage basis. Standard deviations on the latter were routinely calculated; they rarely exceeded $\pm 1\%$ and were often only $\pm 0.5\%$ or less.
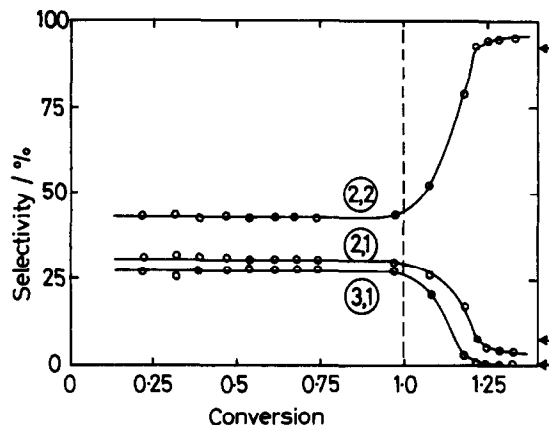

Fig. 2. Dependence of methylbutene isomer selectivities on conversion for $Pd_{20}Au_{80}$. Arrows indicate thermodynamic equilibrium concentrations at 299 K [18].

3. Results

3.1. Tests for mass-transport limitation

A number of tests were performed to ensure that reactions were performed without mass-transport control. Rates varied linearly with catalyst weight (5% Pd/SiO_2) up to ≈ 80 mg, but there was an intercept of ≈ 10 mg due to traces of toxic impurities. Mass-transport limitation obtrudes when the rate of H_2 uptake exceeds a

critical value and its onset is thus a function of both shaker frequency and catalyst weight at constant temperature. In its absence, product composition changes linearly with conversion until almost all the isoprene has reacted (Fig. 1), i.e. values of S and product selectivities remain constant over this period (Fig. 2). Thus for example with $Pd_{50}Au_{50}$, and a shaking frequency of 960 min^{-1}, the reaction was clearly under mass-transport control with 150 mg cata-
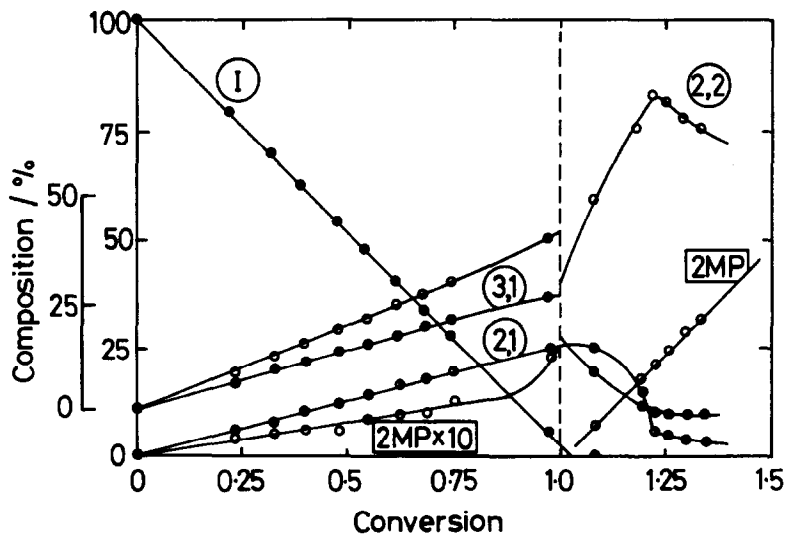

Fig. 1. Variation of % composition with conversion for $Pd_{20}Au_{80}$. For concentration of the 3,1 and 2,2 isomers, the outer scale is for conversions up to 100%.

Table 1
Hydrogenation of isoprene using various palladium catalysts

Catalyst	mol CO/mol Pd	TOF/min^{-1}	Methylbutene isomer selectivity/%			f[a]
			3,1-	2,1-	2,2-	
5% Pd/CaCO$_3$	0.085	289	31.6	25.4	43.1	0.225
3% Pd/BaSO$_4$	0.025	1063	29.9	24.7	45.4	0.15
			29.2	*25.8*	*44.9*	0.15
5% Pd/C	0.125	296	28.8	24.3	46.9	0.10
Pd black	0.0026	1525	29.0	24.6	46.5	0.10
			27.9	*25.6*	*46.5*	0.10
5% Pd/SiO$_3$ [b]	0.136	15.7	26.8	24.1	49.1	0.025
			25.8	*25.2*	*49.1*	0
0.5% Pd/Al$_2$O$_3$	0.57	196	25.3	25.0	49.7	−0.015
5% Pd/SiO$_2$ [c]	0.053	386	25.1	24.3	50.6	−0.015

[a] Methyl group weighting factor, see Discussion.
[b] Prepared using Pd(NO$_3$)$_2$ solution.
[c] Prepared using H$_2$PdCl$_4$ solution.
Calculated distributions in italic type.

lyst (rate, 17 cm^3 min^{-1}) and free of it with 26 mg (rate, 1 cm^3 min^{-1}).

In all cases the rate of H$_2$ consumption declined markedly after the end of the first mole uptake, at which point the methylbutene isomers rapidly changed in concentration (Fig. 1), attained their equilibrium concentrations [18] (Fig. 2) before their hydrogenation was complete.

3.2. The behaviour of various supported Pd catalysts

The results for various supported Pd catalysts, and for Pd black, are contained in Table 1

which also gives the molar CO/Pd ratios derived from chemisorption isotherms. The 0.5% Pd/Al$_2$O$_3$ is the most highly dispersed (57% dispersion assuming the CO to be linearly adsorbed), and also the most active, while the other supported catalysts have dispersions between 2.5 and 14%; there are considerable variations in the rates when expressed as turnover frequencies. Values of S all lay in the range 95–98%.

There are small but significant variations in the relative amounts of the methylbutene isomers formed. Thus for example the yield of the 2-methyl-2-butene isomer varies between 43.1

Table 2
Hydrogenation of isoprene using Pd–Au/SiO$_2$ and Pd–Ag/SiO$_2$ catalysts

%Au	%Ag	10^2 mol CO/mol Pd	TOF/min^{-1}	S/%	Methylbutene isomer selectivity/%			f[a]
					3,1-	2,1-	2,2-	
—	—	5.33	386	98.5	25.1	24.3	50.6	−0.015
20	—	1.98	1326	97.7	27.3	24.9	47.8	0.06
40	—	1.74	2086	95.7	27.9	26.0	46.1	0.11
50	—	1.19	3050	96.1	28.6	26.1	45.3	0.14
60	—	1.06	3630	97.3	29.6	27.3	43.0	0.20
80	—	1.36	373	98.2	30.5	27.2	42.3	0.225
—	20	2.35	648	97.3	25.5	26.3	48.2	0.05
—	40	1.17	1735	96.1	29.1	26.8	44.1	0.17
—	50	2.11	964	98.2	28.3	27.0	44.8	0.15
—	60	1.06	981	97.3	29.5	27.2	43.3	0.20
—	80	2.24	613	95.7	28.2	27.4	44.4	0.185

[a] Methyl group weighting factor, see Discussion.
For calculated distributions, see Fig. 3.

and 50.6%. In general the yield of this isomer is close to 50%, while those of the others are in the region of 25%. A simple model to rationalise these results will be presented below.

3.3. Palladium–gold and palladium–silver on silica catalysts

The results for these catalysts are recorded in Table 2. For the Pd–Au series, the rate expressed per unit mass of Pd increases as the Au concentration arises, but only slowly after the $Pd_{60}Au_{60}$ composition; the TOF however rises by a factor of 10 to a maximum at $Pd_{40}Au_{60}$. Pure Au is inactive. In the Pd–Ag series, the rate per unit mass of Pd shows no regular variation with composition, but the TOF apparently increases four-fold; pure Ag is of course inactive.

In the Pd–Au series there are systematic variations in the composition of the methylbutene isomers, the proportion of the 2-methyl-2-butene isomer decreasing with increasing Pd content from 50.6 to 42.4%. Alkene selectivity is lower in the middle of the series ($\approx 96\%$) than at either end. Changes in the same sense, but somewhat less orderly, are found with the Pd–Ag.

Scheme 2.
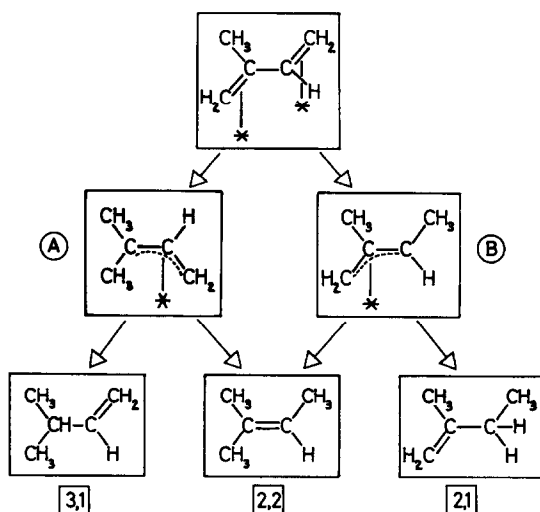
4. Discussion

The chief point of interest in this work is the composition of the products formed during the first mol H_2 uptake, i.e. before the hydroisomerisation of the methylbutenes begins: the reactions of 3-methyl-1-butene have been the subject of a separate study which will be reported on later. More specifically, we shall enquire whether the composition of the methylbutene isomers provides information concerning the nature of the catalytic surface.

4.1. Mechanism of the hydrogenation of isoprene

The mechanism of the hydrogenation of 1,3-butadiene on Pd and Pd–Au catalysts has been thoroughly investigated by Wells et al. [16], who concluded that the molecule is chemisorbed parallel to the surface either in a syn or, predominantly, in an anti conformation by two π-bonds. Attack by an H atom occurs exclusively at a terminal carbon atom, with the formation of corresponding syn or anti π-allylic radicals. Addition of the second H atom then occurs at either end of this species, and the formation of the three isomeric butenes is thereby explained. No conformational interconversion occurs in either the chemisorbed butadiene or in the π-allylic radicals, and no isomerisation of the butene isomers takes place while butadiene remains. The product selectivities thus very directly reflect the structures and reactivities of the intermediates.

We may suppose that isoprene chemisorbs analogously (Scheme 2), but the conformation of the di-π-adsorbed molecule is irrelevant because there can be no geometrical isomerism in the resultant alkenes. If the addition of the first H atom occurs with equal probability at positions 1 and 4, and that of the second H atom equally either at positions 1 and 3 in species A or at positions 2 and 4 in species B (see Scheme

2), the three methylbutene isomers will be formed in the ratio

$$S_{2,2} : S_{3,1} : S_{2,1} = 50:25:25$$

which approximates closely to the distributions found with Pd/Al_2O_3 and the Pd/SiO_2 made from H_2PdCl_4 (Table 1). It is however clear both from Table 1 and from Table 2 that with many of the catalysts the yield of the 2,2 isomer is significantly less than 50% and that those of the 2,1 and especially the 3,1 isomers can exceed 25%. We must therefore enquire how the foregoing assumptions can be modified to account for these divergences.

Since the addition of the first H atom is taken to occur at a terminal, and therefore unsubstituted, carbon atom, it is perhaps safe to retain the assumption that both possibilities are equally likely, and that the species A and B are equal in concentration. The analogous situation certainly applies in the case of butadiene [11]. The terminal carbon atoms of the π-allylic radicals A and B however differ as follows. In A, carbon atom 4 is unsubstituted while number 2 is disubstituted (i.e. it bears two methyl groups); in B, carbon atom 3 is monosubstituted and number 1 is unsubstituted. We therefore define a factor f which reflects the effect of a methyl group on the probability of an H atom adding at a given carbon atom, and we assume that two methyl groups have twice the effect of a single one. The chances of forming the three alkene isomers are then given by

$$S_{3,1} : S_{2,2} : S_{2,1} = (1 + 2f):2:(1 + f)$$

The dependence of the calculated isomer selectivities upon the value of f in the range -0.1 to $+0.5$ is shown in Fig. 3. Clearly when f is zero, we obtain the 25:50:25 composition mentioned above. As f tends to infinity, the selectivities of the 3,1, 2,2 and 2,1 isomers tend respectively to 0.6, zero and 0.3. When f is less than -0.5, the selectivity of the 3,1 isomer becomes zero and when f is -1 only the 2,2 isomer is formed. It is at once evident that this model provides a good description of the results
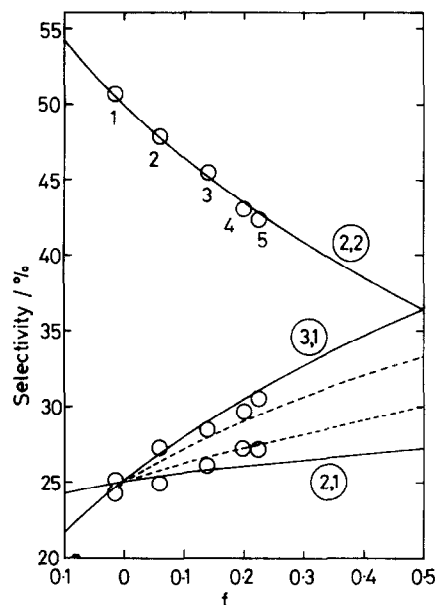

Fig. 3. Calculated dependence of methylbutene isomer selectivities on the parameter f: full lines, basic method; broken lines, modified method (see text). Experimental points superimposed: 1, 0.5% Pd/SiO_2; 2, $Pd_{80}Au_{20}$; 3, $Pd_{50}Au_{50}$; 4, $Pd_{40}Au_{60}$; 5, $Pd_{20}Au_{80}$.

in Tables 1 and 2 with the use of values of f between about zero and 0.3. Optimum values of f to fit each set of experimental results may then be obtained by interpolation into Fig. 3 by inspection, or more objectively by deriving values of f from each isomer's yield from the equations.

$$f_{3,1} = (4S_{3,1} - 1)/(2 - 3S_{3,1})$$

$$f_{2,2} = (2 - 4S_{2,2})/(3S_{2,2})$$

$$f_{2,1} = (4S_{2,1} - 1)/(1 - 3S_{2,1})$$

and taking the average. These optimum values of f are those quoted in Tables 1 and 2, where illustrative examples of calculated distributions are also given (in italic print) to show how close is the agreement with experimental results. In Fig. 3 selected observed distributions from the Pd–Au bimetallic series (Table 2) are shown against the theoretical curves, as a further demonstration of the success of the model. Calculated values for the 3,1 isomer tend to be a little too low and of the 2,1 isomer a little too

high, but the maximum difference between observed and calculated values is usually less than 1% and is often much smaller.

A slight modification to the above calculation has been tried. It follows from what has been said that the π-allyl radical (A) will react more quickly than (B) when f is positive, and so the ratio of their concentrations is likely to change, and can only be maintained via dehydrogenation back to adsorbed isoprene. If the sums of the two reaction paths for each radical are equated, the relative isomer selectivities become

$$S_{3,1}:S_{2,2}:S_{2,1} = \frac{1+2f}{2+2f}:\frac{1}{2+f} + \frac{1}{2+2f}:\frac{1+f}{2+f}$$

The result is the same when f is zero, and the values for the 2,2 isomer are unaltered, but for positive values of f the selectivities of the 3,1 and 2,1 isomers become respectively lower and higher. Fig. 3 also shows the selectivities calculated in this way, but for values of f up to ≈ 0.2 the differences are small and it is difficult to decide which is the better model.

The literature contains only a few papers from which product selectivities in the hydrogenation of isoprene on Pd catalysts can be extracted [19,20]; even so, in most cases they are either not measured or are reported with insufficient accuracy to make detailed analysis profitable. Four sets of results are however given in Table 3, together with corresponding distributions calculated by the first type of model presented above. The agreement with the experimental results is fair to good, although the value

of f for the Pd/C catalyst is larger than that given in Table 1.

The success of this simple model in accounting for the composition of the monoalkenes formed by hydrogenation of isoprene provides strong confirmation of the π-allylic mechanism, and obedience of observed yields to the theoretical relations given above may be taken as a diagnostic test for the mechanism, since on Pt, where a quite difference mechanism operates [21], the product yields are quite different from those expected for π-allylic intermediates [22].
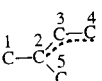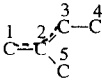
4.2. Quantum mechanical calculations on the π-allylic radicals

We have sought a theoretical basis for our reaction model by calculating spin densities and charges at each atom of the two π-allylic radicals (Scheme 2), using an unrestricted INDO Programme; we have not attempted to calculate how the structures of the radicals might be altered by chemisorption on Pd atoms. The results for both sets of carbon atoms are shown in Table 4. As expected, the free electron spends most of its time at the terminal atoms of the π-allylic bond: the two unsubstituted carbon atoms have similar electronic structures, while those of the methyl-substituted carbons differ significantly. In fact the charge is a quite precise inverse linear function of the number of methyl substituents, due to a partial delocalisation of charge from the π-orbitals into these groups. This latter observation confirms the log-

Table 3
Literature values for product selectivities in the hydrogenation of isoprene, and matching calculations

Catalyst	Methylbutene isomer selectivity /%			S/%	f	Reference
	3,1-	2,1-	2,2-			
5%Pd/C	31.5	25.9	42.6	96.4	–	[19]
Pd/CaCO₃	31.6	26.3	42.1	> 95	–	[19]
	31.3	26.2	42.5	–	0.235	
0.09%Pd/α-Al₂O₃	28	25	47	95.2	–	[20]
	27.5	25.5	47.0	–	0.085	
0.09%Pd/α-Al₂O₃	26	22	52	97.2		[20]
	23.4	24.7	51.9	–	−0.05	

Table 4
Calculated charges and spin densities for the isomeric dimethyl-
π-allyl radicals

Radical	Carbon atom	Charge	Spin density
(structure 1)	1	0.0557	−0.069
	2	0.0029	0.635
	3	0.0393	−0.315
	4	−0.0366	0.662
	5	0.0538	−0.066
(structure 2)	1	−0.034	0.696
	2	0.055	−0.312
	3	−0.013	0.671
	4	0.050	−0.074
	5	0.046	0.032

ical basis for a simple model in which the reactivity of the terminal carbon atoms depends on the number of attached methyl groups. Since values of f are mainly positive, the adding H atom must as expected [23] carry a fractional *negative* charge if it is to discriminate between the various available carbon atoms in the sense of favouring those having the *smaller* negative charges. We may further suppose that the charge that it carries is reflected in the value of f, viz., the greater the charge, the more will addition at the least charged atom be favoured, and hence the greater will be the value of f. We shall therefore explore whether the sign and magnitude of f correlate with predictable differences in the electronegativity of the H atoms.

4.3. Catalytic behaviour of palladium–gold and palladium–silver bimetallic catalysts

It has been clear for some time that the rigid band model is not adequate to describe the catalytic properties of alloys formed between metals of Groups 10 and 11. It is better to regard each component as retaining its essential identity, so that the profound changes which occur with alteration in composition are chiefly attributable to variations in the average size of the active ensemble. However, while there is little evidence of significant ligand effects, the

possibility of smaller second-order effects has not been eliminated and merits continued attention.

Structural examination of the Pd–Au catalysts used in this work has revealed a somewhat complex picture [17]. XPS measurements, which sense only the external surface of the catalyst grain, show Pd enrichment at the Au-rich end, while TEM/EPMA of sectioned grains also shows Pd enrichment in the first 2 μm from the surface: the interior contains smaller particles in which Au predominates. Reaction is likely to take place at the external surface or in the immediate subsurface region. The rate per unit mass of Pd increases by a factor of less than two on passing from Pd to $Pd_{40}Au_{60}$, while the TOF (expressed as mol H_2 consumed per mol CO adsorbed per min) increases almost ten-fold because of the decrease in the amount of CO adsorbed per mol Pd. We cannot however be sure that CO adsorption and isoprene hydrogenation sense the same fractions of the active component, and indeed it is likely that CO by penetrating throughout the catalyst grain gives an integral measure of surface Pd atoms; values of TOF cannot therefore be quantitatively reliable. Calculation of the mass of Pd available to the isoprene reaction from the nominal overall composition may also be over-estimated, so even the increase in rate on this basis may not be wholly valid, although there are numerous reports in the literature of increases in rate as Au is added to Pd [24,25]. In the end however the only reliable parameters on which to base a discussion are those connected with product composition.

The systematic increase in f with Au content implies that the negative change on the H atoms increases as Au is added. This may be a consequence of the progressive isolation of Pd atoms from each other, with a corresponding narrowing of the 3d band and other alterations to electronic structure [25].

Changes in f in the same sense occur as the Ag content of the Pd–Ag bimetallics is increased, but the structural study indicates [11]

that alloying is far from complete. We cannot therefore be so confident of our conclusions with the Pd–Ag series, although similar effects of those found in the Pd–Au series cannot be excluded.

4.4. Supported palladium catalysts

The electronic structure of a surface metal atom may also depend on the size and perhaps on the morphology of its particle: certainly there is much evidence to show that very small particles (< 200 atoms) do not have the band structure characteristic of bulk metals [26], and small Pd particles appear to be electron-deficient [3,27]. Metal–support interactions, weaker than those classified as 'strong', may also generate minor changes in the electron concentration of surface atoms. IFP scientists have shown that hydrogenation of 1,3-butadiene in the liquid phase on Pd/Al_2O_3 and Pd/SiO_2 is structure-sensitive, TOF *decreasing* as dispersion is *increased* [3]. This effect is attributed to the very strong chemisorption of the reactant on atoms of low coordination number, leading in effect to self-poisoning. From the limited range of catalysts we have examined, a similar trend can be discovered (Table 1), but effects due to residual impurities may somewhat obscure the picture. No clear trend of f with dispersion is discernible, but on the highly dispersed (and therefore electron-deficient) Pd/Al_2O_3 f is close to zero, perhaps because negative charge is not then freely available to the H atoms. Similarly, with the Pd/SiO_2 prepared from H_2PdCl_4, residual Cl atoms may withdraw charge from adjacent Pd atoms, thus hindering its movement towards H atoms. The higher values of f are found with the less well dispersed catalysts, as may be expected on this model.

5. Conclusions

The information contained in the product selectivities observed in the hydrogenation of iso-prene can be interpreted in terms of delicate changes in the electronic structure of the active Pd atoms produced by neighbouring Group 11 atoms. Similar differences between various other Pd catalysts may also be due to electronic factors, but the reasons for the variations are less evident.

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