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Reactions of Propane and of *n*-Butane with Hydrogen over Palladium Catalysts†

Geoffrey C. Bond* and Andrea Donato‡
Department of Chemistry, Brunel University, Uxbridge, UK UB8 3PH

On 5% Pd/SiO_2 and 5% Pd/Al_2O_3 catalysts, hydrogenolysis of propane affords ethane in high selectivity ($S_2 \approx$ 0.97–0.98); on the latter, the order in H_2 is −3.0 and the value of S_2 decreases as the H_2 pressure falls. The reaction of *n*-butane with H_2 gives chiefly methane and propane in almost equal amounts, except at the highest temperatures (>650 K) and the lowest H_2 pressure (<0.35 atm): the probability of central bond fission falls as the catalyst becomes deactivated by 'carbon' deposition to a value of *ca.* 0.05. Skeletal isomerisation to isobutane also occurs with low selectivity ($S_i \approx$ 0.07–0.15). Product selectivities from *n*-butane are remarkably unaffected by alteration of temperature and of H_2 pressure, owing to the predominance of a single reaction pathway; the activation energy is high (250–320 kJ mol^{-1}) and the order in H_2 strongly negative (−3.0).

Although hydrogenolysis of alkanes is not of itself of great practical importance, the structure sensitivity shown in this family of reactions has great usefulness in revealing how the structure of the surface of small metal particles depends on their size and earlier history. In previous parts of this series we have examined the reactions of the lower alkanes with H_2 over a number of supported-metal catalysts in order to acquire a body of knowledge of use in rationalising the complex behaviours encountered in these systems. We have put particular emphasis on the analysis of reaction products in terms of the Kempling–Anderson formalism,[1] since this permits the effects of changes in structure and composition to be understood in terms of identifiable unit steps in the overall process. We have not, so far, looked at Pd catalysts, because this metal is the least active of those of Group 8,[2] and the literature on it is sparse. Such few papers as are relevant do, however, suggest that Pd has some unusual features, meriting further study.

Sinfelt and Yates[3] described the hydrogenolysis of ethane on 10% Pd/SiO_2, finding an activation energy of 243 kJ mol^{-1} and orders in ethane and H_2 at 478 K of, respectively, 0.9 and −2.5. Anderson and Avery[4] studied the reaction of *n*-butane and H_2 on Pd films in the range 549–583 K; they determined an activation energy of 159 kJ mol^{-1}, and at H_2 pressures exceeding 45 Torr,§ orders in *n*-butane and H_2 of, respectively, −0.3 and *ca.* 0. The chief products were methane and propane, with only 1% isomerisation to isobutane. A more detailed study[5] of this reaction was subsequently made, using Pd black as catalyst; rates and product selectivities as a function of H_2 pressure and of temperature between 537 and 589 K were reported. Isomerisation selectivity increased with H_2 pressure, but a notable feature of the results was that methane selectivity rose markedly as the H_2 pressure was lowered, especially at the highest temperature.

The preference for Pd catalysts to attack terminal C—C bonds is also apparent from work on *n*-hexane and *n*-heptane.[6,7] With the former,[6] reaction with H_2 on Pd black at 648 K showed the following relative bond reactivities: C(1)—C(2), 2.61; C(2)—C(3), 0.33; C(3)—C(4), <0.05. With the latter,[7] reaction with H_2 over Pd powder at 573 K afforded 46% each of methane and hexane, and 4% each of ethane and pentane; isomerisation selectivity was only 0.06. The hydrogenolysis and isomerisation of methylcyclopentane and the methylpentanes on a number of Pd/Al_2O_3 catalysts of different dispersions have very recently been described,[8] and once again the superior reactivity of terminal C—C bonds (for example, in 2-methylpentane) has been demonstrated.

We now report a short study of the reactions of propane and of *n*-butane with H_2 over Pd/SiO_2 and Pd/Al_2O_3 catalysts. Because of the somewhat high temperatures which have to be used, deactivation due to 'carbon' deposition created difficulties for accurate determination of reaction kinetics; however, the use of a short reaction-pulse technique previously developed[9] enabled kinetic measurements to be made at H_2 : alkane ratios greater than 3 : 1. We have also been able to establish how 'carbon' deposition affects product selectivities.

Experimental

Materials and Methods

The 5% Pd/SiO_2 catalyst had been prepared by Dr. A. F. Rawle[10] by impregnating Davison 70 SiO_2 gel (322 m^2 g^{-1}) with an aqueous solution of $[Pd(NH_3)_4](NO_3)_2$, followed by reduction with N_2H_4 HCl. The 5% $Pd/\gamma\text{-}Al_2O_3$ catalyst was made by impregnating Degussa Aluminium Oxide C (100 ± 15 m^2 g^{-1}) with aqueous $PdCl_2$ solution, followed by drying and reduction in H_2 for 2 h at 500 K. Before using them as catalysts, both were calcined for 1 h in air at 763 K, then purged with N_2 for 1 h at 673 K before being reduced in H_2 for 1 h at 763 K: they were then cooled to reaction temperature in H_2. All flow rates were 20 cm^3 min^{-1}. CO chemisorption isotherms were determined volumetrically at room temperature after reduction in H_2 (1 h at 293 K) and outgassing (2 h at 670 K); a CO : Pd_s ratio of 2 : 1 was assumed. The 5% Pd/SiO_2 catalyst had a dispersion of 1.9%, while that of the 5% Pd/Al_2O_3 was 10.1%.

A sample of 1% $Pd/\alpha\text{-}Al_2O_3$ was kindly provided by Dr. B. Coq (ENSCM, Montpellier). This had been prepared by impregnating Rhône–Poulenc $\alpha\text{-}Al_2O_3$ SCS9 with a solution of $Pd(acac)_2$;[11] the dispersion was estimated by H_2 chemisorption as 50%.

Reactions were conducted in the microprocessor-controlled apparatus previously described.[12] The catalysts (*ca.* 200 mg) were pretreated as above, and were then exposed to a reactant stream comprising alkane, 10; H_2, 100; N_2, 30 cm^3

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‡ On leave of absence from the Facoltà di Ingegneria, Università di Reggio Calabria, 48 Via Emilio Cuzzocrea, 89128 Reggio Calabria, Italy.

§ 1 Torr = (101 325/760) Pa.

min^{-1}. The reactor temperature was raised in steps of 10 K and a single sample was analysed near the end of each intervening 20 min isothermal period: this constituted stage 1 of the reaction, after which the temperature was lowered in a similar stepwise manner and further results collected (stage 2). Sometimes a further thermal cycle was performed. Temperatures were generally in the range 530–670 K. By this procedure[12] it was possible to assess quickly the effect of deactivation occurring at high temperature on rates and product selectivities; 627 K was used as the standard temperature for comparison. Isothermal measurements were also carried out to ascertain how deactivation depended on the H_2 : alkane ratio used: samples were taken for analysis at 20 min intervals. The dependence of rate on H_2 pressure was determined using the short reaction-pulse technique,[9] in which reactants flowed over the catalyst for only 1 min, at the end of which time a sample was taken for analysis, and the alkane flow was diverted from the reactor. The standard H_2–N_2 flow was then restored for 20 min, after which the H_2 flow was adjusted to that required for the next measurement. The alkane flow remained constant at 10 $\text{cm}^3\ \text{min}^{-1}$ and the N_2 flow was changed to compensate for the changes in H_2 flow. This procedure minimised but did not always eradicate deactivaton caused by 'carbon' deposition; it was also used on occasions in thermal cycling experiments.

Treatment of Results

Rates are expressed as mmol alkane reacted (g Pd)$^{-1}$ h^{-1}; for *n*-butane, the number of moles converted, A, is given by

$$A = \frac{1}{4} \sum_{j=1}^{j=3} jC_j$$

The selectivity of product j is then defined as

$$S_j = c_j/A$$

where c_j is the molar fraction of products containing j carbon atoms ($j < 4$). The isomerisation selectivity S_i is the fraction of *n*-butane converted to isobutane. Analogous definitions apply to the reaction of propane.

The reactions can be represented by 'rake' mechanisms,[1] in which for *n*-butane an adsorbed C_4 species can suffer either central fission (chance F) or terminal fission (chance 1-F). First-order rate constants are assigned to each possible step, primed constants relating to reactive desorption of an adsorbed species having j carbons and starred constants to further C—C bond breaking. Then

$$T_j = k'_j/(k'_j + k^*_j)$$

($j = 2$ or 3). Steady-state analysis of this scheme, first described by Kempling and Anderson,[1] leads to expressions for the selectivities S_1, S_2 and S_3 as functions of conversion and of T_2 and T_3. These simplify at low conversions to

$$S_2/T_2 = 1 + F - S_3$$

$$S_3/T_3 = 1 - F$$

There are insufficient known parameters to estimate all the unknowns, so elsewhere we have either taken T_2 to be unity[13] or have used its value as found in hydrogenolysis of propane,[12] where $T_2 = S_2$. For reasons given below, the former procedure is used here; the constants F and T_3 are then distinguished by primes. It is unnecessary to tabulate all the selectivities, since for propane, $S_1 + 2S_2 = 3$, and for *n*-butane, $S_1 + 2S_2 + 3S_3 = 4$.

Results

Pd/SiO$_2$

The rate of propane hydrogenolysis over 5% Pd/SiO$_2$ was low, and in the course of two thermal cycles its value at 627 K decreased by *ca.* 50%. However, reliable activation energies were obtained in the range 600–665 K; these were in the range 304–319 kJ mol^{-1} (mean, 312 kJ mol^{-1}). Values of S_2 at the top of the temperature range were 0.97–0.98.

As we have found with other catalysts,[12,13] *n*-butane caused more rapid deactivation than propane, so that with 5% Pd/SiO$_2$ after stage 1 rates could be measured accurately only above *ca.* 640 K; results obtained in stage 1 are shown in Table 1. Isothermal experiments were then performed at 622 K: with H_2 : *n*-butane = 10 : 1, rates remained constant after 1 h on stream [*ca.* 4.6 mmol (g Pd)$^{-1}$ h^{-1}] and product selectivities were also unchanged, agreeing well with those found in the thermal cycling experiment (see Table 1). However, on changing the H_2 : *n*-butane ratio to 2 : 1, rates decreased over 2 h from 11 to 6.4 mmol (g Pd)$^{-1}$ h^{-1}. There were accompanying slight changes in selectivities, S_1 decreasing from 0.97 to 0.91 and S_3 increasing from 0.82 to 0.85; these seemed to be due more to changes in T'_3 than in F'. Table 1 shows the average of the results found after 80–140 min on stream. Use of the short reaction-pulse method in a thermal cycling experiment resulted in a rate of 3.6 mmol (g Pd)$^{-1}$ h^{-1} at 627 K; above this temperature, S_i and S_2 increased, and S_1 and S_3 decreased, with rising temperature.

The value of T_3 obtained by assuming T_2 to be unity, *viz.* T'_3, was also in most cases within an error of unity; taking the value of S_2 in the hydrogenolysis of propane under the same conditions as T_2 would therefore have led to T_3 values greater than unity. We therefore concluded that it is not appropriate to proceed in this way with this system, and we therefore only report values of F' and T'_3.

The effect of varying the H_2 pressure on the rate of *n*-butane hydrogenolysis and on the product selectivities was

Table 1 Reaction of *n*-butane and H_2 over Pd/SiO$_2$ and Pd/Al$_2$O$_3$ catalysts: thermal cycling and isothermal experiments

catalyst	mode[a]	stage	T range/K	E/kJ mol^{-1}	ln A[b]	r[b,c]	S_2	S_3	F'	T'_3	S_i
5% Pd/SiO$_2$	C	1	577–627	259 ± 25	47.5	2.3	0.095	0.957	0.052	1.01	0.16
	C/I[d]	—	622	—	—	4.6	0.103	0.947	0.050	1.00	0.15
	P	1	589–638	246 ± 13	45.4	3.6	0.129	0.934	0.063	1.00	0.07
5% Pd/Al$_2$O$_3$	P	1	568–627	279 ± 11	55.0	97	0.212	0.894	0.106	1.00	0.16
	C	2	587–665	319 ± 6	60.8	13	0.079	0.964	0.043	1.01	0.17
1% Pd/Al$_2$O$_3$	P	1	538–649	263 ± 5	50.7	141	0.115	0.943	0.060	1.01	0.08
	C	2	568–669	285 ± 5	54.1	59	0.048	0.974	0.022	1.00	0.05
	C	3	568–639	282 ± 9	53.5	57	0.063	0.977	0.022	1.00	0.06

[a] Reaction modes: C, continuous flow; C/I, continuous flow, isothermal; P, short reaction-pulse. [b] A and r (=rate) in mmol (g Pd)$^{-1}$ h^{-1}. [c] Rate and all selectivity parameters at 627 K. [d] Rate and selectivity parameters: average for 80–140 min period.

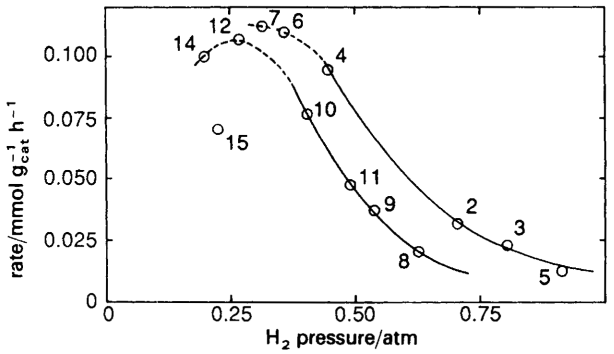

Fig. 1 Dependence of rate of *n*-butane hydrogenolysis on H_2 pressure at 619 K, with 5% Pd/SiO_2. The numbers against the points give the sequence in which the measurements were made.

then examined at 619 K, using the short-reaction pulse method. Rates were adequately reproducible when the H_2 pressure was more than *ca.* 0.35 atm† (pressure of *n*-butane = 0.089 atm throughout), but at lower H_2 pressures there was some deactivation which was not completely removed by the intervening H_2 treatment. The form of the results (Fig. 1) suggests, however, that continued use of higher H_2 pressures results in a continued slow recovery of activity. It was, however, impossible to locate the position of the maximum rate, although measurements were made down to 0.018 atm H_2 pressure.

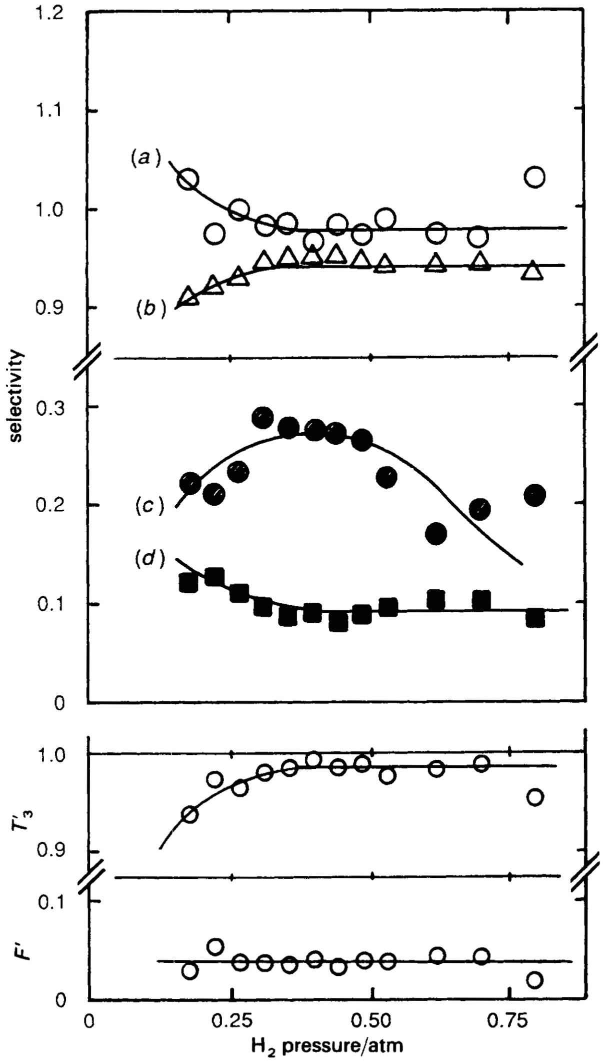

Fig. 2 Dependence of product selectivities and of Kempling–Anderson parameters on H_2 pressure at 619 K, with 5% Pd/SiO_2: (*a*) S_1, (*b*) S_3, (*c*) S_i, (*d*) S_2

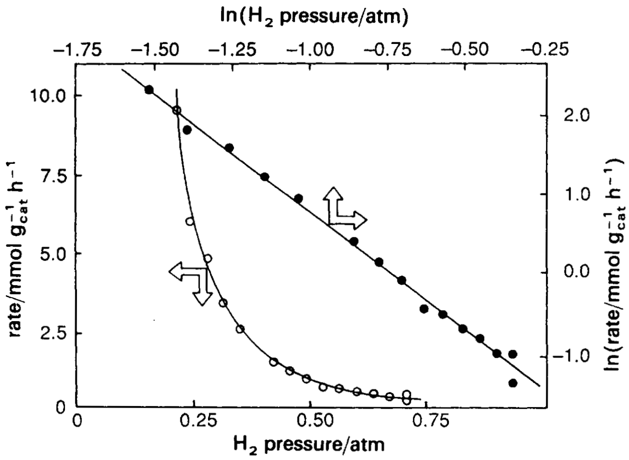

Fig. 3 Dependence of rate of propane hydrogenolysis on H_2 pressure at 608 K, with 5% Pd/Al_2O_3, and the corresponding log–log plot

These activity changes were, however, without major effect on product selectivities (Fig. 2). Only the values of S_i were a little scattered in consequence of the effect of the deactivation noted above; even so, the use of short reaction-pulses mitigates the worst effects of deactivation. After elimination of the results obtained (i) at the highest H_2 pressure, and (ii) after using the lowest H_2 pressures, on the grounds that they were unreliable owing to the very low conversion, we find that the values of S_1, S_2 and S_3 are independent of H_2 pressure above 0.3 atm, but that below this pressure S_3 slowly falls and S_1 rises: this is associated with a decrease in T'_3, but F' is not altered (Fig. 2). S_i seems to pass through a broad maximum, but its sensitivity to the condition of the surfaces makes this uncertain.

Pd/Al_2O_3

The 5% Pd/Al_2O_3 catalyst was initially *ca.* 100 times more active for propane hydrogenolysis than 5% Pd/SiO_2, but it was also deactivated (by *ca.* 70%) after two thermal cycles. Reliable activation energies were measured between 560 and

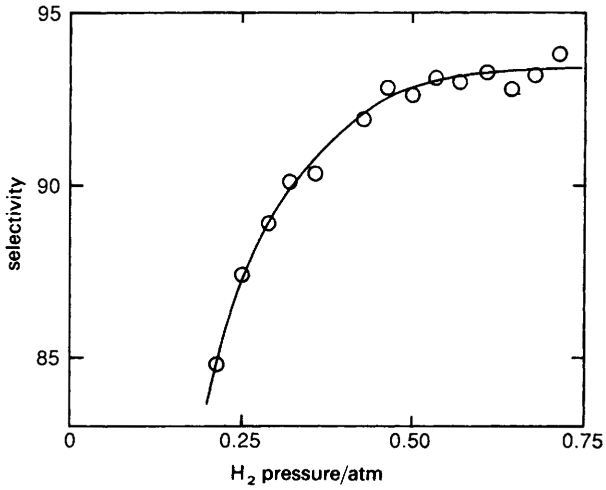

Fig. 4 Dependence of S_2 in propane hydrogenolysis on H_2 pressure at 608 K, with 5% Pd/Al_2O_3

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† 1 atm = 101 325 Pa.

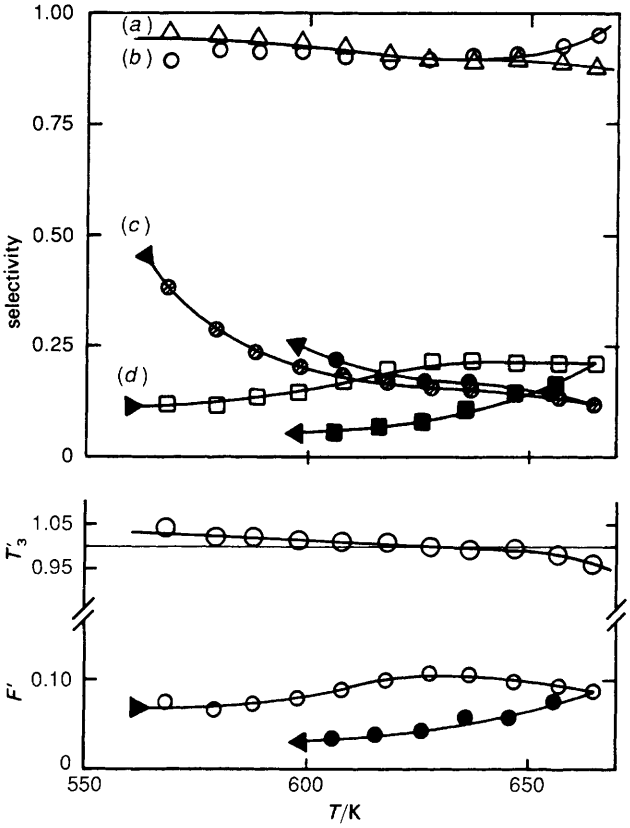


Fig. 5 *n*-Butane hydrogenolysis on 5% Pd/Al_2O_3: selectivity parameters as a function of temperature. Stage 1 (rising temperature), reaction-pulse mode; stage 2 (falling temperature), continuous-flow mode. (*a*) S_3, (*b*) S_1, (*c*) S_i, (*d*) S_2. Note: where results for both stages are shown, the direction of temperature change is indicated, and the stage 2 data points are filled. In the other cases, results for the two stages are indistinguishable.

660 K; these were in the range 304–330 kJ mol^{-1} (mean, 315 kJ mol^{-1}). Values of S_2 were *ca.* 0.975 and decreased slightly above this temperature.

In view of the difficulties experienced with deactivation when trying to determine the dependence of rate on H_2 pressure with the Pd/SiO_2 catalyst, we prefaced our attempt to perform similar experiments with propane using 5% Pd/Al_2O_3 with isothermal measurements conducted over an 80 min period, using various H_2 : alkane ratios and analysing samples at 20 min intervals, in order to delineate the region where severe deactivation was encountered, so that it might

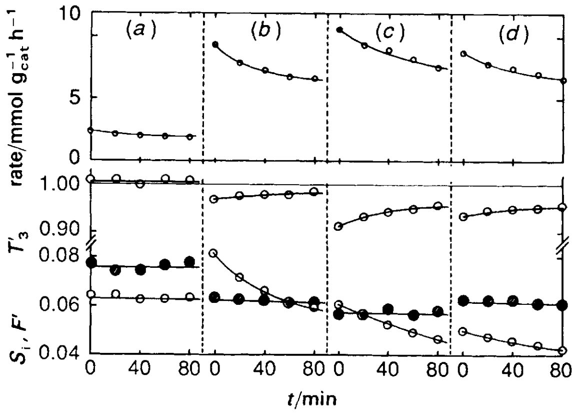


Fig. 6 Variation of rates and selectivity parameters with time-on-stream for *n*-butane hydrogenolysis at 608 K on 5% Pd/Al_2O_3, using different H_2 : *n*-butane ratios: (*a*) 10 : 1, (*b*) 5 : 1, (*c*) 3 : 1, (*d*) 2.5 : 1. Hatched points, S_i; open points, F'.

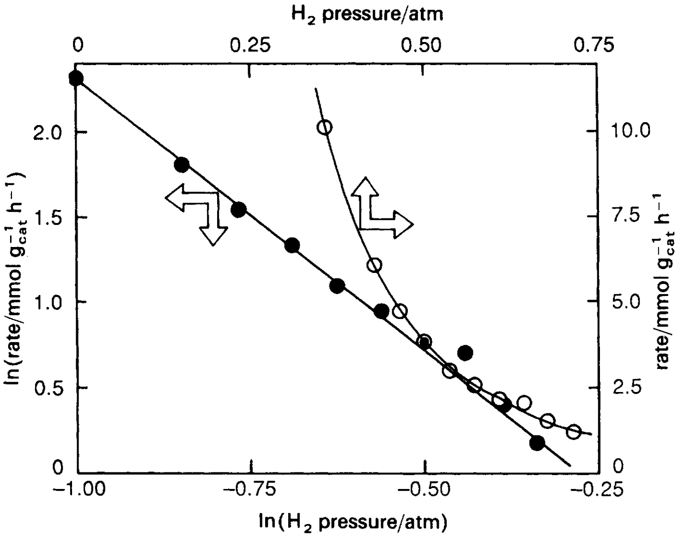


Fig. 7 Dependence of rate of *n*-butane hydrogenolysis at 608 K, with 5% Pd/Al_2O_3, and the corresponding log–log plot

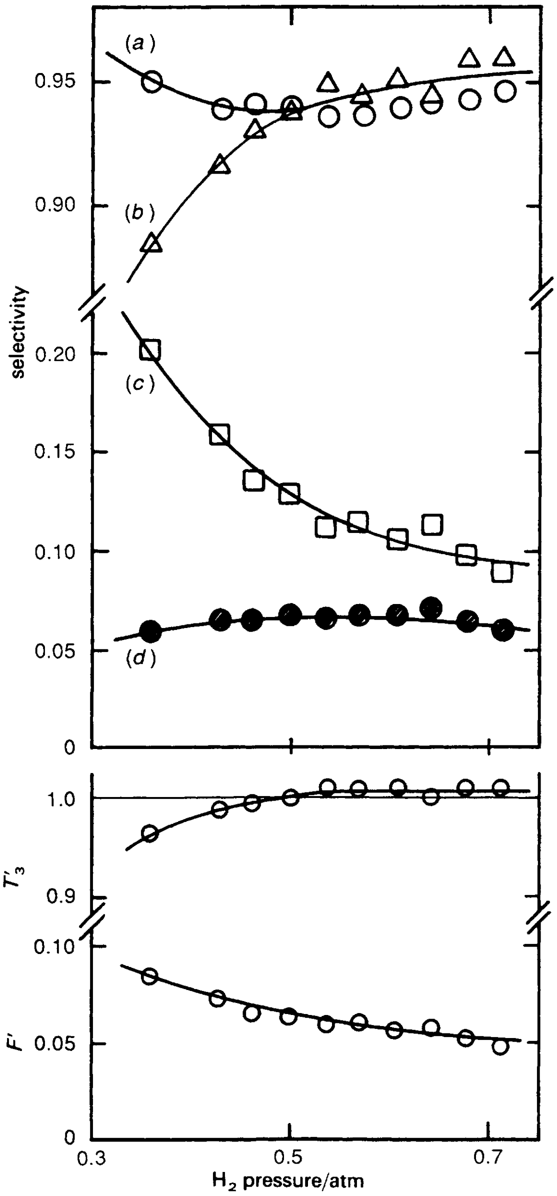


Fig. 8 Dependence of product selectivities and of Kempling–Anderson parameters on H_2 pressure at 608 K, with 5% Pd/Al_2O_3: (*a*) S_1, (*b*) S_3, (*c*) S_2, (*d*) S_i

be avoided. At 608 K, there was no loss of activity with H_2 : propane ratios of 10 and 5 : 1, but with a ratio of 2.5 : 1 some 40% of activity was lost within 80 min. When determining the effect of H_2 pressure on rates and selectivities, H_2 : propane ratios of less than 3 : 1 were therefore not used. The results are shown in Fig. 3 and 4. There is very little scatter in the rate measurements, which give an excellent linear log–log plot, corresponding to an order in H_2 of -3.0 (Fig. 3). The values of S_2 fall with decreasing H_2 pressure (Fig. 4).

In the thermal cycling experiment with *n*-butane, the 5% Pd/Al_2O_3 catalyst suffered marked deactivation, even though stage 1 was performed in the pulse-reaction mode; the results recorded in stages 1 and 2 are shown in Table 1 and Fig. 5. Deactivation caused a decrease in S_2, and hence in F', to values similar to those found with Pd/SiO_2; S_i did not, however, decrease. The same trends were disclosed in an isothermal experiment at 608 K (Fig. 6), where loss of activity occurred at all H_2 : alkane ratios less than 10 : 1, this also caused T'_3 to increase. Hydrogenolysis selectivities have low temperature coefficients, although S_i decreases significantly with rising temperature (Fig. 5).

However, by operating in the reaction-pulse mode, reliable results were obtained for the dependence of rate and selectivities on H_2 pressure (Fig. 7 and 8). The variation of rate with H_2 pressure showed minimal scatter, and a good log–log plot results, giving an apparent order in H_2 of -3.0 (Fig. 6). The manner of the variation of the selectivities and the derived Kempling–Anderson parameters (Fig. 8) closely resembles that found with Pd/SiO_2 (Fig. 2): S_1 is almost constant (0.935–0.950), as is S_i (0.06–0.07), while S_3 decreases and S_2 increases with decreasing H_2 pressure. Significant excess methane formation is seen only at the lowest H_2 pressures. T'_3 is within error of unity, but F' increases as the H_2 pressure is lowered. It is possible, but risky, to use the results in Fig. 6 to project what might happen at even lower H_2 pressures. Taking the initial values, it seems that S_2, and hence F', may pass through a maximum as the H_2 pressure falls, while S_i remains close to 0.06 and T'_3 stays high (>0.9).

A single thermal cycling experiment was carried out with the 1% Pd/Al_2O_3 catalyst; the first stage employed the short reaction-pulse mode, but in later stages continuous flow was used. This catalyst was *ca.* 50% more active per g Pd than the 5% catalyst, and its activity stabilised after stage 1 (see Table 1). Deactivation once again caused a decrease in S_2 and hence also in F', and an increase in activation energy; S_i was low (0.05–0.08) and unaffected by deactivation.

Discussion

Catalyst Deactivation

The type of support exerts a marked influence on the activity and rate of deactivation of the Pd particles: the activity of the 5% Pd/Al_2O_3 is 50 to 100 times higher than that of the 5% Pd/SiO_2 (Table 1), this being only partially due to the difference in active areas. Although it suffers some deactivation (Fig. 6) it is much less than that experienced by the SiO_2-supported catalyst, the low activity of which may be a direct consequence of its propensity of deactivate, as it may lose much of its activity in the first few seconds of use. The higher proportion of Pd atoms of low coordination number present in the smaller particles in the 5% Pd/Al_2O_3 may retain their activity better than those in the low-index planes which will predominate in the large particles found in the Pd/SiO_2.[14] A similar difference in activity between Pd/SiO_2 and Pd/Al_2O_3 catalysts has been noted before;[15] the lower activity shown by the former may also be ascribed to the formation of the PdSi alloy during high-temperature reduction.[16]

The loss of activity in the continuous-flow mode is greater the lower the H_2 : alkane ratio (Fig. 6), so it must be caused by formation of strongly absorbed and dehydrogenated derivatives of the alkane, which may be in short referred to as 'carbon'. While the use of the short reaction-pulse technique allows useful kinetic results to be obtained over a quite wide range of H_2 : alkane ratios, the effect of 'carbon' formation on product selectivities can help to specify the number of different kinds of active centre, or, at the very least, the way in which 'carbon' influences the behaviour of neighbouring sites. Thus in the case of the Pd/SiO_2 catalyst, product selectivities are very little changed by deactivation at constant temperature, while with both Pd/Al_2O_3 catalysts there is clear evidence for a decrease in S_2 (and hence in F') as deactivation proceeds (Table 1 and Fig. 5 and 6). At least at higher H_2 : alkane ratios, S_2 seems to reach a limiting value, associated with attainment of a finite but partial coverage of the active surface by 'carbon', this being determined by the temperature used. However, the isomerisation selectivity does not change, and hence we can conclude that central bond breaking and isomerisation are not mechanistically linked.

Supported Pt catalysts have shown similar changes of F with 'carbon' content, although subtle differences exist between Pt/SiO_2 (EUROPT-1)[17] and Pt/Al_2O_3 (*e.g.* EUROPT-3).[9,12] The former suffers a limited deactivation and a slight decrease in F after thermal cycling, and shows quite high isomerisation activity ($S_i \approx 0.1$–0.4), while the latter is deactivated continuously under comparable conditions, with larger but limited reductions in F: isomerisation is negligible. Qualitative models involving two types of active centre have been proposed to account for these observations.[12,17]

Product Selectivities

Apart from their different activities and rates of deactivation, and the different effects of 'carbon' on the value of S_2, the three Pd catalysts show a number of marked similarities, in respect of activation energies and product selectivities. The latter define the characteristic properties of Pd in alkane hydrogenolysis; these are summarised as follows. (1) There is significant isomerisation of *n*-butane to isobutane on all catalysts, but least with 1% Pd/Al_2O_3 (Table 1) which has the highest dispersion. (2) The terminal position is predominant for bond breaking in *n*-butane (to the extent of at least 95%). (3) Over a wide range of conditions, there is little if any excess formation of methane, *i.e.* each residence on the surface results in only a single C—C bond fission, and intermediate C_2 and C_3 species are desorbed in preference to suffering further hydrogenolysis (Table 1, Fig. 2 and 8). These observations are in harmony with previous work,[3–8] briefly summarised in the Introduction.

All of these statements are, however, capable of further refinement, especially with respect to the effects of temperature and pressure. In the *n*-butane reaction at low H_2 pressures (<0.5 atm on Pd/Al_2O_3, Fig. 8, and <0.3 atm on Pd/SiO_2, Fig. 2), S_3 begins to decrease, and S_1 and S_2 to increase: these changes are specifically connected with the T_3 term rather than with F, so that further cracking of C_3 and C_2 intermediates is favoured as the surface becomes depleted in H atoms. The desorption step, *i.e.* the conversion of an adsorbed intermediate into the corresponding gaseous alkane, clearly requires more H atoms than its further hydrogenolysis. Unfortunately, the extensive deactivation encountered at low H_2 pressures has prevented us from obtaining kinetic results in this region (<0.35 atm for Pd/Al_2O_3, <0.2

atm for Pd/SiO_2), and so we cannot extract the functional relationship between T_3 and H_2 pressure. Results analogous to these were reported with evaporated Pd films as the catalyst.[4]

Although the constraints of low activity and fast deactivation at high temperatures limited the range of temperature that could be investigated, it was clear that there was no rapid escalation of methane formation as the temperature was raised, as is often observed with other metals;[12,13] excess methane is seen only above *ca.* 650 K (Fig. 5). Our work with Ru[13] has suggested that such behaviour is characteristic of a heavily contaminated surface because a larger site is required for further bond-breaking than for reactive desorption; this is not, however, necessarily the case here. The very high values of T'_3, based, it must be remembered, on the assumption that T_2 in the reaction of *n*-butane is unity, imply that propane or the adsorbed C_3 species derived therefrom are much less reactive than *n*-butane or the adsorbed C_4 species. Measured rates of propane hydrogenolysis are, however, only five to ten times smaller at 627 K than those of *n*-butane, and such factors are hardly sufficient to account for values of T'_3 which are generally within an experimental error of unity. We return to this point later.

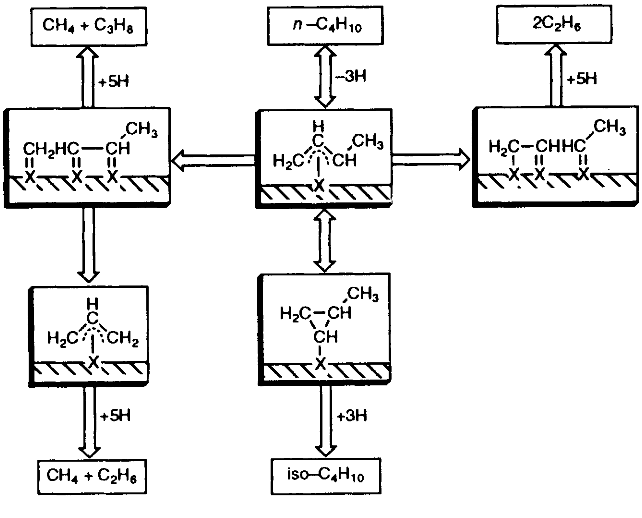
Another unusual observation needs to be noted. In the case of other metals for which we have comparable results, T_2 in the reaction of propane is usually higher than T_3;[12,13] this difference is especially noticeable with Pt,[17] and reflects the greater stability of the C_2 species. Here, on the other hand, T_2 is slightly but significantly lower than T'_3, and hence by implication lower than both T_3 and T_2 in the *n*-butane reaction. However, in the region where T_3 is close to unity, and F' being only *ca.* 0.05, no further reaction of C_3 species occurs, and the concentration of C_2 species formed by central bond fission is low: T_2 in the *n*-butane reaction is thus, in effect, indeterminate. It is for this reason, *i.e.* doubt concerning whether S_2 from the propane reaction may be legitimately taken as T_2 in the *n*-butane reaction, that we have not performed this substitution here.

There is one other remarkable circumstance meriting attention. With both of the 5% Pd catalysts in the higher H_2 pressure range, the product selectivities and derived parameters for the *n*-butane reaction are almost independent of H_2 pressure, although the rate is severely inhibited by H_2, the order in H_2 being *ca.* -3 (Fig. 1–3, 7 and 8). Therefore, while the number of locations at which reaction can occur is a strong negative function of H_2 pressure, the composition of such locations in terms of the number of H and C atoms entering the transition state for the rate-determing step is more or less the same. Under these conditions the slow step may have to be sought in the opening steps of the reaction sequence, *e.g.* in the interaction of the gaseous alkane with a vacant surface site to give a chemisorbed alkyl radical, which can then quickly undergo dehydrogenation until an intermediate is formed which is sufficiently strained or reactive to undergo hydrogenolysis. Excessive dehydrogenation results in species too strongly attached to the surface;[12] these are responsible for deactivation. Since the rate of conversion of the adsorbed C_3 species into gaseous propane is so much favoured over its further cracking (because it is relatively weakly bonded to the surface), no competitive pathways exist for a differential dependence on H atom concentration to be shown, and hence no change in product selectivity is possible until the H_2 pressure falls below the point at which the rate of C_3 desorption begins to be limited by the availability of H atoms. This corresponds to the point at which the rate is a maximum. With propane as reactant, however, the C_2 intermediate is more strongly held than the corresponding C_3 species; alternative pathways are therefore available, and S_2 decreases as the H_2 pressure is lowered (Fig. 4) because, as noted above, further C—C bond breaking needs fewer H atoms than the reactive desorption step. The effect of varying the H_2 pressure on rates and selectivities is unfortunately often ignored (see, however, ref. 4 and 5); the use of a constant and high H_2 : alkane ratio evades the question of how the reactions which follow the first bond breakage occur.

Reaction Mechanisms

It remains to try to meld those observations into a coherent reaction mechanism, aided by suggestions from the literature.[3–8,16] There is much evidence to suggest the participation of π-alkene and π-alkene-σ-alkyl species in reactions of alkanes over Pd, and of metallocycles over both Pd[8] and Pt.[18] Cyclic species are not, however, essential for describing the reactions of the lower alkanes[12,17] and are inapplicable in the case of ethane. Common intermediates for both hydrogenolysis and isomerisation of *n*-butane have been proposed,[8,18] and mechanisms based on them have an appealing elegance and simplicity; this does not, however, mean that they are right. The ability of Pd catalysts to effect a near-totally selective hydrogenolysis of terminal C—C bonds in *n*-alkanes without excessive methanation is unique amongst the metals of Group 8. This may be explained by supposing either that essentially the same species exist on all metals and that they react in a way which depends on the surface chemistry of each particular metal; or alternatively, and we think more probably, that distinctly different intermediate species are formed on metals showing different catalytic behaviour. This latter view seems to reflect current thinking.[8]

The older literature stresses the wide-ranging role played by π-allylic species in both homogeneously[19] and heterogeneously[20] catalysed reactions involving Pd, although they are inexplicably absent from recent mechanistic discussions.[8] We try in Scheme 1 to show how an adsorbed 1-methyl-π-allyl radical might dissociate by alternative paths to give either $C_1 + C_3$ or two C_2 fragments, and through a cyclic intermediate lead to the formation of isobutane. The reasons for preferring a π-allylic intermediate are as follows. (i) We doubt whether a metallocyclobutane is sufficiently dehydrogenated to account for the large negative orders in H_2 (Fig. 1, 3 and 7), and excluding work on ethane[3,21] there has been no quantitative kinetic analysis of the reactions of higher alkanes: indeed this might prove difficult to do, because of



Scheme 1

the difficulty of measuring rates of low H_2 pressures. (ii) Linear multiply bonded species have been advocated to interpret reactions on Pt catalysts,[12,17] and on the basis of the argument presented above they may not be suitable for describing the special behaviour of Pd. (iii) π-Allylic species are also commonly associated with organometallic complexes of Ni, and this metal shows some similarity to Pd in its preference for terminal-bond fission.[22,23]

The unsymmetrical structure of the 1-methyl-π-alkyl radical (Scheme 1) may explain the preferred mode of bond breaking. Quantum-mechanical calculations[24] on the related 1,1- and 1,2-dimethyl-π-allyl radical have shown that charge is delocalised into the methyl groups, and that the highest concentration of charge lies on the unsubstituted terminal carbon atom. An analogous effect in the 1-methyl-π-allyl radical will assist the formation of the C=M double bond in the adsorbed methylene group (Scheme 1) which we may suppose triggers C—C bond breaking. The alternative fission mode is then less probable.

The occurrence of homologation of C_4 to C_5 species has been observed[23] and has been mechanistically associated with isomerisation, thought to be proceeding by a methylene-reinsertion mechanism.[18] Numerous alternative mechanisms for isomerisation have been proposed in the literature,[18,25] and it is difficult to discriminate between them in the case of the butanes, where isotopic tracing cannot assist. The evidence from the present work is that isomerisation proceeds by the same kinetics as hydrogenolysis and that the same intermediate is involved. We cannot, however, eliminate methylene reinsertion into a π-alkenic species from consideration.

Two small matters still require attention: the effect of H_2 pressure (Fig. 8) and of 'carbon' coverage (Fig. 6) on F' in the *n*-butane reaction. We note that the former is shown only with the Pd/Al_2O_3 catalyst and not with the Pd/SiO_2, which has larger particles (*cf.* Fig. 2 and 8). We believe that this less favourable mode of C—C bond breaking is helped by a higher concentration of electrons at the neighbouring Pd atom where the multiple C=M bond is to be formed. The presence of adjacent strongly bonded 'carbon' species, also held to the surface by multiple C=M bonds, will also increase the electron density at the above-mentioned free Pd atom. It is then possible that the decrease in the H atom coverage will, for small Pd particles only, increase the electron concentration at free Pd atoms, hence also facilitating central bond breaking.

Finally, it is worth stressing that very similar patterns of behaviour are shown by Pd catalysts of different particle size,[8] on different supports (this work) and with different *n*-alkanes (see the Introduction). Other more complex mechanisms which are available to the higher alkanes, and which are required to explain isomerisation, are not therefore needed to account for hydrogenolysis. The persistence of the preferred terminal C—C bond fission in the higher (C_6 and C_8) alkanes implies that the same type of intermediate as that shown in Scheme 1 is at work, and that the tendency to form 1-alkyl-π-allyl radicals rather than other isomers which would lead to internal fission may be due to steric as well as electronic effects.

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