# Reactions of n-Hexane and Methylcyclopentane on Alumina-supported Platinum–Rhenium Catalysts

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Received 16th February, 1982

Reactions with excess hydrogen of n-hexane and of methylcyclopentane at 550 K have been studied in a static reactor system on a series of platinum-rhenium catalysts containing 0.5% metal by weight. The various reactions which took place have been grouped into two main categories according to the pattern of activity found across the series of catalysts. (1) Ring opening of methylcyclopentane, and the minor process of its demethanation, and 1,5 cyclization of n-hexane occurred readily over platinum but activity decreased steadily with increase of rhenium content and was low for pure rhenium. (2) Skeletal isomerization of n-hexane than with methylcyclopentane and general hydrogenolysis (more important with n-hexane than with methylcyclopentane) were catalysed most effectively by catalysts with about equal amounts of the two metals and less rapidly on the platinum-rich or rhenium-rich catalysts. It is suggested that the first category of reactions involves either 1,5 or 1,2 adsorbed hydrocarbon species whereas the second category is dependent on the formation of 1,3 adsorbed species.

Alumina-supported platinum-rhenium catalysts are used extensively in the commercial reforming of hydrocarbons.<sup>1, 2</sup> Their principal advantages, when compared with catalysts containing only a single metal, are longer life and higher selectivity.

Several types of reactions have been investigated in detail on catalysts based on platinum and rhenium. These include the hydrogenolysis and isomerization of n-butane,<sup>3, 4</sup> cyclopentane,<sup>4</sup> 2,2-dimethylpropane<sup>5</sup> and n-pentane<sup>6</sup> together with the exchange of methane<sup>3</sup> and benzene<sup>4</sup> with deuterium. The catalytic characteristics of platinum-rhenium catalysts depend markedly on the nature of the reaction being investigated. For example, the rate of exchange of methane with deuterium is high on pure platinum and decreases monotonically with the addition of rhenium<sup>3</sup> while the rates of hydrogenolysis of n-butane<sup>3</sup> and 2,2-dimethylpropane<sup>5</sup> are a maximum at a catalyst composition of *ca*. 60% rhenium.

In contrast to the behaviour of n-butane<sup>3</sup> and 2,2-dimethylpropane, Tournayan *et al.*<sup>6</sup> have reported that the turnover numbers for the reaction of n-heptane with hydrogen at 673 K decreased linearly with the addition of rhenium to platinum, with the selectivities towards hydrogenolysis and cyclization passing through a maximum for a catalyst composition of *ca.* 85% rhenium.

The object of the present work was to examine the reactions of the two  $C_6$  hydrocarbons, n-hexane and methylcyclopentane, on our series of platinum-rhenium catalysts<sup>3,5</sup> for comparison with published results, already described, for  $C_4$ ,  $C_5$  and  $C_7$  hydrocarbons. We chose the reaction temperature of 550 K rather than the higher temperature of 673 K used by Tournayan *et al.*<sup>6</sup> partly to have a better chance of measuring the initial rates of the various types of reaction and partly to enable us to make valid comparisons with our results for the smaller hydrocarbons.

#### EXPERIMENTAL

The preparation of the six supported platinum-rhenium catalysts from chloroplatinic acid, perrhenic acid and Condea Pural SB  $\gamma$ -alumina (260 m<sup>2</sup> g<sup>-1</sup>) has been described.<sup>3</sup> The weighed quantity of catalyst used in each experiment was in the range 0.02-0.2 g as appropriate for accurate determination of reaction rate.

Methylcyclopentane and n-hexane (Puriss grade, Koch-Light Laboratories) were degassed and purified by vacuum distillation. Hydrogen (B.O.C.), used in the reduction of catalysts, was purified by passage through a Deoxo (Engelhard) unit, a bed of 4A molecular sieve and a trap at 77 K. Hydrogen for use in preparing reaction mixtures was purified by diffusion through a heated palladium-silver membrane and a trap at 77 K.

All reactions were carried out in a static reaction system<sup>7.8</sup> with a facility for analysis of samples of the reaction mixture by gas chromatography. Before use, each catalyst sample was purged with flowing hydrogen ( $15 \text{ dm}^3 \text{ h}^{-1}$ ) in the reaction vessel (volume 180 cm<sup>3</sup>) for 30 min, heated to 573 K for 45 min and then reduced for 16 h at 753 K, still in flowing hydrogen, before cooling to reaction temperature and evacuation of the gas-phase hydrogen. For each reaction the charge of hydrocarbons in the reaction vessel was 560 Pa and sufficient hydrogen was added, along with the hydrocarbon, to yield a hydrogen: hydrocarbon ratio of 10:1; the charge gave  $1.6 \times 10^{19}$  molecules of hydrocarbon in the reaction vessel.

Reactions were followed by periodic withdrawal of samples of gas into an evacuated sample loop (volume 0.5 cm<sup>3</sup>) and analysis using a Perkin-Elmer type F11 gas chromatograph fitted with a flame ionization detector. As no chromatographic column which could separate all of the products formed during reaction was available, two reactions, analysed using different columns, were performed for each catalyst-hydrocarbon-hydrogen combination. Methylcyclopentane, cyclopentane and acyclic hydrocarbons with carbon numbers between one and six were separated on an 8 m column of propylene carbonate operated at 296 K. An 8 m column of bentone-1, also at 296 K, separated methylcyclopentane, cyclohexane, cyclohexene, benzene and the methylcyclopentenes.

The integrated peak areas from each reaction were appropriately corrected for sensitivity (using methylcyclopentane as a standard to link each pair of experiments, as it was separated by both columns) and used to express the amount of each hydrocarbon present as a percentage of the total carbon in the gas phase.

#### RESULTS

#### **REACTION OF n-HEXANE WITH HYDROGEN**

As an example of a typical experiment, the reaction of n-hexane on the pure platinum catalyst at 550 K is given in fig. 1. The distribution of products is presented in the terms of the four main reactions which occurred with n-hexane; these were: (1) isomerization (I) forming 2-methylpentane and 3-methylpentane, (2) 1,5 cyclization giving methylcyclopentane, (3) general hydrogenolysis forming smaller hydrocarbons with less than six carbon atoms (n-pentane, 2-methylbutane, n-butane, 2methylpropane, propane, ethane and methane), (4) isomerization (II) forming 2,2dimethylbutane. It may be seen from fig. 1 that the main initial products on platinum were those associated with isomerization (I). Furthermore, the shape of the curve for the formation of 2,2-dimethylbutane indicates that isomerization (II) was largely a consecutive reaction from the products of isomerization (I) with little direct reaction from n-hexane.

From plots of the product distributions as a function of time the initial rates of each reaction were determined by constructing tangents at zero time. Such rates, for each of the principal types of reaction occurring, are presented in table 1. The initial product distributions of molecules containing less than six carbon atoms formed by hydrogenolysis are presented in table 2, together with R, the ratio of the rates of



FIG. 1.—Reaction of n-hexane with hydrogen on the 100% Pt catalyst at 550 K expressed as percentages of the total carbon present in the gaseous compounds: ×, n-hexane; ●, products from isomerization (I); △, methylcyclopentane; ○, products from general hydrogenolysis; ▲, 2-2-dimethylbutane.

TABLE I. INTIAL KAILS FOR THE REACTION OF HERAND WITH HIDROGEN AT 55	TABLE	1	-INITIAL	RATES <sup>a</sup>	FOR	THE REACTI	ON OF	n-HEXANE	WITH	HYDROGEN	AT	550	Κ
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catalyst composition Pt/Re	disappearance of n-hexane	isomerization (I)	methyl- cyclopentane formation <sup>b</sup>	general hydrogenolysis	2,2- dimethylbutane formation	ratio of 3-MP to 2-MP
100/0	0.73	0.49	0.17	0.06	0.01	0.66
80/20	1.37	0.82	0.36	0.18	0.01	0.71
60/40	2.04	1.75	0.03	0.23	0.03	0.75
40/60	1.43	1.06	< 0.01	0.36	0.01	0.77
20/80	0.34	0.23	< 0.01	0.10	0.01	0.80
0/100	0.13	0.05	< 0.005	0.08	0.002b	0.71

<sup>*a*</sup> In terms of the total carbon content of the gas phase, in units of  $\% \min^{-1} (0.2 \text{ g of catalyst})^{-1}$ ; <sup>*b*</sup> difficult to determine with accuracy.

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catalyst	initial percentages <sup>a</sup>									
Pt/Re	n-pentane	isopentane	n-butane	isobutane	propane	ethane	methane	Rb		
100/0	9	2	10	1	16	16	46	0.01		
80/20	7	1	14	1	16	21	40	0.07		
60/40	11	1	14	1	14	18	41	0.10		
40/60	5	2	4	1	12	22	54	0.56		
20/80	7	2	7	1	11	17	56	1.40		
0/100	1	1	3	1	4	13	77	2.70		

 TABLE 2.—INITIAL DISTRIBUTIONS OF PRODUCTS FROM n-HEXANE CONTAINING LESS THAN SIX

 CARBON ATOMS

<sup>a</sup> In terms of mole percentages of hydrogenolysis products; <sup>b</sup> Ratio of the rate of methane production from the hydrogenolysis of n-hexane to the rate of exchange of methane with deuterium.



FIG. 2.—Reaction of methylcyclopentane with hydrogen on 60% Pt, 40% Re catalyst at 550 K expressed as percentages of the total carbon present in the gaseous compounds: ×, methylcyclopentane; ♦, benzene and cyclohexane; △, products from ring opening; ●, cyclopentane and methane; ○, products from general hydrogenolysis.

methane production from n-hexane hydrogenolysis to the ratio of methane exchange with deuterium.<sup>3</sup>

Small traces of cyclopentane (< 0.1%) were observed on the catalysts containing 100, 80 and 60% platinum. No 1,6 cyclization to yield cyclohexane or benzene, or the formation of 2,3-dimethylbutane was detected on any catalyst.

#### REACTION OF METHYLCYCLOPENTANE WITH HYDROGEN

The four main types of reaction of methylcyclopentane with hydrogen observed on the platinum-rhenium catalysts at 550 K were: (1) ring opening forming n-hexane, 2-methylpentane and 3-methylpentane, (2) C<sub>6</sub> ring formation to cyclohexane and benzene, (3) demethanation forming cyclopentane and methane, (4) general hydrogenolysis forming smaller hydrocarbons with less than six carbon atoms as observed with n-hexane (but excluding the products of demethanation). The course of a typical reaction, on a 60% platinum-40% rhenium catalyst, is shown in fig. 2, where the gas-phase composition in the reaction vessel is plotted as a function of time. Methylenecyclopentene, the only olefinic product detected, was formed on all catalysts except pure rhenium but to an extent which never exceeded 0.9% before decreasing again.

TABLE 3.—INITIAL RATES<sup>a</sup> for the methylcyclopentane/hydrogen reaction at 550 K

catalyst	overall	ring	benzene	e	general
Pt/Re	reaction	opening	formation	demethanation	genolysis <sup>b</sup>
100/0	1.13	1.07	0.02	0.03	0.02
80/20	0.93	0.68	0.05	0.03	0.03
60/40	0.88	0.40	0.38	0.02	0.06
40/60	0.38	0.21	0.08	0.02	0.06
20/80	0.31	0.08	0.14	0.01	0.05
0/100	0.011	0.005		—	0.005

<sup>*a*</sup> In units of  $\% \min^{-1} (0.2 \text{ g catalyst})^{-1}$ , and in terms of the total carbon present in the system; <sup>*b*</sup> excluding the methane produced with cyclopentane in the demethanation.

The initial rates of the main processes occurring, with methylcyclopentane as reactant, are presented in table 3 for the range of catalysts studied. Further information, namely the relative amounts of products of ring opening and the benzene:cyclohexane ratio, are given in fig. 3. Cyclohexane was only observed on the 60, 40 and 20% platinum catalysts, and like methylenecyclopentene passed through a maximum of < 1% as the reaction proceeded. Owing to the small extent of general hydrogenolysis, product distributions were not determinable with accuracy but were similar to those given in table 2 for n-hexane.

In no case was 2,2-dimethylbutane detected before 50% of the methylcyclopentane had been converted, and it was thus considered a product of sequential reaction of the ring-opening products.



FIG. 3.—Further details of product distributions from the reaction of methylcyclopentane with hydrogen on the catalysts: ratios of n-hexane: 3-methylpentane,  $\bigcirc$ , and 3-methylpentane: 2-methylpentane,  $\bigcirc$ , from ring opening; ratio of benzene: cyclohexane at the stage when the maximum amount of cyclohexane was formed,  $\times$ .

# DISCUSSION

Evidence from temperature-programmed reduction and other techniques<sup>9, 10</sup> suggests that the platinum and rhenium atoms are in contact in bimetallic clusters in catalysts similar to ours even up to relatively high rhenium content provided that the catalysts have not been exposed to oxygen at 473 K or above before reduction. The objective of the present work was to derive information about the properties of the bimetallic catalysts by comparing the relative rates of different reactions on the same series of catalysts. As the reactions of the C<sub>6</sub> hydrocarbons are complex the rates of each different type of reaction will be discussed in turn. One advantage of this approach is that it is relatively simple to decide whether thermodynamic constraints are influencing the course of the reaction or limiting the percentages of any of the products formed.

# ISOMERIZATION (I) OF n-HEXANE

It can be seen from table 1 that the predominant mode of reaction of n-hexane (n-H) is skeletal isomerization to yield as initial products 2-methylpentane (2-MP) and 3-methylpentane (3-MP). The expected composition at equilibrium<sup>11</sup> at 550 K for this limited isomerization would be 26.3% n-H, 49.5% 2-MP and 24.2% 3-MP. We suggest that the decreasing rate of this isomerization with time shown in fig. 1 was caused

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by the approach to equilibrium. This was confirmed by treating the conversion of n-hexane to the two products as a reversible first-order reaction and plotting  $\ln(x - x_e)$  against time, where x is the percentage of n-hexane (taking the amounts of the three compounds as 100%) and  $x_e$  the corresponding value at equilibrium. Typical plots for two of the catalysts are shown in fig. 4 and the linear plots confirm that the decrease



FIG. 4.—Plots to confirm that the isomerization of n-hexane to 2-methylpentane and 3-methylpentane was a reversible first-order reaction; x is the percentage of n-hexane at time t and  $x_e$  the equilibrium percentage (26.3%):  $\Box$ , 40/60 catalyst;  $\bigcirc$ , 80/20 catalyst.

in rate with time in fig. 1 was caused by the approach to equilibrium and not by poisoning of the catalyst as the reactions proceed. Furthermore, the rates of reaction derived from the plots agree with the initial rates obtained directly from the composition against time graphs like fig. 1. Table 1 shows that activity for skeletal isomerization, which was relatively high on platinum, rose through a maximum at the 60/40 catalyst and then decreased sharply at the rhenium end of the series. This behaviour is similar to that reported previously for the isomerization of n-butane<sup>3</sup> but contrasts with results for n-heptane at 673 K found by Tournayan *et al.*,<sup>6</sup> for which skeletal isomerization only occurred to *ca.* 20% of the total rate of reaction and showed little variation across the series. The initial experimental ratio of the products 3-MP: 2-MP from skeletal isomerization was *ca.* 0.75 and showed comparatively little variation across the series (table 1); this value was greater than the equilibrium value of 0.49, suggesting that there may have been some preferential formation of 3-MP, but the effect was not marked.

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### ISOMERIZATION (II)

On thermodynamic grounds the further isomerization of 2-MP and 3-MP should lead to the formation of both 2,3-dimethylbutane and 2,2-dimethylbutane, but only the latter was observed, possibly because the presence of the quaternary atom made it less easily removed by hydrogenolysis than the 2,3-DMB. The amount of 2,2-DMB formed directly from n-hexane was small but most noticeable on the 60/40 catalyst; no direct formation of 2,2-DMB occurred from methylcyclopentane but it was produced by subsequent reaction of the products of ring opening.

#### GENERAL HYDROGENOLYSIS

No thermodynamic limitations were important in relation to general hydrogenolysis, because with the hydrogen-rich mixtures we used the equilibria favour the smaller hydrocarbon molecules. The reaction occurred to a substantially greater extent with n-hexane than with methylcyclopentane and a maximum activity was observed with the 40/60 catalyst. The character of the hydrogenolysis of n-hexane on the platinum and platinum-rich catalysts was mild, with only ca. one C-C bond per molecule being broken and significant amounts of n-pentane and n-butane were formed as products (table 2). The depth<sup>12</sup> of hydrogenolysis was greater on the 40/60 and 20/80 catalysts and noticeably more significant over rhenium, which gave large amounts of methane and some ethane as the two main products. Previously<sup>3</sup> we have proposed that the ratio of the rate of production of methane by hydrogenolysis to the rate of exchange of methane with deuterium may be used to differentiate between the breaking of C-C bonds and the removal of C<sub>1</sub> fragments from the surface as rate-limiting steps in hydrogenolysis. In the present study this ratio, R, has been calculated for the hydrogenolysis of n-hexane using rates of methane exchange extrapolated from published data<sup>3</sup> and the values are given in table 2. Since R is < 1 on the platinum-rich catalysts the fission of the C-C bond is likely to limit the overall rate but with the 20:80 catalyst and pure rhenium giving R > 1 the slow step is the removal of methane from the surface. This conclusion is in agreement with previous results on the hydrogenolysis of n-butane<sup>3</sup> and of 2,2-dimethylpropane<sup>5</sup> and the pattern of activity across the series of catalysts was broadly similar for each reactant. The maximum activity found in each case with the 40/60 catalyst was associated with values of  $R \approx 1$ and a change in the nature of the rate-determining step with catalyst composition. There are some differences in detail between the rates of hydrogenolysis of n-hexane and n-butane: both compounds reacted at similar rates on platinum at 550 K but the reaction of the smaller molecule was some 20 times faster on rhenium, possibly an indication that more strongly adsorbed species may form on that metal from n-hexane.

# 1,5 CYCLIZATION OF n-HEXANE AND RING OPENING OF METHYLCYCLOPENTANE

It is appropriate to consider these reactions together, as one involves the reverse of the other. If we consider methylcyclopentane and the three products formed by ring opening, the equilibrium<sup>11</sup> at 550 K and under the conditions we used favour the non-cyclic molecules; the calculations indicate 8.6% MCP, 24.1% n-H, 45.3% 2-MP and 22.1% 3-MP. We start with the ring-opening reaction of methylcyclopentane, which was the major process occurring with the platinum-rich catalysts. Now although this reaction is nominally a hydrogenolysis, since it involves the addition of hydrogen and the breaking of a C—C bond, it was clearly a different process from the hydrogenolysis of n-hexane or the other non-cyclic hydrocarbons. For these general hydrogenolyses the best catalyst was the 40/60 one but for ring opening platinum was most active and the rate of reaction fell steadily with increasing rhenium content and then sharply from the 20/80 catalyst to pure rhenium.

If the bonds in the positions  $\alpha$ ,  $\beta$  and  $\gamma$  to the side group in methylcyclopentane opened at the same rate, the relative amounts of n-H:2-MP:3-MP would have been 2:2:1. The experimental ratio (fig. 3) for 3-MP:2-MP was *ca*. 0.6 and changed relatively little across the series of catalysts, suggesting that the  $\gamma$ -bond opened slightly more rapidly than the  $\beta$ -bond. The experimental ratio for n-H:3-MP never approached the value of 2 for equal reactivity of bonds, but was highest on platinum and close to the equilibrium<sup>11</sup> ratio of 1.09 and dropped to 0.44 on rhenium. Thus the  $\alpha$ -bond opened more slowly than the  $\gamma$ -bond, particularly as the rhenium content of the catalysts increased.

The 1,5 cyclization reaction of n-hexane started rapidly but then the rate decreased sharply with time on platinum, as shown in fig. 1. Obviously thermodynamic considerations were responsible for the shape of the curve. If we were concerned only with n-hexane and methylcyclopentane some 26% of the latter might have been formed, but because of subsequent ring opening of MCP to form 2-MP and 3-MP as well the MCP could not attain a higher percentage than 8.6% of the amount of the former compounds. So the very sharp curvature of the percentage of methylcyclopentane with time was a consequence of its rapid ring-opening reaction and the low equilibrium value. The curvature made it impossible to determine the initial rate of formation of methylcyclopentane accurately. The activity for 1,5 cyclization of n-hexane was high on the platinum-rich catalysts but fell off rather more sharply with increasing rhenium content than would have been expected on the basis of the pattern of activity for ring opening of methylcyclopentane. Two factors may have caused this to occur. First, on the principle of microscopic reversibility, we note that the conversion of n-hexane to methylcyclopentane involves the formation of the C-C bond in the  $\alpha$ -position of the ring compound, and this reaction was therefore probably less easy as the rhenium content of the catalyst increased. Secondly, the increasing amount of isomerization (I) of n-hexane with rhenium content may have limited the possibility of reaction of adsorbed hexane in other directions.

# DEMETHANATION OF METHYLCYCLOPENTANE

The rate of the minor reaction of demethanation of methylcyclopentane fell steadily with addition of rhenium to platinum, and the activity pattern was similar to that for ring opening and different from that for general hydrogenolysis. The amount of cyclopentane levelled off after a small percentage had been formed (fig. 2) or even, as was clearer with other catalysts, passed through a maximum. This behaviour was probably a consequence of the high chance of further reaction of cyclopentane by ring opening; it was not due to a thermodynamic limitation on demethanation as the equilibrium is well over to the side of methane and cyclopentane. We believe that the similar activity patterns for ring opening and demethanation may arise because both processes involve 1,2 adsorbed intermediates rather than the 1,3 adsorbed species<sup>13</sup> responsible for general hydrogenolysis and for isomerization of n-hexane.

We believe that the formation of trace amounts of methylenecyclopentane may have arisen as a by-product of the slow demethanation reaction. Although it was observed on all catalysts except pure rhenium there was evidence that the amount of methylenecyclopentane rose more rapidly on the platinum-rich catalysts. Since the demethanation reaction was itself slow it is reasonable to suggest that dehydrogenation occurred as an alternate reaction path from the relevant 1,2 adsorbed intermediate.

The fact that methylenecyclopentane, which is the least stable<sup>14</sup> of the various

alkenes which can arise from dehydrogenation of methylcyclopentane, was the only such product to be observed is interesting. We suggest that the ring-opening reaction, which was ca. 20 times faster than demethanation, may have occurred preferentially from any adsorbed intermediates which would otherwise have given rise to dehydrogenation to a methylcyclopentene. In making this suggestion we are emphasising again that the formation of the exocyclic alkene was a special reaction arising from the very limited rate of hydrogenolysis associated with intermediates for demethanation.

# Formation of $C_6$ ring compounds

Thermodynamic factors are relevant to this aspect of the results. Under the conditions we used the equilibrium between n-hexane and cyclohexane was 92.4% n-H and 7.6% CH, but for formation of cyclohexane from methylcyclopentane the equilibrium was 81.2% MCP and 18.8% CH. However, because of the relative low pressures of hydrogen in our system the equilibrium ratio of benzene: cyclohexane was > 400:1 at 550 K.

The production of a C<sub>6</sub> ring compound from methylcyclopentane (ring enlargement) may be considered to be a simple skeletal isomerization, and by analogy with the isomerization of n-hexane it is not surprising that the rate of this process was a maximum on the 60/40 catalyst. The relative amounts of benzene and cyclohexane formed from methylcyclopentane are shown in fig. 3, and it was only on the 60/40catalyst that the equilibrium ratio was approached. The extent of dehydrogenation to the aromatic compound was markedly reduced as the rhenium content of the catalysts increased.

The absence of detectable amounts of cyclohexane or benzene formed directly from n-hexane over any of the catalysts is particularly interesting. Although the equilibrium is not very favourable it would have been possible to detect cyclohexane if it had been formed from n-hexane, and we believe that its absence indicated that 1,6 cyclization of n-hexane was not a significant reaction on our catalysts. This may have been caused by a kinetic preference for the relevant intermediate to give 1,5 ring closure rather than 1,6. However, we also have to explain why it was not possible to form the  $C_6$ ring compounds from n-hexane by the consecutive route

# n-hexane $\rightarrow$ methylcyclopentane $\rightarrow$ cyclohexane

and the answer is to be found in tables 1 and 3. The only catalysts which were efficient for the first stage of this sequence were the platinum and 80/20 catalysts; the only catalysts which were active for the second stage were those from 60/40 to 20/80; and so none of the catalysts showed good activity for the overall process.

#### COMPARISON WITH OTHER WORK AND GENERAL CONCLUSIONS

The mechanisms proposed for skeletal isomerization of  $C_6$  or larger hydrocarbons over platinum have included a 1,3 bond-shift mechanism<sup>13</sup> and also the route through  $C_5$  ring compounds.<sup>15, 16</sup> The results that we have obtained with our catalysts containing a comparatively low loading of 0.5% by weight of metal on alumina clearly show a dominance of a bond-shift mechanism under our conditions for the isomerization of n-hexane.

Comparisons with the literature reveal that the method of preparation of the catalysts, whether monometallic or bimetallic, has a great bearing on both activity and selectivity. The hydrogenolysis of methylcyclopentane has been studied by Glassl et al.<sup>17</sup> on platinum on alumina catalysts prepared by different methods and of different particle sizes. They found that the relative amounts of the three isomeric  $C_6$ products from the ring opening of methylcyclopentane depended strongly on metal particle size when the support alumina was prepared by evaporation of aluminium in oxygen, but such dependence was much less pronounced when alumina was prepared by anodic oxidation. They also reported some modification of the isomerization activity for the alumina-supported platinum catalysts by the addition of ammonia to the reactant methylcyclopentane; thus, part of the isomerization activity may be dependent on acid sites on the support.

We do not consider that a valid comparison can be made between our results and those reported by Tournayan *et al.*<sup>6</sup> for the reaction of n-heptane on platinum–rhenium, since the conditions used were different in a number of respects and they concluded that their metal surfaces were at least partially covered with carbon.

In addition to the part played by a bond-shift mechanism for isomerization of n-hexane we would stress the two different patterns of activity across the series of catalysts that have emerged from our results. Pattern A corresponds to maximal activity at the platinum end of the series decreasing steadily with increase of rhenium content and sharply from the 20/80 catalyst to pure rhenium. This pattern holds for ring opening of methylcyclopentane, 1,5 cyclization of n-hexane and demethanation of methylcyclopentane. It seems likely that the types of intermediates invoked in these processes are either 1,2 adsorbed species or 1,5 adsorbed species.

Pattern B correspons to maximal activity for catalysts such as the 60/40 or 40/60 and applies to skeletal isomerization of n-hexane, ring enlargement with methylcyclopentane and to general hydrogenolysis, which was more significant with n-hexane than with methylcyclopentane. There is some suggestion from the results that there may be two versions of pattern B, with a peak at the 60/40 catalyst for the isomerization processes and with a peak at the 40/60 catalyst for hydrogenolysis. We believe that the relevant intermediates for these reactants may involve 1,3 adsorbed species. The maximum in activity for hydrogenolysis has been associated<sup>3</sup> with a catalyst composition which gives equal rates of C-C bond fission and product desorption. Catalysts of other compositions are less efficient for one or other of these reactions, platinum-rich being less active for bond fission and rhenium-rich for product desorption. However, we believe on the basis of the two different activity patterns that it is relevant to distinguish between C-C bond breaking in ring-opening reactions for which platinum is the best catalyst and the other type of bond breaking involved in general hydrogenolysis for which the activity increases with rhenium content of the catalysts.

We thank the Agricultural Division of Imperial Chemical Industries Ltd for preparing the catalysts and for financing a studentship for I.H.B.H.

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