Reactions of Hexanes, Unlabeled and Labeled with ^{13}C, on Alumina-Supported Palladium–Gold and Platinum–Gold Alloys

A. O'CINNEIDE AND F. G. GAULT

Laboratoire de Catalyse, Université Louis Pasteur de Strasbourg,
4 rue Blaise Pascal, Strasbourg, France

The isomerization and hydrocracking of unlabeled and labeled hexanes have been investigated over palladium–gold and platinum–gold alloys (10% of metal on alumina).

The palladium–gold catalysts are substantially less active than pure palladium, even after activation in air at 400°C. However, no noticeable change in selectivity is observed when alloying gold and palladium. For both palladium and alloy catalysts, selective demethylation is the main reaction occurring and the mechanism of hexane isomerization is essentially "cyclic."

On the contrary, dramatic changes in reaction mechanisms are observed when alloying platinum with gold: while the mechanism of hexane isomerization on platinum is mostly "bond-shift," on the 15% platinum–gold alloy, only the "cyclic" mechanism takes place. Similarly a nonselective ring opening of methylcyclopentane occurs on the platinum–gold alloy, while on platinum, only the CH_2–CH_2 secondary–secondary bonds are broken.

The 15% platinum–gold alloy is active only after pretreatment by air and is deactivated in the presence of hydrogen. Activation and deactivation are time-dependent, temperature-dependent and reversible. No change in selectivity and mechanism is observed during the activation and deactivation processes.

It is therefore concluded that a high dispersion of the platinum atoms and the presence of oxygen ions in their immediate vicinity are both required to induce the cyclic mechanism of hexane isomerization and the nonselective hydrogenolysis of methylcyclopentane.

INTRODUCTION

The mechanisms of skeletal rearrangements of hydrocarbons on metals, the cyclic and "bond-shift" mechanisms, are now well characterized. Extensive work on supported platinum catalysts and platinum films has shown that hydrogenolysis of methylcyclopentane, isomerization of hexanes and aromatization are very sensitive to surface structure and especially to metal particle size (*1–3*) in contrast to the case of reactions involving carbon hydrogen bonds (*4*).

This has naturally led several authors to use these structures sensitive reactions as model reactions to study alloy catalysts (*5–7,31,32*).

Furthermore, the introduction of a new parameter, namely, the alloy composition, may provide additional data capable of throwing a new light on the intimate reaction mechanisms of skeletal rearrangement (*8*).

In this work, both experiments with labeled and unlabeled molecules have been carried out; as has been pointed out earlier (*9*), simple considerations of product distributions are not sufficient in themselves to distinguish between the isomerization mechanisms.

Similarly the choice of the two catalytic

311

systems, 15% Pt–Au and Pd–Au alloys
has been influenced by mechanistic consid-
erations. Reaction paths for isomerization
on platinum are very intricate, and we felt
it would be interesting to investigate
whether alloying this metal would change
the relative contribution of the various ex-
isting mechanisms. On the other hand, Pd
and Au appear from the literature to be
very distinct in their catalytic properties.
C_6 skeletal isomerization is essentially cy-
clic on Pd (10) and Au was reported to
catalyze the neopentane to isopentane
isomerization (11), whose mechanism is
necessarily bond-shift. It would therefore
be of interest to see which type of mecha-
nism would operate on a Pd–Au alloy.

Another attractive aspect of our choice
lies in the physical properties of these
alloys. The Pd–Au system is well known
to be a thermodynamically stable, one-
phase alloy throughout the composition
range and a recent surface study suggests
that the surface composition of this system
may be approximately the same as the
bulk composition (12). As for the 15%
Pt–Au alloy, the system is not expected to
exhibit phase separation at equilibrium
(13). Moreover, in a random substitutional
binary alloy A–B, the relative abundance
of isolated surface A atoms (i.e., A atoms
all of whose nearest neighbors on the sur-
face are B atoms) is greatest at a surface
composition of 15–20% A (14,15).

Although our primary interest was in
product distribution and in the position of
the labeled carbon atoms, some reactivity
measurements were also performed and in
some cases an unusual dependence of
catalyst activity upon in situ pretreat-
ment was observed.

EXPERIMENTAL METHODS

Catalysts

All catalysts were prepared by co-
impregnation (or impregnation in the case
of pure metals) of the same nonacidic inert

alumina support which has been described
in previous publications (16), by aqueous
acidified solutions of the metal chlorides.
After slow evaporation to dryness the
preparation was completed by the follow-
ing three consecutive steps:

i. reduction of the chlorides to the metal
in flowing hydrogen at 200°C for 24 hr;

ii. overnight calcination in air at 770°C;

iii. further reduction in flowing H_2 at
200°C for 6 hr.

In preliminary work with some Pd–Au
alloys the X-ray diffraction profiles were
examined after step (i). Pronounced broad-
ening of the diffraction peaks of the alloys
(relative to those of the pure Pd and pure
Au catalysts, similarly treated) was ob-
served. Since there seems no reason to
suppose that the alloys should be more dis-
persed than the pure metals prepared by
an identical impregnation technique, the
possibility that the broadening of the dif-
fraction peaks was caused by very small
metallic crystallites was rejected and it
was concluded that after step (i) alloying is
still incomplete. The diffraction patterns
remained unchanged after a second reduc-
tion, this time at 550°C for 12 hr, and it
was only after the introduction of step (ii)
into the preparative procedure that satis-
factorily sharp X-ray peaks were observed
at the expected Bragg angle. Thus the
standard preparative procedure sum-
marized in the 3 steps above was arrived
at and all catalysts finally used (including
Pt and 15% Pt–Au alloy) were prepared in
this way, after which the X-ray diffraction
patterns were recorded. They were then
stored in air. All catalysts contained 10%
by weight of metal. When prepared in this
way the X-ray line width of the catalysts
was in most cases only marginally greater
than the instrumental line width. Hence
the average particle size was at least sev-
eral hundred angstroms. This in turn im-
plies that most of the metal must be depos-
ited outside of the pore system of the
alumina since the average pore diameter of

the support is 70 Å. Thus, in contrast to some literature reports on the preparation of supported alloy catalysts (17–19), our experience suggests that co-impregnation followed by reduction (at temperatures ≤550°C) does not always automatically result in satisfactory alloying of the metal components.

Materials

The unlabeled hydrocarbons used (2-methylpentane, n-hexane and methylcyclopentane) were Fluka puriss grade and were used without further purification. The ^{13}C-labeled hydrocarbons used (2-methylpentane-2-^{13}C, 2-methylpentane-4-^{13}C and 3-methylpentane-3-^{13}C) were prepared by synthetic methods already described (16,20). The isotopic purity was in some cases around 60% and in some cases around 90%.

Apparatus and Procedure

The catalytic reaction were carried out in an all-glass, grease-free flow system at a hydrogen pressure of 1 atm, the catalyst being held between glass wool plugs in a Pyrex U-tube reactor. The catalyst bed was isothermal, isobaric and operated under differential reaction conditions. Activity differences among the catalysts were compensated for by using different quantities of catalysts and different flow rates so that comparative studies could be performed at the same temperature, e.g., 500 mg of the 15 atom% Pt–Au alloy had approximately the same activity as 20 mg of the pure Pt catalyst (diluted with 480 mg of the support) at 300°C. Calculations based on the method of Wheeler (21) indicated that under reaction conditions the fraction of the catalyst surface which was available to the reactants was very close to unity. Hence we believe that the measured activities were uninfluenced by diffusion limitations. Small quantities (2–4 μl) of the reacting hydrocarbons were injected into the hydrogen flow upstream of the catalyst

bed. Before reaching the catalyst, the injected hydrocarbon passed through a coil cooled to −45°C which produced a close approximation to a square-wave hydrocarbon pulse passing over the catalyst at a constant partial pressure (~3 Torr for n-hexane and methylcyclopentane, and ~4 Torr for 2-methylpentane and 3-methylpentane). After leaving the reactor, the gas flow entered one cell of a katharometer. Thus the square-wave pulse could be observed shortly after leaving the catalyst bed, and it was verified that no tailing of the pulse took place. Samples for chromatographic analysis were removed directly from the gas-phase by a gas-syringe as the pulse passed a rubber septum located close to the katharometer. Under typical reaction conditions the square-wave pulse took several minutes to flow past a given point.

Gas Chromatographic Analysis

All gas chromatographic separations were performed on a 5 m × ⅛ in. Silicone DC200/firebrick column operated at 15°C. Occasionally some difficulty was experienced in the precise estimation of methane, since the products for analysis were injected into the chromatograph in a large excess of hydrogen and the sensitivity of the hydrogen flame ionization detector changes momentarily as the hydrogen peak (with the methane peak closely following) is eluted. Thus, for example, we believe that the value for methane marked with footnote d in Table 1 is less than the true value. The glc data were converted into molar concentrations using the sensitivity data of Dietz (22) for the hydrogen flame detector. In presenting the results, we have used the parameters α = total conversion, S = selectivity for C_6 formation and r_w = reaction rate (molecules/sec) per gram of catalyst as already defined by Ponec and Sachtler (6). C_i denotes the molar concentration of a hydrocarbon with i carbon atoms. Summation over j is performed for all detected

TABLE 1

REACTIONS OF 2-METHYLPENTANE ON Pd–Au ALLOYS AT 350°C ACTIVITIES, PRODUCT DISTRIBUTIONS AND EFFECT OF PRETREATMENT CONDITIONS

Catalyst	In situ pretreatment (°C)	α (%)[a]	Concn (mole%)													S (%)[b]	r_w[c]
			C_1	C_2	C_3	iso-C_4	C_4	iso-C_5	C_5	cyclo-C_5	2,3-DMB	3MP	n-Hex	MCP		
100% Pd	H$_2$ at 350	7.9	26.7	1.4	1.5	1.6	0.5	11.2	15.9	1.4	0.3	6.9	5.7	27.1	57	5.6×10^{17}
100% Pd	Air at 400 + H$_2$ at 350	7.0	30.6	1.3	1.2	1.4	0.5	9.8	13.7	1.6	0.4	6.0	5.0	28.5	58	7.1×10^{17}
50% Pd–Au	Air at 400 + H$_2$ at 350	6.8	29.0	2.7	1.1	3.1	0.6	10.8	12.2	1.2	0.2	6.5	6.5	26.2	58	2.0×10^{16}
35% Pd–Au	H$_2$ at 350	4.75	32.8	3.1	2.4	3.8	0.8	12.6	13.9	0.9	0.2	3.3	2.7	23.5	47	6.5×10^{15}
35% Pd–Au	Air at 400 + H$_2$ at 350	4.95	16.6[d]	2.2	1.1	2.7	0.5	9.1	10.2	0.9	0.3	6.5	5.7	44.1	71	2.5×10^{16}
35% Pd–Au	Air at 400 + H$_2$ at 350	9.75	24.2	2.3	1.7	2.2	0.8	7.2	8.9	1.8	0.4	9.4	9.5	31.7	69	1.5×10^{16}

[a] α = total conversion.
[b] S = selectivity for C_6 formation.
[c] r_w = rate (molecules/sec) of overall reaction per gram of catalyst.
[d] Approximate value.

isomers of each C_i hydrocarbon. The subscript k denotes the hydrocarbons in the feed.

$$\alpha = \frac{100 \sum\limits_{i=1}^{6} \sum\limits_{j, j \neq k} iC_i^{(j)}}{\left\{ \sum\limits_{i=1}^{6} \sum\limits_{j, j \neq k} iC_i^{(j)} + 6C_6^{(k)} \right\}},$$

$$S = \frac{600 \sum\limits_{j, j \neq k} C_6^{(j)}}{\sum\limits_{j, j \neq k} \sum\limits_{i=1}^{6} iC_i^{(j)}},$$

$$r_w = \frac{F \, \alpha}{w \times 100} \text{ molecules sec}^{-1} \text{ g}^{-1} \text{ catalyst,}$$

where F = flow rate of reactant (molecules/sec^{-1})

w = weight of catalyst sample (g).

Since we were interested exclusively in the carbon skeleton and since small amounts of olefins were sometimes produced at higher temperatures (despite the large excess of hydrogen) a small charge of reduced platinum oxide (Adams' catalyst) was placed close to the exit of the reactor and maintained at 80°C. This converted all unsaturated hydrocarbons (except, in some cases, benzene) to the corresponding alkanes without altering the carbon skeleton.

Experiments with Labeled Compounds: Procedure

If the reacting hydrocarbon was labeled with ^{13}C, the pulse was trapped after leaving the katharometer cell, a preliminary chromatographic separation was performed, and the fraction containing the C_6 isomerized products (including a small quantity of the starting compound) was brought to a coupled glc–ms unit for final separation and recording of the mass spectra of the isomers. The mass spectrometer used was a CH7 Varian-Mat apparatus operating with 70 eV and a trap current of 300 μA. A relatively low resolution was used (ca. 800) to increase the sen-

sitivity. The gas chromatograph was connected to the mass spectrometer through a Biemann separator which eliminated 90% of the helium used as a carrier gas. With a pressure of 2 atm at the entrance of the chromatographic column (5 m × 1/8 in., 5% DC200 on 50–80 mesh a.w. firebrick) and a flow rate of 8 ml/min, the pressure in the source of the mass spectrometer was about 10^{-6} Torr. The temperature of the chromatograph (−10°C) was adjusted so that the retention times of the hexanes lay between 50 and 80 min. The scanning time, 1.2 sec/decade, was a compromise so that (a) the accuracy of the measurement on the mass spectra was only limited by the determination of the height of the peaks, (b) the change of the total ion current was smaller than 0.5% for a group of 10 masses, even on the steepest part of the chromatographic elution peak.

The chromatography resulted in a partial separation of the light and heavy molecules (about 10% enrichment in the heavy molecules towards the front of the elution peak), but it was checked that no change in the composition of the isotopic varieties resulted from this effect.

Finally, several blank spectra were recorded between consecutive elution peaks, in order to make an accurate estimation of the "true" background, mostly due to a memory effect; this background was never higher than 2% of the recorded peaks.

The mass spectra were recorded in the parent, $-CH_3$, and $-C_2H_5$ regions. After correction for fragmentation due to loss of hydrogen, natural abundance of ^{13}C and deuterium, and the lack of 100% isotopic purity of the starting labeled compounds, the parameters a_5 and a_4 (the fractional abundance of ^{13}C in the C_5 and C_4 mass spectral fragments, respectively) were determined. By comparison with the known a_5 and a_4 values of all the ^{13}C labeled hexane isomers, the analysis of the mixture of isotopic varieties could then be achieved in a manner which has already

been described (20). In the case of the n-hexane, the amounts of the three ^{13}C positional isomers may be determined. In the case of the methylpentanes, only the total amounts of the 2-methylpentane-2-^{13}C and -3-^{13}C or of the 3-methylpentane-1-^{13}C and -2-^{13}C are obtained.

The estimated error limit for this techniques is ±5%, which explains the slightly negative values obtained on a few occasions, and also a value slightly greater than 100% obtained in one instance.

RESULTS AND DISCUSSION

The Influence of "in Situ" Pretreatment

It was initially verified that the alumina support itself is inactive under reaction conditions and also that the Au–Al$_2$O$_3$ catalyst was inactive up to 400°C, irrespective of pretreatment conditions. In separate experiments, however, in a high vacuum apparatus, we observed some cracking and isomerization on an evaporated Au film at temperatures ≥400°C. This lends support to the original report of Boudart and Ptak (11) that this metal has some catalytic activity for these reactions.

Initially an "in situ" reduction in flowing hydrogen at 350°C for 30 min was employed as pretreatment for all catalysts. Anomalously low values of S (the selectivity for C$_6$ formation) were observed on the 35 atom% Pd–Au alloy, and in the case of the 15 atom% Pt–Au alloy there was a complete absence of activity. We then repeated the experiments beginning with an in situ oxidation of the catalysts in air (400°C, 30 min) followed, after a brief evacuation, by the same reduction as before. The preoxidation had relatively little effect on the activity of the pure metals Pd and Pt. The 35 atom% Pd–Au alloy, however, became noticeably more active and its S value also increased. The 15 atom% Pt–Au alloy was most dramatically affected, displaying activity for the first time; furthermore with this catalyst the activating effect of heating in air was found to be both time dependent and temperature dependent. Figure 1 summarizes this effect in a semiquantitative way. Preheating in air (1 atm) at 400°C for 30 min followed by reduction in flowing hydrogen at 350°C (30 min) was eventually adopted as the "standard" pretreatment which was used for all experiments reported in Tables 3, 4, and 5.
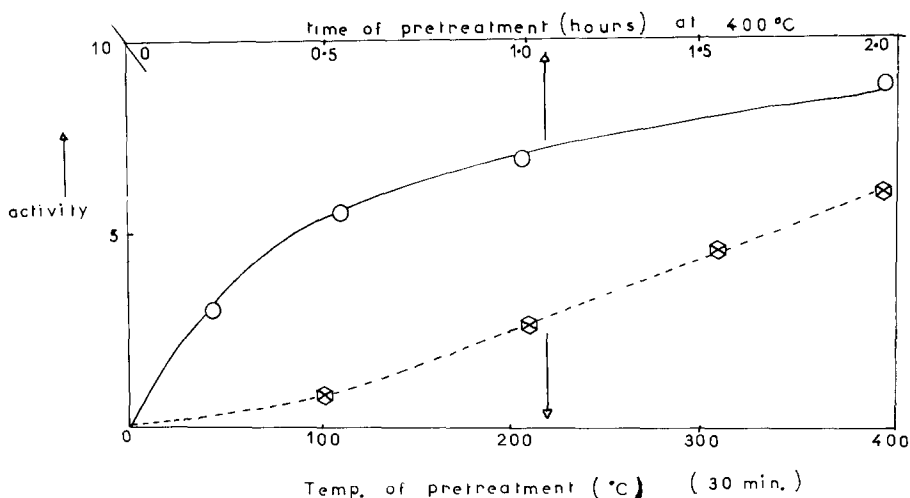

FIG. 1. 15% Pt–Au alloy activation by preheating in air: (open circle) activity vs time of pretreatment at 400°C; (cross in hexagon) activity vs temperature of pretreatment.
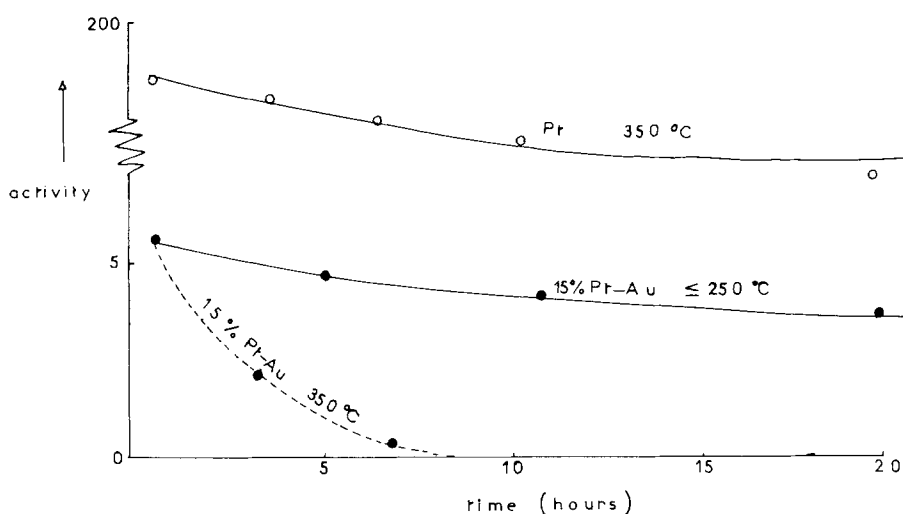
FIG. 2. Catalyst deactivation in presence of hydrogen: (O) Pt; (●) 15% Pt–Au alloy.

It was also observed that the activity of the 15% Pt–Au catalyst declined and eventually disappeared upon continued exposure to flowing hydrogen at 350°C, whereas if the catalyst was maintained in hydrogen at temperatures $< \sim 250°C$ (and heated to reaction temperature only for the duration of the reaction) the activity remains fairly constant with time. The pure Pt catalyst was largely unaffected by high temperature exposure to hydrogen. These findings are summarized (again in a semi-quantitative way) in Fig. 2. We think it unlikely that the deactivation phenomenon is due to poisons either in the hydrogen or on the support. The hydrogen carrier gas was purified by passage through activated silica gel traps cooled to $-196°C$, and in any case the pure Pt catalyst was not similarly deactivated. We shall comment on these unusual activation–deactivation phenomena again below.
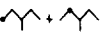
### Reaction with Unlabeled Compounds

Tables 1, 2 and 4 contain the product distributions obtained using the unlabeled hydrocarbons. Tables 1 and 2 include results obtained both with and without a preoxidation included in the pretreatment. Although most distributions were obtained at low conversions, they are initial dis-

TABLE 2

REACTIONS OF n-HEXANE ON Pd–Au ALLOYS AT 350°C ACTIVITIES, PRODUCT DISTRIBUTIONS AND EFFECT OF PRETREATMENT CONDITIONS

Catalyst	In situ pre-treatment[a]	α (%)	C_1	C_2	C_3	iso-C_4	C_4	iso-C_5	C_5	cyclo-C_5	2-MP	3-MP	MCP	Be + CH	S (%)	r_{ic}
100% Pd	H_2	8.25	37.1	3.8	3.8	Tr	3.8	0.8	19.7	0.8	3.8	2.3	15.2	8.3	30	1.5×10^{17}
80% Pd–Au	H_2	8.60	33.6	3.1	3.1	Tr	3.1	0.8	21.9	1.6	4.7	3.1	15.6	10.2	34	3.7×10^{16}
50% Pd–Au	H_2	9.4	24.6	3.2	4.0	Tr	2.4	0.8	15.1	0.8	11.1	5.5	22.2	10.3	49	6.4×10^{15}
35% Pd–Au	H_2	3.35	32.8	7.7	13.0	Tr	6.5	Tr	16.5	1.0	2.2	1.7	13.0	5.5	22	0.8×10^{15}
35% Pd–Au	Air + H_2	26.5	29.5	4.8	5.8	0.3	5.6	1.6	20.4	1.3	7.3	4.3	6.5	12.5	48	2.7×10^{16}

[a] H_2 at 350°C; or air at 400°C and H_2 at 350°C.

TABLE 3

REACTIONS OF 2-METHYLPENTANE-2-C[13] ON Pd–Au ALLOYS AT 330°C
LABELING OF THE ISOMERIZATION PRODUCTS

Catalyst	3-Methylpentanes			n-Hexanes			α (%)
100% Pd	−1	84	17	4	90	6	6.7
35% Pd–Au	−1	82	19	0	94	6	6.8

tributions only in an approximate sense since methylcyclopentane is always present in significant amounts among the reaction products and the hydrogenolysis of methylcyclopentane is more rapid than the other cracking and isomerization reactions.

It is clear that within the Pd–Au series neither the distribution of cracking products (among which methane and pentanes are dominant) nor that of the C_6 products is radically changed upon addition of Au to Pd. The S value, however, does show a tendency to increase (after "standard" pretreatment in the case of the 35% Pd–Au alloy) an effect that has already been demonstrated more dramatically in the case of the Ni–Cu alloy system by Ponec and Sachtler (6).

In contrast, significant changes in product distribution are observed between Pt and the 15% Pt–Au alloy (Table 4). Whereas on the latter catalyst the hydrogenolysis of methylcyclopentane occurs nonselectively, leading to a 2-methylpentane:3-methylpentane:n-hexane ratio very close to 2:1:2 (similar to what has already been observed for highly dispersed Pt catalysts), on the pure Pt catalyst the n-hexane yield is very small.

A sharp difference between the Pt and 15% Pt–Au catalysts is also apparent among the C_6 isomerization products of 2-methylpentane, e.g., the 3-methylpentane/n-hexane ratio on pure Pt is $\simeq 3$, whereas on the alloy it is $\simeq 0.5$. The latter

value is the same as the one obtained on a highly dispersed 0.2% Pt–Al_2O_3 catalyst (24).

It is interesting to note that the product distribution obtained from 2-methylpentane on a 15% Pt–Au catalyst which has been partly deactivated by exposure to hydrogen at 350°C is the same as the one on an activated catalyst. The deactivation effect of the high temperature hydrogen treatment is therefore to decrease only the number of sites and not to alter their nature.

As far as cracking products are concerned, the (already high) S value on Pt appears to be only marginally influenced by alloying with Au. The distributions in Table 4 show that bond fission tends to be more internal than terminal on Pt in contrast to, for example, Pd and Ni. However, while propane, resulting presumably from a one-step rupture of the tertiary–secondary C–C bond is the main hydrocracking product from 2-methylpentane on Pt, on a 15% Pt–Au alloy it represents only a minor reaction product, as has already been observed on a highly dispersed Pt catalyst (25). Relative ease of splitting of the tertiary–secondary C–C bond in an acyclic molecule on Pt catalyst of low dispersion contrasts with the difficulty of rupture of the analogous bond in methylcyclopentane. That seems to indicate that ring opening and hydrocracking do not involve the same sites of the metal surface.

To summarize, the following conclu-

TABLE 4

COMPARISON OF PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF 2-METHYLPENTANE, n-HEXANE AND METHYLCYCLOPENTANE ON Pt AND ON 15% Pt–Au ALLOY

Reactant	Catalyst	Temp (°C)	α (%)	Concn (mole%)																
				C_1	C_2	C_3	iso-C_4	C_4	iso-C_5	C_5	cyclo-C_5	2,2-DMB	2,3-DMB	2MP	3MP	n-Hex	MCP	Bc/CH	S (%)
⋀⋀	Pt	300	8.6	3.0	3.6	8.0	2.8	0.4	1.0	1.8	0.4	0.2	–	–	39.8	13.6	25.4	–	88
	15% Pt–Au	300	2.65	5.1	4.5	1.7	4.2	–	1.4	3.6	–	–	–	–	14.7	24.8	39.9	–	87
⋁⋁⋁	Pt	300	8.3	3.1	4.1	9.9	0.2	3.6	–	3.2	–	–	2.0	38.2	26.0	–	7.4	2.3	85
	15% Pt–Au	300	6.95	2.4	3.3	6.8	–	2.7	–	1.9	0.4	–	1.0	24.0	18.5	–	24.8	14.2	91
⬠	Pt	170	2.2	Tr	–	–	–	–	–	–	–	–	–	71.3	24.3	4.4	–	–	100
	Pt	280	6.5	Tr	–	–	–	–	–	–	Tr	–	–	72.9	23.8	3.3	–	–	100
	15% Pt–Au	280	5.55	Tr	–	–	–	–	–	–	Tr	–	–	44.2	19.1	36.6	–	–	100

ᵃ Tr trace quantity.

sions emerge from an inspection of the product distribution obtained with unlabeled compounds:

i. the character of Pd as a catalyst for cracking, isomerization and cyclization reactions remains largely unchanged upon alloying with Au;

ii. the 15% Pt–Au alloy is significantly different from the Pt catalyst of low dispersion used in this study as far as ring opening, isomerization and hydrocracking reactions are concerned.

For all three reactions the 15% Pt–Au alloy behaves like a highly dispersed Pt catalyst.

Reactions with Labeled Compounds

Tables 3 and 5 contain the results of experiments performed with ^{13}C labeled hexanes. In these experiments interest was confined exclusively to the isomerized C_6 products with the object of determining unequivocally the relative contributions of the two possible isomerization mechanisms (the "bond-shift" and "cyclic" mechanisms). In all cases the labeling of the unconverted reactant was found to be unchanged after reaction. For the conversion of 2-methylpentane-2-^{13}C to 3 methylpentane, the bond-shift mechanism should give 3-methylpentane-2-^{13}C, whereas the

"cyclic" mechanism should give 3-methylpentane-3-^{13}C.
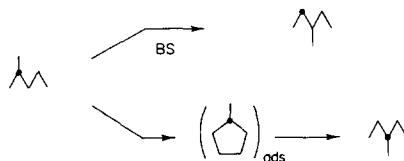
Hence Table 3 illustrates that for both Pd and 35% Pd–Au the cyclic mechanism is dominant for this conversion. The contribution of the bond-shift mechanism is in both cases smaller than 20%. This confirms the conclusion arrived at earlier that the addition of Au to Pd does not radically change the character of Pd as a catalyst for these reactions.

As can be seen from Table 5, when the same conversion occurs on pure Pt (of low dispersion) at 300°C, the bond-shift mechanism accounts for about 60% of the isomerization. This is in fairly good agreement with previous results obtained at lower temperatures (270°C) on a similar 10% Pt–Al$_2$O$_3$ catalyst of low dispersion (26), where the bond-shift mechanism accounted for about 70% of the 3-methylpentane formed. It is also consistent with recent kinetic data obtained in this laboratory for the corresponding reactions of pentanes (27) which show that the appar-

TABLE 5

REACTIONS OF ^{13}C LABELED METHYLPENTANES ON Pt AND ON 15% Pt–Au ALLOY AT 300°C: RELATIVE ABUNDANCE OF THE VARIOUS ISOTOPIC SPECIES OF THE ISOMERIZED PRODUCTS

| Reactant	Catalyst	2-Methylpentanes			3-Methylpentanes			n-Hexanes			α (%)
	Pt				−2	43	59	−2	88	14	7.5
	15% Pt–Au				3	74	23	9	91	0	3.0
	15% Pt–Au				−1	−2	103	0	49	51	4.2
	15% Pt–Au	4	94	1				−1	99	2	1.8

ent energy of activation is greater for the cyclic mechanism than for the bond-shift mechanism.

A striking change occurs, however, in going from the Pt catalyst to the 15% Pt–Au alloy. On the latter, the cyclic mechanism becomes dominant, accounting for 74% of the 2-methylpentane → 3-methylpentane conversion. A similar difference has already been observed between Pt catalysts of low and high dispersion. Hence, although the metallic crystallites are very large, the Pt–Au alloy behaves in this respect as also in the case of the hydrogenolysis of methylcyclopentane like a highly dispersed Pt catalyst.

The main interest in the reaction of 2-methylpentane-4-^{13}C lies in the labeling of the n-hexane formed. The bond-shift mechanism should give 100% n-hexane-2-^{13}C and the cyclic mechanism should give a 50–50 mixture of n-hexane-2-^{13}C and n-hexane-3-^{13}C. Hence the results in Table 5 indicate that on the alloy the 2-methylpentane conversion to n-hexane is almost entirely cyclic in character.

(scheme: 2-methylpentane-4-^{13}C, BS → n-hexane; cyclic → (methylcyclopentane)$_{ads}$ → n-hexane (1/2) + n-hexane (1/2))
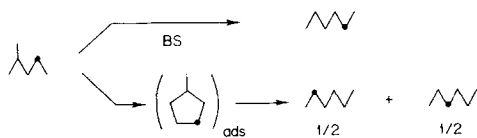
As far as the reaction of 3-methylpentane-3-^{13}C is concerned the main interest lies in the labeling of the n-hexane formed. Whereas the bond-shift mechanism would provide only the n-hexane-3-^{13}C, n-hexane-2-^{13}C should be obtained by a cyclic mechanism.

(scheme: 3-methylpentane-3-^{13}C, BS → n-hexane; cyclic → ( )$_{ads}$ → n-hexane)
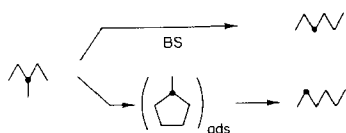
It is known from unpublished work in this laboratory that ~ 60% of the n-hexane is formed by a cyclic mechanism on a Pt–Al$_2$O$_3$ catalyst of low dispersion

(170 Å). The n-hexane obtained on the 15% Pt–Au alloy is only labeled on carbon 2 and therefore results from a pure cyclic mechanism, as happens also on ultrahighly dispersed catalyst (16).

Another interesting point is the labeling of the 2-methylpentane formed. The bond-shift mechanism should give 2-methylpentane-3-^{13}C and the cyclic mechanism should give 2-methylpentane-2-^{13}C. 2-Methylpentane-2-^{13}C and 2-methylpentane-3-^{13}C cannot be distinguished by this technique. Hence for this reaction the existence of significant amounts of 2-methylpentane labeled in positions other than positions 2 and 3 would indicate the existence of consecutive rearrangements occurring during a single sojourn of the reactant molecule on the surface. Such consecutive rearrangements have already been detected for these reactions on Pt catalysts of low dispersion (26) (but not, however, on highly dispersed Pt catalysts). Table 5 shows that they are not important in the case of the 15% Pt–Au alloy.

CONCLUSION

It goes without saying that the surfaces of supported catalysts used in a conventional flow system are unlikely to be perfectly clean. In addition there must be some uncertainty concerning the surface composition of the alloys we have used in this investigation. However, without being blind to these limitations, we believe that the results obtained constitute a useful contribution to our knowledge of the characteristics of these reactions. The surface compositions of some unsupported Pd–Au alloys have been determined by Auger electron spectroscopy (28). Within the experimental errors it is approximately the same as the bulk and is largely insensitive to thermal treatment and exposure to different gases. Also it should be borne in mind that these catalysts were calcined in air at 770°C during their preparation. Ef-

fects such as "Gibbs adsorption," which can cause surface enrichment in one component, are likely to be less important at higher temperatures where the energetics are dominated by the entropy term (which disfavors surface enrichment) (29). Thus we feel moderately confident in saying that, as far as the 35% Pd–Au and 15% Pt–Au catalysts are concerned, we are dealing with surfaces which contain Pd and Pt atoms, respectively, in a gold rich environment.

The data on the relative activities of the catalysts is rather scanty and complicated by the critical dependence of activity on *in situ* pretreatment. However, it seems clear that the alloys are substantially less active than the pure Pd and Pt catalysts, even taking into account the smaller amounts of Pd and Pt present in the alloys. Although the classical "band" theory of alloys is perhaps not completely irrelevant, a more localized model seems to be required for a detailed explanation of product distributions and mechanistic changes.

For example, the fact that the 15% Pt–Au catalyst (despite its large crystallites) behaves exactly like a highly dispersed Pt catalyst, which is perhaps the most striking result of this work, is best understood on the assumption that the catalytic behavior of the majority of its surface Pt atoms is primarily determined by the fact that they are surrounded by inert Au atoms. Thus the bond-shift mechanism which apparently demands doublet or triplet sites on Pt is disfavored, as also are consecutive rearrangements, which imply a certain surface mobility of the adsorbed hydrocarbons. The third similarity between 15% Pt–Au and highly dispersed Pt catalysts is the nonselective hydrogenolysis of methylcyclopentane in both cases as opposed to the difficulty of formation of *n*-hexane in the same reaction on Pt catalysts of low dispersion. The implication seems to be that when quasi-isolated Pt

atoms only are present, nonselective ring opening and its reverse 1,5 cyclization (probably the rate-determining step in "cyclic" isomerization) are mandatory, but when doublet or triplet sites are present another mechanism for ring opening and ring closure, involving attachment at more than one Pt atom and resulting in selective hydrogenolysis (or dehydrocyclization) away from the tertiary carbon, becomes preferred.

Besides these simple "ensemble" effects, it is also clear that more subtle electronic effects are important in these reactions. Thus, for example, on both the 35% Pd–Au and the pure Pd catalyst the cyclic mechanism is dominant even though there should be no shortage of doublet or triplet sites on the latter. Another effect which could well be classified as electronic is the dramatic influence of adsorbed oxygen on the activity of the 15% Pt–Au alloys. The first results of an Auger study of oxygen adsorption on alloys (28) indicate a strong chemical shift of the KLL transition from 517 to 508 eV. This oxygen therefore appears to be very strongly bonded as in silicates and alumina (30) and is presumably of ionic character; furthermore, the adsorbed oxygen is not easily removed by exposure to H_2 at temperatures around 300–400°C. Therefore, not only a quasi-atomic dispersion of the platinum atoms, but also the presence of oxygen ions in their immediate vicinity seems to be necessary to promote some reactions like cyclic type isomerization and nonselective methylcyclopentane hydrogenolysis. O^{2-} ions are available in the supported platinum catalysts (Pt–Al_2O_3, Pt–SiO_2) which, when they are in a high degree of dispersion, promote the very same reactions. It is tempting, therefore, to suggest that the catalytic sites in these systems are not really small platinum crystallites, but active systems where platinum atoms are surrounded by oxygen ions. The zero oxida-

tion state of the metal atoms in such systems could therefore well be questioned.

REFERENCES

1. (a) Maire, G., Plouidy, G., Prudhomme, J. C., and Gault, F. G., *J. Catal.* **4**, 556 (1965); (b) Gault, F. G., *Ann. Chim.* (Paris) p. 645 (1960); (c) Corolleur, C., Gault, F. G., Juttard, D., Maire, G., and Muller, J. M., *J. Catal.* **24**, 406 (1972).
2. Anderson, J. R., McDonald, R. J., and Shimoyama, Y., *J. Catal.* **20**, 147 (1971).
3. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).
4. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
5. Reman, W. G., Ali, A. H., and Schuit, G. C. A., *J. Catal.* **20**, 374 (1971).
6. Ponec, V., and Sachtler, W. M. H., *Proc. Int. Congr. Catal., 5th, 1972* p. 645 (1973).
7. Moss, R. L., and Whalley, L., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 22, p. 115. Academic Press, New York, 1972.
8. Anderson, J. R., Comment on paper No. 43. *Proc. Int. Congr. Catal., 5th, 1972* p. 655 (1973).
9. Gault, F. G., Comment on paper No. 47. *Proc. Int. Congr. Catal., 5th, 1972* p. 707 (1973).
10. Hajek, M., Maire, G., O'Cinneide, A., Corolleur, C., and Gault, F. G., *J. Chim. Phys.* **71**, 1329 (1974).
11. Boudart, M., and Ptak, C. D., *J. Catal.* **16**, 90 (1970).
12. Sancier, K. M., Nishiyama, Y., and Wise, H., presented: 33rd Annu. Conf. Physical Electronics, Berkeley, Cal. 1973.
13. Bouwman, R., and Sachtler, W. H. M., *J. Catal.* **19**, 127 (1970).
14. Dowden, D. A., *Proc. Int. Congr. Catal., 5th, 1972* p. 621 (1973).
15. Moss, R. L., *Platinum Metals Rev.* **17**, 137 (1973).
16. Corolleur, C., Corolleur, S., and Gault, F. G., *J. Catal.* **24**, 385 (1972).
17. Joice, B. J., Rooney, J. J., Wells, P. B., and Wilson, G. R., *Discuss. Faraday Soc.* **41**, 223, (1966).
18. Bartholomew, C. H., and Boudart, M., *J. Catal.* **25**, 173 (1972).
19. Anderson, J. R., Conn, P. J., and Brandenberger, S. G., *J. Catal.* **16**, 326 (1970).
20. Corolleur, C., Corolleur, S., and Gault F. G., *Bull. Soc. Chim. Fr.* **1970**, 158.
21. Wheeler, A., *in* "Advances in Catalysis (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Eds.), Vol. 3, p. 249. Academic Press, New York, 1953.
22. Dietz, W. A., *J. Gas Chromatogr.* **68** (1967).
23. Anderson, J. R., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 23, p. 59. Academic Press, New York, 1973.
24. Barron, Y., Maire, G., Muller, J. M., and Gault, F. G., *J. Catal.* **5**, 428 (1966).
25. Corolleur, C., PhD thesis, Caen, 1969.
26. Corolleur, C., Tomanova, D., and Gault, F. G., *J. Catal.* **24**, 401 (1972).
27. Garin, F., and Gault, F. G., unpublished data.
28. Gault, F. G., Legare, P., Maire, G., and O'Cinneide, A., unpublished data.
29. Bartholomew, C. H., and Boudart, M., *J. Catal.* **29**, 278 (1973).
30. Carriere, B., Deville, J. P., and Goldsztaub, S., *C. R. Acad. Sci. Ser. B* **274**, 415 (1972); Joyce, B. A., and Neave, J. H., *Surface Sci.* **27**, 499 (1971).
31. Dessing, R. P., Ponec, V., and Sachtler, W. M. H., *Chem. Commun.* 880 (1972).
32. Ponec, V., and Sachtler, W. M. H., *J. Catal.* **28**, 381 (1973).