# Gas-chromatographic Studies of Hydrocarbon Hydrogenolysis on a Ni/SiO<sub>2</sub> Catalyst

BY KEVIN F. SCOTT AND COURTENAY S. G. PHILLIPS\* Inorganic Chemistry Laboratory, Oxford University, Oxford

Received 20th June, 1979

The hydrogenolysis of hydrocarbons on a Ni/SiO<sub>2</sub> catalyst has been studied using a wide variety of unconventional gas-chromatographic techniques, especially those involving the gas-chromatographic properties of the catalyst itself. Under 1 atm of hydrogen, reaction takes place via terminal cleavage with an unusually high apparent activation energy, which suggests a mechanism involving the breaking of many C—H bonds before the C—C bond. This is supported by the lowering of this activation energy at lower hydrogen pressures (0.01 atm) when the rate-determining step becomes defined as the generation of methane from the surface. At very low hydrogen pressures (nitrogen carrier gas) various surface rearrangement reactions have been observed giving chiefly C<sub>5</sub> and C<sub>6</sub> rings in addition to methane.

The hydrogenolysis of hydrocarbons by hydrogen is catalysed by a large number of metals. These appear to fall into two groups.<sup>1, 2</sup> The metals of the first group, within which Pt is the best-studied example, cause cleavage of all C—C bonds with almost equal ease. Those in the second group, typified by Ni, lead to a marked preference for cleavage of the terminal C—C bond of an alkane chain. Our results on Ni/SiO<sub>2</sub> indicate an apparent exclusivity of this terminal attack under appropriate conditions of temperature (low) and pressure (1 atmosphere of hydrogen).

Most of the literature studies have been carried out using the microreactor technique,<sup>3</sup> in which gas passes through a short bed of reactor into an analytical gas-chromatographic column; the chromatographic properties of the catalyst are not used and are often negligible. One of the main purposes of our study has been to show how information can be usefully obtained from a much wider variety of chromatographic techniques <sup>4</sup> specifically developed for catalystic studies and in most of which the chromatographic properties of the catalyst itself are investigated and utilised. These techniques are described very briefly at the end of the experimental section.

In a number of studies,<sup>5-7</sup> the kinetics of the hydrogenolysis reaction of Ni are represented by a rate law of the form

rate = 
$$k p_{hydrocarbon}^n p_{H_2}^{-m}$$

where *n* has a value between 0.8 and 1.0 and *m* lies between 0.7 and 2.6. Apparent activation energies are quite high and in the range 100-250 kJ mol<sup>-1</sup>. The larger values of *m* and of the activation energy appear to occur at higher pressure of hydrogen  $(e.g., 0.1-0.5 \text{ atm}).^5$  Our values for *m* lie within the published range, but we have encountered much higher apparent activation energies. In part, this is associated with the higher hydrogen pressure of 1 atm which we have employed.

The mechanism of the reaction has been much discussed in the literature and there is still some disagreement on its details. The suggested steps are chemisorption

(possibly in several dissociative stages), C—C bond cleavage and, finally, product desorption (involving hydrogenation). Sinfelt <sup>8</sup> and Guczi *et al.* <sup>6</sup> have held that the C—C bond cleavage is rate-determining, while, *e.g.*, Frennet *et al.* <sup>9</sup> suggest that the hydrogenation-desorption step can be the controlling one in many cases. Our own work throws further light on these kinetic aspects. It proves convenient to group the experimental data and the discussion into three sections, distinguished by the hydrogen pressures involved.

# EXPERIMENTAL

The supported nickel catalyst was prepared as follows. Sufficient nickel nitrate (AnalaR grade, B.D.H.) to provide 2 % by weight of nickel on silica was dissolved in a small volume of distilled water and then added to the appropriate weight of silica support (Porasil A or C, 80-100 BSS mesh, Phase Separations). Distilled water was then added to make a thin slurry and this was agitated to assist even distribution of the salt on the silica. The water was slowly evaporated off under vacuum and gentle heating with constant gentle agitation. The catalyst was packed into a gas-chromatographic column (glass, normally 1 m long, 0.45 cm i.d. and fitted with a glass-metal seal at the exit) and reduced *in situ* with a stream of pure hydrogen (20-60 cm<sup>3</sup> min<sup>-1</sup>) at 350-400°C.

Traces of oxygen were removed from all carrier gases with MnO/Celite which reduces the oxygen content to lower than 1 part in 10<sup>9.5</sup>.<sup>10</sup> All the chromatographic apparatus involved only relatively minor modifications of conventional Pye-104 gas chromatographs (Pye-Unicam) with flame-ionisation detectors (or a katharometer detector for hydrogen determination).

The hydrocarbons were mostly supplied by Koch Light and their purity checked by gas-liquid chromatography; where necessary they were further purified by gas chromatography. Experiments involving constant hydrocarbon feeds made use of cylinders of gas mixtures specially prepared by British Oxygen.

### CHROMATOGRAPHIC TECHNIQUES

Apart from the analysis of trapped products which was carried out by conventional gas-liquid or gas-solid chromatography, several other chromatographic techniques were employed. These are outlined beow: details will be found in the references cited.

### (1) ELUTION (WITH REACTION)

This is equivalent to the "normal" gas-chromatographic technique in which a small sample is injected into a gas stream at the beginning of the column. When a catalyst is used as the column material, the resulting "reaction" chromatogram can provide information about the reaction occurring on the column<sup>11</sup> and, from the shape and retention time of the eluted peak of unreacted sample, information about the adsorption of the sample molecules on the catalyst surface. This latter information includes the adsorption isotherm<sup>12</sup> and enthalpies and entropies of adsorption. If the sample molecules react completely before emerging from the normal catalyst column, this adsorption information can usually be obtained by suitable extrapolation from measurements carried out at lower temperatures and/or with faster gas flow rates and shorter column lengths. In particular, the residence time of the reactant on the catalyst surface and its distribution between the gas and the solid surface will always be known from the chromatographic retention times on the catalyst.

### (2) DEUTERIUM EXCHANGE

A small sample of deuterium gas is injected into a hydrogen carrier gas stream passing through the catalyst and its emergence (as HD) followed with a katharometer. The retention of the deuterium then measures the exchange of deuterium with adsorbed hydrogen, water and hydrocarbons.<sup>13, 14</sup>

685

# (3) MICROCATALYTIC <sup>3</sup>

### (4) REACTOR-STOP

This is just a simple modification of (3) in which the reactant is stopped on a (longer) reactor for varying periods of time and then swept off with the products to the analytical gas-chromatographic column. In experiments described in this paper, the stop-time was long compared to the elution time so that the experiment was effectively a static one.

# (5) STOPPED-FLOW <sup>15</sup>

This is a variation of (1) in which the gas flow through the reactor column is stopped from time to time so that the chromatographic process is switched off while the reaction is allowed to continue. Each time the gas flow is restarted, sharp chromatographic peaks are generated on top of the normal "reaction" chromatogram, each peak corresponding to one volatile product of the reaction formed during the stop period. Here again, in this work, detailed kinetic information was extracted from results obtained when the reacting species was stationary in the column, leading to a simpler kinetic treatment.

# (6) SAMPLE-VACANCY <sup>16</sup>

Reactant is fed continuously (in a carrier gas) through a reactor and then an analytical gas-chromatographic column. Samples of the feed are switched periodically into the gas flow between the reactor and chromatographic columns to generate a differential chromatogram, in which the positive peak measures the amount of reactant which has reacted, the negative peaks the amounts of the various volatile products and the difference the amount of involatile product (polymer, coke *etc.*).

# (7) HEATER-DISPLACEMENT<sup>17</sup>

Samples are driven through the catalyst by means of a carrier gas and an external moving heater. This technique is primarily designed for preparative reaction and separation, but some experiments carried out with a  $Ni/SiO_2$  catalyst in this mode support the general results reported in this paper.

# RESULTS

# CHROMATOGRAPHIC CHARACTERISATION OF THE CATALYST

As a preliminary to the studies of the hydrogenolysis reaction on  $Ni/SiO_2$ , the catalyst itself was characterised by treating it as a chromatographic stationary phase. This procedure has the advantage that the interaction of reactants *etc.* with the catalyst surface (expressed, for example, in the form of adsorption isotherms, see below) can be studied close to the reaction temperatures and under other conditions in common with those of the reaction.

The catalyst was first characterised by elution chromatography of reactants below the reaction temperature and the results compared to those obtained on the support material alone. The chromatographic properties are described at length in ref. (4) but, in general, the addition of nickel to the surface increased the alkane retention and rendered the eluted chromatographic peaks more asymmetric. Thus, for example, a sample of n-hexane corresponding to  $10^{-12}$  mol g<sup>-1</sup> adsorbent was eluted symmetrically from Ni/SiO<sub>2</sub> (Porasil "C") in 2 column dead volumes of carrier gas at 174°C and in 1 column dead volume from SiO<sub>2</sub> under the same conditions. Moreover, although symmetrical peaks could be obtained from the SiO<sub>2</sub> up to sample sizes of  $10^{-6}$  mol g<sup>-1</sup> adsorbent, they could only be obtained from the catalyst at or below  $10^{-11}$  mol g<sup>-1</sup>.

In cases where the peaks were asymmetric the adsorption isotherm for the hydrocarbon reactant on the catalyst surface was obtained from the form of the elution profile using the simple method of Huber and Keulemans.<sup>12</sup> This allowed the total

surface concentrations of hydrocarbon reactant on the catalyst to be determined and also the effective contact times for reactants could be calculated. The isotherms, determined at different temperatures, gave values for the isosteric heats of adsorption, for example, at a surface coverage of  $3 \times 10^{-9}$  mol g<sup>-1</sup> of n-hexane, 43.1 kJ mol<sup>-1</sup> on Ni-Porasil "C" and 30 kJ mol<sup>-1</sup> on Porasil "C" alone. The difference between the two isotherms gave an approximate isotherm for the hydrocarbon on the metal alone and from this it was determined that, under the conditions of the hydrogenolysis experiments at 1 atm hydrogen pressure, the metal surface concentration of hydrocarbon reactant was substantially independent of the total hydrocarbon concentration.

The interaction of hydrogen with the catalyst surface was studied in three ways. First, the catalyst, previously heated to 350°C under hydrogen to activate it and then under nitrogen at 350°C to remove adsorbed hydrogen and finally cooled under nitrogen to 100°C, was titrated with small aliquots of hydrogen of approximately  $5 \times 10^{-6}$  mol g<sup>-1</sup>. This hydrogen could be removed by heating to 350°C under nitrogen, or chemically using a hydrocarbon reactant (see below).

The second method involved the extraction of the adsorption isotherm for hydrogen from the elution profile as employed in the case of hydrocarbons above. In this case the hydrogen measured was adsorbed in a different manner to that determined by titrations in that the heat of adsorption determined for isotherms between 200 and 300°C was only 7.8 kJ mol<sup>-1</sup>. Adsorptions of this kind (weak chemisorptions having a heat of adsorption some 10-20 times the latent heat of sublimation of hydrogen) have been observed in the literature [see, e.g., ref. (18)], mostly at low temperatures, and have been called Type "C" adsorptions.

The third method by which the interaction of hydrogen with the catalyst has been observed is deuterium exchange chromatography first introduced by Ozaki et al.<sup>13</sup> This is the subject of another paper.<sup>14</sup> The important result for the purposes of this discussion is that the exchange of deuterium with hydrocarbons has been found to become significant in the same temperature range as the hydrogenolysis reaction itself. Thus the deuterium exchange with n-heptane increased sharply with temperature above 140°C.

# **REACTIONS UNDER 1 atm HYDROGEN PRESSURE**

On our  $Ni/SiO_2$  catalyst, the hydrogenation of alkenes under hydrogen is rapid and quantitative even at room temperature. Aromatic hydrogenation is markedly slower; thus the hydrogenation of benzene to cyclohexane proceeds sufficiently slowly at 80°C for the reaction to be studied quantitatively from the chromatographic profile resulting from benzene injection on to a reactor column under hydrogen carrier gas. Hydrogenolysis under 1 atm pressure of hydrogen does not begin until a temperature in the range 170-220 $^{\circ}$ C is reached and then the rate increases so rapidly with temperature that the hydrogenolysis of any particular hydrocarbon type may be thought of as "switching-on" at one particular temperature. Thus hydrocarbons with a  $-CH_2$ .  $CH_3$  termination react at  $\approx 170^{\circ}C$  while those with a  $CH \cdot CH_3$ termination react at  $\approx 217^{\circ}$ C, at about the same temperature as C<sub>5</sub> and C<sub>6</sub> rings are opened.

The hydrogenolysis of n-alkanes proceeds by a markedly simple series of terminal cleavage reactions [compare ref. (13), (18) and (19)]. Thus for small amounts of reaction, at low temperatures ( $\approx 170^{\circ}$ C) the products from a C<sub>x</sub> hydrocarbon are almost entirely the  $C_{x-1}$  n-alkane and  $CH_4$ , with successively very small amounts of the  $C_{x-2}$ ,  $C_{x-3}$  etc. n-alkane with no  $C_2H_6$ ,  $C_3H_8$  etc. formed directly by cleavage from the end of a longer chain.<sup>4</sup>

The kinetics of the hydrogenolysis of n-dodecane were studied in detail using the reactor-stop technique. Sufficient sample (0.2 mg) was used for each experiment so that the metal surface concentration (see above) reached the plateau value. This was then stopped in the middle of a 1.5 m long reactor column for varying periods of time, the reaction products and unchanged reactant being then swept off into a trap and analysed in a normal gas-chromatographic column.

A typical set of results are given in table 1. The decay of the n-dodecane at each temperature was found to follow reasonable first-order kinetics, but this has no great mechanistic significance since the total n-alkane concentration (reactant plus "heavy" products) remains constant throughout any experiment. However, by varying the quantity of reactant the reaction was shown to follow first-order kinetics. The results as a whole can be reasonably interpreted (*e.g.*, the figures calculated and given in brackets in table 1) in terms of a series of successive first-order reactions

$$C_{12}H_{26} + H_2 \rightarrow C_{11}H_{24} + CH_4 \dots k_{12}$$
  

$$C_{11}H_{24} + H_2 \rightarrow C_{10}H_{22} + CH_4 \dots k_{11}$$
  

$$C_{10}H_{22} + H_2 \rightarrow C_9H_{20} + CH_4 \dots k_{10}$$

with steadily decreasing velocity constants.

TABLE	1.—HYDROGENOLYSIS	OF n-D	ODECANE	ON	Ni/SiO <sub>2</sub>	UNDER	1 atm	HYDROGEN	AT
$177^{\circ}\mathrm{C}$ —fitting the data to a theoretical model									

	$product/10^{-7}$ mol						
stop-time/min	C <sub>12</sub>	C <sub>11</sub>	C10	Cو			
0	4.4 (3.6)	3.5 (3.9)	0.70 (0.37)	0.24 (0.004)			
20	1.5 (1.8)	4.2 (4.6)	2.5 (2.0)	0.79 (0.28)			
40	0.93 (0.9)	4.3 (3.8)	2.9 (3.2)	1.2 (1.0)			
60	0.11 (0.47)	3.8 (2.9)	3.4 (3.8)	1.8 (1.9)			
70	0.35 (0.34)	3.4 (2.4)	3.5 (3.8)	2.1(2.3)			
80	0.26 (0.24)	3.0 (2.0)	3.6 (3.7)	2.2(2.7)			
120	0.01 (0.06)	1.1 (0.86)	2.5 (2.8)	2.5 (3.4)			
140	0.12 (0.03)	0.79 (0.55)	2.0 (2.2)	2.5 (3.3)			

The effective reaction time for each hydrocarbon was taken as the sum of the stop-time and a calculated retention time. The rate constant for the  $C_{12-r}$  hydrocarbon,  $k_r$ , was assumed to fall exponentially with increasing r, since gas-surface distribution coefficients fall in a similar way with increasing r.

The rate constants increase sharply with temperature as is shown, for example, in table 2, from which one calculates the very high apparent activation energy of  $390 \text{ kJ mol}^{-1}$ . These experiments were repeated on the same catalyst to ensure that the activity of the catalyst was not changing significantly. Although a fresh sample of catalyst shows a fairly rapid drop in activity over the first 3 h of use and treatment with  $10^{-4}$  mol of hydrocarbon reactant, it was found that thereafter the activity changed only very slowly with time and hydrocarbon treatment; indeed, its activity towards the hydrogenolysis reaction after the experiments described above was indistinguishable within experimental error from that before.

Similar studies were made with ethylcyclohexane (at 170°C losing one carbon atom to give only methylcyclohexane and methane), 2,3-dimethylbutane (no terminal  $-CH_2CH_3$ ) and cyclohexane (ring-opening and as an example of a hydrogenolysis reaction which cannot take place on a terminal carbon atom). The results are summarised in table 3.

temperature/°C	first-order rate constant/min-
177	3.38×10 <sup>-2</sup>
184	$1.05 \times 10^{-1}$
188	$1.70 \times 10^{-1}$
194	1.10
198	2.59

TABLE 2.—KINETIC	RESULTS	FOR T	HE HYDI	ROGENOLYS	SIS OF	n-DODECANE
ON	Ni/SiO <sub>2</sub>	UNDE	r 1 atm	HYDROGE	N	

TABLE 3.—Effect of temperature on hydrogenolysis reactions with  $Ni/SiO_2$  under 1 atm HYDROGEN

reactant	temperature/°C for $k = 10^{-2} \min^{-1}$	change in rate for 10°C	activation energy /kJ mol <sup>-1</sup>
n-dodecane	174	× 8.4	392
2,3-dimethylbutane	215	×4.6	296
ethyl cyclohexane	163	× 5.3	305
cyclohexane (ring opening)	219	× 21	556

# REACTIONS UNDER 1 % HYDROGEN

A series of experiments were carried out using as carrier gas a mixture of 1 % hydrogen in nitrogen. A number of reactions were studied using the microreactor technique (a 20 cm long reactor leading directly on to the analytical column without trapping). As expected there was an enormous increase in reaction rates and the reaction was now conveniently studied at very significantly lower temperatures ( $\approx 120^{\circ}$ C). There was a lower apparent activation energy of 200 kJ mol<sup>-1</sup> for the alkane cleavage step.

A reaction chromatogram resulting from the injection of purified n-hexane on to the reactor at 142°C is shown in fig. 1. It brings out a number of features which contrast with the results found under 1 atm hydrogen pressure. (a) For a similar rate of reaction the temperature is now  $\approx 70^{\circ}$ C lower. (b) In addition to the sharp peaks resulting from the rapidly formed hydrogenolysis products ( $C_{x-1}$ ,  $C_{x-2}$ ) etc.) there is an underlying profile (dotted line) which results from the slow production of methane which continues for some considerable time after the reactant has left the reactor column. (c) The amounts of intermediate hydrocarbons were now found to be slightly greater indicating some departure from the simple terminal cleavage mechanism. More detailed investigations were made using the hydrogenolysis of ethyl benzene (under these conditions of temperature and hydrogen pressure the aromatic is just thermodynamically stable with respect to the cycloalkane) which is particularly simple as it yields only toluene and a very little benzene

with the associated reaction profile of methane, see fig. 2. The kinetics of this methane production were followed by stopped-flow chromatography. Samples of ethyl benzene were injected into a reactor column connected in series with a KCl/ $Al_2O_3$  analytical gas-chromatographic column operated at 40°C. This latter column retained the reactant and the toluene and benzene products for a very long period, thus allowing the methane profile to be studied without interference. The stopped-flow chromatograms also provided further proof that the profile consisted entirely of methane as only methane stopped-flow peaks were obtained. They also showed that the methane-generating species was stationary in the reactor column.



FIG. 1.—Microreactor chromatogram of the hydrogenolysis of n-hexane on Ni/SiO<sub>2</sub> at 142°C under 1 % hydrogen in nitrogen (total pressure 1 atm). (20 cm length of catalyst in the reactor followed by squalane/Celite analytical gas-chromatographic column.)

The rates of production of methane are plotted in fig. 3 as a function of time for three different reactor temperatures. The general pattern seems to be an initial increase in reaction rate (noticeable in the lower temperature results) to a maximum, an approximately first-order region (linear logarithmic plot) and a final flattening towards a zero-order condition. Very analogous results have been obtained by us for the reduction of CO to  $CH_4$  on the same catalyst and suggest perhaps an initial self-poisoning of the surface by high concentration of reactant. From the linear portions of the plots, first-order velocity constants were determined which allowed an activation energy of 77 kJ mol<sup>-1</sup> and a pre-exponential factor of  $2 \times 10^8$  min<sup>-1</sup> to be calculated.

The effect of changing the carrier gas from 1 % hydrogen to pure nitrogen was investigated at the linear portion (fig. 3) of the methane formation reaction. The rate of production of methane was found to drop immediately to a very low value.



FIG. 2.—Microreactor chromatogram of the hydrogenolysis of ethylbenzene on Ni/SiO<sub>2</sub> at 141°C under 1 % hydrogen in nitrogen (total pressure 1 atm). (20 cm length of catalyst in the reactor followed by squalane/Celite analytical gas-chromatographic column.) (a) ethyl benzene, (b) toluene, (c) benzene and (d) methane profile.



FIG. 3.—Kinetics of methane production in the hydrogenolysis reaction of ethylbenzene under 1 % hydrogen in nitrogen. (Stopped-flow chromatography.) ○, 122; □, 133 and ●, 165°C.

After 40 min the nitrogen was replaced by 1 % hydrogen when the methane production rate was restored to its previous value and the kinetic plot continued as though the reaction had not been interrupted. This demonstrates the absence of significant side reactions of the  $C_1$  surface species to give non-hydrogenateable products.

The rate of formation of methane and the rate of the hydrogenolysis reaction itself were similarly studied using hydrogen pressures (in one atmosphere of nitrogen) varying from 0.44 to 14 %. The total amount of methane produced for the same sample size of ethyl benzene and the same contact time was found to decrease with temperature; this was taken as a measure of the rate of the hydrogenolysis reaction.



log10 (hydrogen pressure)

FIG. 4.—Log-log plot of total methane yield against hydrogen pressure for the hydrogenolysis reaction.

A plot of the logarithm of the hydrogenolysis rate against the logarithm of the hydrogen pressure (fig. 4) has a slope of -1.7, showing that over this hydrogen pressure range the order of the hydrogenolysis reaction with respect to hydrogen pressure is thus -1.7. By comparing the hydrogenolysis rate of an n-alkane at 142°C under 1% hydrogen with that calculated for 1 atm of hydrogen (*i.e.*, by extrapolation from the results obtained at higher temperatures) the order of the hydrogenolysis reaction 0.01 to 1 atmosphere was found to be -2.3 with respect to the hydrogen pressure. These values are in general agreement with those in the literature and fit well with the mechanism proposed below involving successive stages of C—Ni bond formation with release of gaseous hydrogen before the activated C—C cleavage step.

From the linear middle portions of the curves in fig. 3, the velocity constants for the  $C_1$  hydrogenation step to  $CH_4$  can be calculated. From the variation of these with hydrogen pressure, an order with respect to hydrogen pressure for this step can then be separately evaluated. This order was found to be  $\approx +1$  at low hydrogen pressures (below 0.02 atm). With increasing hydrogen pressure the order tends

towards zero. This change in order parallels the change in surface hydrogen concentration from partially covered to effectively fully covered shown by the hydrogen adsorption isotherms previously determined.

If the  $C_1$ -fragment hydrogenation rate increases with hydrogen pressure while the hydrogenolysis decreases, it is clear that the kinetic distinction between the two steps will only become apparent at the lower hydrogen pressures. In all the experiments under 0.01 atmosphere hydrogen pressure there was, as under 1 atm of hydrogen, only a very small loss of hydrocarbon to the column as polymer and coke.

### **REACTIONS UNDER NITROGEN CARRIER GAS**

A third series of experiments were carried out using cylinder nitrogen as carrier gas, *i.e.*, with a pressure of hydrogen  $\approx 5 \times 10^{-8}$  atm. Under these conditions, as well as the hydrogenolysis reaction of alkanes, it was also possible to investigate the reaction of methane, olefins and benzene with the Ni/SiO<sub>2</sub> surface, all of which throw some light on the mechanism of the hydrogenolysis reaction itself. Most of these measurements were made using sample-vacancy chromatography.<sup>16</sup>

### ALKANES

A preliminary investigation was made by injecting a series of equal-sized samples of propane on to a 1.5 m reactor column and determining the amount eluted at different temperatures. Fig. 5 shows the result of this experiment. It will be observed that chemical interaction with the surface begins to be significant at  $\approx 110-115^{\circ}$ C and above these temperatures progressively more reaction takes place, until very little propane emerges from an injection at 180°C. In each case the column was previously heated in hydrogen at 350°C for 1 h, cooled in hydrogen and the carrier gas then changed to nitrogen. If the amount of propane permanently retained by the column is taken as a measure of the rate of reaction, then the apparent activation energy for chemisorption from the gas phase is  $\approx 100 \text{ kJ mol}^{-1}$ .

A more detailed study was made with a constant feed of n-hexane in nitrogen (195 v.p.m. from a specially prepared cylinder) using sample-vacancy chromatography.



FIG. 5.—Consumption of propane during its elution through Ni/SiO<sub>2</sub> under nitrogen.

A 1.5 m reactor column was followed by a 1.5 m analytical column packed with 10 % squalane on Celite. Before reaction the catalyst was treated in one of two ways: either the activated column was cooled to the reaction temperature (157°C) under hydrogen and the carrier gas then changed briefly to nitrogen to sweep out gaseous and weakly-adsorbed hydrogen or the reactor containing the catalyst was first heated to 350°C under nitrogen for an hour to remove much of the more strongly adsorbed hydrogen and then cooled in nitrogen to the reaction temperature.

In each case the n-hexane reacted to give methane and no intermediate  $C_2-C_5$  hydrocarbons, although small amounts of benzene (rising to a maximum of 10 % yield from hexane) were formed in the latter stages of the reaction as the hexane itself began to emerge from the reactor. A typical reaction profile is shown in fig. 6 for the case where the surface was initially covered with chemisorbed hydrogen.



time/min

FIG. 6.—Hydrogenolysis of n-hexane on Ni/SiO₂ at 157°C under nitrogen as revealed by sample-vacancy chromatography. ●, Rate of uptake of C<sub>6</sub>H<sub>14</sub>; ○, rate of production of CH<sub>4</sub>. (195 v.p.m. of n-hexane in nitrogen through a 1.5 m reactor column followed by a 1.5 m squalane/Celite analytical gas-chromatographic column.) Inset shows benzene production × 2.5.

When the surface had been pretreated at  $350^{\circ}$ C in nitrogen the pattern was similar with much the same plateau value of methane production, but the amount of methane generated was less and the hexane broke through the reactor earlier. This suggests that the reaction is essentially the same in the two circumstances, the reaction occurring mainly in a zone of the reactor column being built up until A in fig. 6 and emerging from the column between the dotted line and B ahead of the hexane front, the plateau value of methane being controlled by the feed rate of n-hexane to the column.

When the reaction had effectively ceased, the n-hexane-nitrogen feed was cut off and the column gas cleared with pure nitrogen. The carrier gas was then switched to hydrogen when a further quantity of methane (stage 2) was produced, most of which appeared immediately as a sharp peak, although a small amount occurred in a trail which was shown to be of kinetic origin by means of stopped-flow chromatography.

----

#### 694 **GAS-CHROMATOGRAPHIC STUDIES OF HYDROGENOLYSIS**

The stoichiometries of the reaction for five separate experiments are given in table 4. Unlike the experiments at 1 and 0.01 atm pressure of hydrogen, there is now significant permanent loss of carbon to the catalyst. This is only removed slowly by hydrogen at 400°C and rather more rapidly by steam at 400°C.

The fact that no intermediate  $(C_2-C_5)$  hydrocarbons are produced under conditions when (for example) a propane injection would yield 10 % unreacted propane on passage through the whole reactor length must mean that the C--C bond breaking process now takes place without the formation of free  $C_{x-1}$  alkane. Thus the intermediate C5-C2 fragments are presumably attached firmly to the surface via C-Ni bonds until all the C-C bonds have been broken.

		carbo	n atoms/10-	<sup>6</sup> mol g <sup>-1</sup>		
	Ni pi	retreated wit	$h H_2$	Ni pretreated with N <sub>2</sub>		
	1	2	3	1	2	
total hexane take-up	9.9	10.2	9.6	5.8	7.5	
methane (stage 1)	2.6	2.5	2.5	0.9	1.4	
benzene	0.4	0.4	0.44	0.4	0.3	
methane (stage 2)	5.6	5.6	6.3	4.0	5.2	
C permanently retained	1.4	1.7	0.3	0.4	0.6	

TABLE 4.—STOICHIOM	ETRY OF TH	E HYDROGENOLY	SIS REACTION	OF n-HEXANE	ON $N1/S1O_2$ A	١T
		157°C under n	ITROGEN			

Some light may be thrown on the nature of the surface species by the results of further experiments which were carried out by injecting small quantities of hydrogen into the reactor when the reaction had ceased, but while n-hexane was still being fed to the column. Apart from methane and traces of  $C_2$ - $C_4$  hydrocarbons, the main products were cyclopentane and methylcyclopentane with smaller amounts of n-pentane. When hydrogen injections were made at regular intervals  $(0.15 \text{ cm}^3)$ every 800 s) the yields of reaction products from the column at 159°C came to a steady state corresponding to 5 % conversion to cyclopentane and methylcyclopentane, 1 % methane and 94 % unreacted n-hexane. The ratio of the yields of hydrocarbons was found to be largely independent of the temperature at which this hydrogenation was carried out, but the total yield increased with temperature (e.g.,from 0.5 % conversion at  $120^{\circ}$ C to 6 % at  $160^{\circ}$ C).

### BENZENE

The (non-hydrogenolysis) reactions of benzene, olefins and methane with the  $Ni/SiO_2$  catalyst under nitrogen carrier gas were also studied. In each case the surface was activated in hydrogen at 350°C, cooled in hydrogen to the operating temperature and then flushed with nitrogen before the reactant was introduced. Sample-vacancy-chromatographic studies were carried out with a steady feed of benzene (200 v.p.m.) in nitrogen over the temperature range 107-248°C. At the lowest temperature the benzene broke through the reactor as a sharp front and on switching to nitrogen the bulk of the adsorbed benzene was rapidly recovered and was thus presumably physisorbed. As the temperature was raised, the benzene front became more diffuse and more benzene was left (chemisorbed) on the column on switching to nitrogen. This diffuse front reflects the slow chemisorption process and itself becomes sharper again as the temperature rose still further. No methane

# K. F. SCOTT AND C. S. G. PHILLIPS

or other volatile hydrocarbons were found in any of these experiments, but hydrogen was displaced from the surface corresponding to approximately  $3 \times 10^{-6}$  mol per g of catalyst (the total benzene adsorbed was  $5 \times 10^{-7}$  mol<sup>-1</sup> or  $3 \times 10^{-6}$  mol of carbon per g). Under these conditions the hydrogenation of benzene to cyclohexane would be thermodynamically unfavourable.

The species remaining on the surface were investigated by injecting hydrogen after any physisorbed benzene had been removed by flushing the column with nitrogen. The product from the column treated at 248°C was almost exclusively methane, but from columns treated with benzene (and then hydrogen) at lower temperatures a variety of hydrocarbons were formed as is shown in table 5.

	carbon atoms/mol per g catalyst					
hydrocarbon	yield from column treated at 104°C	yield from column treated at 151°C				
methane	2.2×10 <sup>-9</sup>	1.6×10 <sup>-7</sup>				
cyclohexane	$4.0 \times 10^{-7}$	3.6×10 <sup>-7</sup>				
benzene	$1.1 \times 10^{-7}$	$1.6 \times 10^{-7}$				
cvclopentane	$7.2 \times 10^{-9}$	$1.2 \times 10^{-8}$				
pentane	$4.6 \times 10^{-9}$	1.1×10 <sup>-8</sup>				
total	$5.2 \times 10^{-7}$	$7.0 \times 10^{-7}$				
benzene chemisorbed	$3 \times 10^{-6}$	$3 \times 10^{-6}$				

TABLE 5.—HYDROCARBONS FROM THE HYDROGENATION OF CATALYST SURFACES TREATED	WITH
BENZENE AT DIFFERENT TEMPERATURES UNDER NITROGEN	

These figures show that the most dramatic change with temperature is the yield of methane which is  $\approx 70$  times greater at the higher temperature (associated with a greater degree of C—C bond cleavage on the surface) while, in comparison, all the other yields are changed rather little. About 20 % of the chemisorbed benzene was recovered in this way, a large proportion of the remainder being removed at higher temperatures (350°C) as methane with hydrogen.

### OLEFINS

Similar experiments were carried out with propene and pent-1-ene (both 200 v.p.m. in nitrogen) at 107°C. In each case the olefin was rapidly chemisorbed at this low temperature (contrast propane) but a proportion was converted to the corresponding alkane. A typical result is shown in fig. 7. In the case of pent-1-ene, the samplevacancy chromatogram was more complex as considerable isomerisation to the pent-2-enes occurred. The propane and pentane produced corresponded to  $2.5 \times$  $10^{-6}$  mol per g of catalyst, while the hydrocarbon chemisorption corresponded to an average of  $2.5 \times 10^{-6}$  mol of carbon per g. The species remaining on the surface were again investigated either by hydrogen injections or by changing to hydrogen carrier gas. A large number of hydrocarbons were identified including methane, straight and branched alkanes and  $C_5$  and  $C_6$  rings with their methyl derivatives. At 107°C, 36 % of the chemisorbed material was recovered as methane, 53 % as higher hydrocarbons and 11 % was not removed from the surface. The yield of ring compounds and branched-chain isomers did not change appreciably with reaction and hydrogenation temperature, but the yield of n-alkanes dropped at the higher temperatures as expected from their ready hydrogenolysis.



FIG. 7.—Interaction of propene with Ni/SiO<sub>2</sub> under nitrogen. (107°C, 200 v.p.m. of propene in nitrogen.) ○, Propene; ●, propane.

### METHANE

Methane was found to chemisorb on to the Ni/SiO<sub>2</sub> surface only at temperatures higher than those required for alkanes and thus markedly higher than those required for olefins or benzene. Fig. 8 illustrates the result of feeding methane (1000 v.p.m. in nitrogen) on to a 1.5 m reactor column at 198°C. The slow ascent of the effluent methane concentration indicates that the chemisorption reaction is slow at this temperature. From the variation with temperature of the methane adsorbed at equilibrium  $(3.7 \times 10^{-8}, 9.8 \times 10^{-9} \text{ and } 4.9 \times 10^{-9} \text{ mol g}^{-1}$  at 241, 287 and 319°C, respectively) the effective heat of adsorption of methane was calculated as 67 kJ mol<sup>-1</sup>.



FIG. 8.—Adsorption of methane on Ni/SiO<sub>2</sub> at 198°C under nitrogen.

### K. F. SCOTT AND C. S. G. PHILLIPS

697

When the methane feed was interrupted and the carrier gas changed to nitrogen, the methane was slowly desorbed and the kinetics of this desorption were followed by stopped-flow chromatography. Approximately 10 % of the adsorbed methane was recovered in this way (e.g., in 500 min at 200°C) and the remaining 90% on changing to hydrogen carrier gas. The kinetics of the desorption reaction were also studied under 1 % hydrogen in nitrogen. The order of the reaction with respect to hydrogen pressure was found to be  $\approx +0.3$ . The activation energy of the reaction appears to change from  $\approx 170$  kJ mol<sup>-1</sup> under nitrogen to  $\approx 40$  kJ mol<sup>-1</sup> under 1 % hydrogen. During the desorption process, small quantities ( $\approx 1$  % of the methane) of higher hydrocarbons were generated. These were mainly cyclopentane, methylcyclopentane, dimethylcyclopentane, cyclohexane, methyl cyclohexane, benzene and toluene when the desorption process was carried out under 1 % hydrogen. Under hydrogen the benzene and toluene were hydrogenated to increase the sizes of the cyclohexane and methylcyclohexane peaks.

# DISCUSSION

The results obtained under 1 % hydrogen show that the overall reaction can be divided into two kinetically distinguishable stages, namely (1) "Hydrogenolysis", in which the C—C bond is broken and the  $C_{x-1}$  paraffin desorbed. The rate of this reaction decreases rapidly with hydrogen pressure, the average order being  $\approx$  -2 over the range 0.01-1 atm but probably, as the literature suggests, becoming increasingly negative with increasing hydrogen pressure. (2) "Methanation", in which the C<sub>1</sub> surface species is hydrogenated to gaseous CH<sub>4</sub>. The rate of this reaction increases with hydrogen pressure.

At 1 atm pressure of hydrogen the second stage will occur so much faster than the first that hydrogenolysis must be rate-determining. The marked effect of hydrogen pressure suggests that the active species in stage 1 is formed by loss of hydrogen atoms from the adsorbed paraffin with the formation of C—Ni bonds. Thus, at 1 atm pressure of hydrogen, the predominant adsorbed species may, for example, be II or III while the C—C bond breaking actually occurs via V or VI.



We suggest that the initial steps in this stage are essentially under thermodynamic control, while the C—C cleavage is kinetically controlled. Such a mechanism could then account for the very large apparent activation energies which have been found, values which are clearly too high for any plausible one-step process. Note that, since we are concerned with reactant on the surface, the activation energies discussed here are for the surface reactions; they have no significant contribution from the heat of adsorption as is so often the case when heterogeneous reactions are studied in terms of gas-phase concentrations.

Thus if [X] represents the concentration of the surface species involved directly in the C—C cleavage reaction, this will be formed from the predominant surface species,

**F** • **T** 

### 698 GAS-CHROMATOGRAPHIC STUDIES OF HYDROGENOLYSIS

A, with the release of n molecules of H<sub>2</sub>, where, for example, n would be 3 if X were V and A were II. We might then expect the rate of the reaction to be given approximately by

rate = 
$$\frac{kT}{h} \exp(S^{\dagger}/R) \exp(-E^{\dagger}/RT) [X][H_2]^{y}$$

where  $S^*$  and  $E^*$  are, respectively, the entropy of activation and the energy of activation of the C—C cleavage step and where the order of this step with respect to hydrogen pressure is y. Furthermore

$$\frac{[X][H_2]^n}{[A]} = \exp(\Delta S^{\Theta}/R) \exp(-\Delta H^{\Theta}/RT)$$

where  $\Delta S^{\ominus}$  and  $\Delta H^{\ominus}$  are, respectively, the standard entropy and enthalpy changes for the overall reaction

so that

$$A \rightarrow X + nH_2$$
,

rate = exp 
$$[(\Delta S^{\ominus} + S^{\dagger})/R]$$
 exp  $[-(\Delta H^{\ominus} + E^{\dagger})/RT] \frac{[\Lambda]}{[H_2]^{n-y}}$ .

For the n-dodecane case  $(\Delta S^{\ominus} + S^{\pm})$  would then be  $\approx 550 \text{ J deg}^{-1} \text{ mol}^{-1}$ . Now, if the activated cleavage step involves the release of both CH<sub>4</sub> and the C<sub>x-1</sub> alkane, then the maximum entropy release would be  $\approx 200 \text{ J deg}^{-1} \text{ mol}^{-1}$ . However, for each of the individual steps leading up to this, *e.g.*,



 $\Delta S^{\oplus} \approx 130 \text{ J deg}^{-1} \text{ mol}^{-1}$ , so that the observed apparent entropy of activation suggests that 3-4 steps are involved between A and X, *i.e.*, the active species for the C—C cleavage step might well be VI.

Since the active species is presumably only present in very small amounts in relation to the predominant adsorbed species A, these individual steps are thermodynamically unfavourable, so that if they have favourable entropy changes  $\approx 130 \text{ J}$  deg<sup>-1</sup> mol<sup>-1</sup> they must be endothermic to the extent of more than 60 kJ mol<sup>-1</sup>. If 4 steps were indeed involved this would mean that the "true" activation energy for the final C—C bond breaking would be reduced from 390 kJ mol<sup>-1</sup> to less than 150 kJ mol<sup>-1</sup>, which is much more reasonable for a reaction proceeding quite smoothly just below 200°C.

By similar mechanistic analyses to that used above for n-alkane hydrogenolysis, the apparent entropies of activation for the reactions of 2,3-dimethylbutane and cyclohexane would suggest that the final C—C bond cleavage occurred with surface species such as VII and VIII, respectively.



### K. F. SCOTT AND C. S. G. PHILLIPS

Attack at non-terminal carbon atoms (e.g., cyclohexane) was so much slower under 1 atm of hydrogen that it was a negligible reaction in the normal hydrogenolysis of an n-alkane. However, cyclohexane ring-opening was shown to have a higher apparent activation energy and, therefore, a greater apparent entropy of reaction, suggesting that cleavage of a non-terminal C-C bond necessitates the formation of a greater number of C-Ni bonds. The effect of reducing hydrogen pressure should, therefore, have an even more marked enhancement of the attack on non-terminal C-C bonds. This was shown directly by the fact that the cyclohexane (and more so the cyclopentane) ring were opened readily under 1 % hydrogen ; indeed the distinction between n-alkane and ring-opening reaction was now much less marked than it had been under 1 atm of hydrogen.

The literature studies of hydrogenolysis on supported Ni surfaces have commonly been carried out at pressures of hydrogen between 0.01 and 0.1 atm so that the peculiarly high selectivity for the terminal C-C bond cleavage which we have observed at 1 atm of hydrogen may be largely a result of this sensitivity to hydrogen pressure.

As the hydrogen partial pressure was reduced, the formation of methane became kinetically distinguishable from the release of the major alkane fragment in the cleavage reaction: that is, hydrogenation of the  $C_1$  fragment from the surface became slow and measurable.

Simple kinetic analysis now leads to an activation entropy  $\approx -130 \text{ J deg}^{-1} \text{ mol}^{-1}$ , which could correspond to



but less plausibly to

 $\begin{array}{ccc} \text{CH}_3 & \text{H} \\ | & +\text{H}_2 \rightarrow | +\text{CH}_4 \ (\approx 10^{-5} \text{ atm}) \\ \text{Ni} & \text{Ni} \end{array}$  $\Delta S^{\ominus} \approx 130 \text{ J deg}^{-1} \text{ mol}^{-1}$ .

At the very low hydrogen partial pressure associated with nitrogen carrier gas, activated chemisorption of hydrocarbons occurred at 100°C and above, leading to considerably dissociated adsorbed species which underwent rearrangement on the surface to give a range of products on hydrogenation. Presumably at this hydrogen pressure the dehydrogenation of the adsorbed species proceeds beyond the species VI described above, yielding a multiply-bonded carbonaceous residue which can rearrange.

The work was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. K. F. S. was the holder of a British Petroleum Research Studentship.

- <sup>4</sup> K. F. Scott and C. S. G. Phillips, J. Chromatog., 1975, 112, 61.
- <sup>5</sup> F. E. Shephard, J. Catalysis, 1969, 14, 148.
- <sup>6</sup> L. Guczi, B. S. Gudkov and P. Tetenyi, J. Catalysis, 1972, 24, 187.
- <sup>7</sup> J. H. Sinfelt, J. L. Carter and D. J. C. Yates, J. Catalysis, 1972, 24, 283.

<sup>&</sup>lt;sup>1</sup> H. Matsumoto, Y. Saito and Y. Yoneda, J. Catalysis, 1970, **19**, 101. <sup>2</sup> E. Kikuchi, M. Tsorumi and Y. Morita, J. Catalysis, 1971, **22**, 226.

<sup>&</sup>lt;sup>3</sup> R. T. Kokes, H. Tobin and P. H. Emmett, J. Amer. Chem. Soc., 1955, 77, 5860.

<sup>8</sup> J. H. Sinfelt, J. Catalysis, 1972, 27, 468.

- 9 A. Frennet, L. Degols, G. Lienard and A. Crucq, J. Catalysis, 1974, 35, 18.
- <sup>10</sup> C. R. McIlwrick and C. S. G. Phillips, J. Phys. (E), 1973, 6, 1208.
- <sup>11</sup> M. van Swaay, in Advances in Chromatography, ed. J. C. Giddings and R. A. Keller (Marcel Dekker, New York, 1969), p. 363.
- <sup>12</sup> J. F. K. Huber and A. I. M. Keulemans, in Gas Chromatography 1962, ed. M. van Swaay (Butterworths, London, 1962), p. 26.
- <sup>13</sup> A. Ozaki, F. Nozaki, K. I. Maruya and S. Ogaswara, J. Catalysis, 1967, 7, 234.
- <sup>14</sup> K. F. Scott and C. S. G. Phillips, J. Catalysis, 1978, 51, 131.
- <sup>15</sup> R. M. Lane, B. C. Lane and C. S. G. Phillips, J. Catalysis, 1970, 18, 281.
- <sup>16</sup> C. S. G. Phillips and C. R. McIlwrick, Analyt. Chem., 1973, 45, 782.
- <sup>17</sup> C. M. A. Badger, J. A. Harris, K. F. Scott and C. S. G. Phillips, J. Chromatog., 1976, 126, 11.
   <sup>18</sup> A. Ozaki, Y. Shigehara and S. Ogaswara, J. Catalysis, 1967, 8, 22.
- <sup>19</sup> J. A. Rijks and C. A. Cramers, Chromatographia, 1974, 7, 99.

# (PAPER 9/954)