JOURNAL OF CATALYSIS **64**, 448–463 (1980)

Skeletal Reactions of Hydrocarbons over Supported Iridium–Gold Catalysts

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Received December 3, 1979; revised February 29, 1980

The reactions of *n*-butane, neohexane, and neopentane have been studied over dispersed, supported, iridium–gold catalysts having gold contents in the range 0–86 mol%, and which were characterized by electron microscopy, hydrogen adsorption, and temperature-programmed desorption of hydrogen. The hydrocarbon reactions fell into one of two classes. Within each class the activation energy was independent of gold content, but the classes were distinguished by differing modes of variation of frequency factor (rate per surface iridium) with gold content. Neohexane (bond rupture within the ethyl group only) and *n*-butane reacted with similar Arrhenius parameters (activation energy 170 ± 10 kJ mol^{-1}), and the basic hydrogenolysis reaction was in the C_2-unit mode over the entire gold content range. Hydrogenolysis of neopentane occurred in the iso-unit mode over the entire gold content range (activation energy 242 ± 15 kJ mol^{-1}). It is concluded that hydrogenolysis in the iso-unit mode requires a single surface iridium atom as the active site, while hydrogenolysis in the C_2-unit mode requires more than one surface iridium atom as the active site (probably two adjacent iridium atoms). Under appropriate circumstances, iso-unit hydrogenolysis is accompanied by a bond-shift isomerization component, and C_2-unit hydrogenolysis is accompanied by a C_5-carbocyclic isomerization component. These mechanistic relationships are formulated, and the way in which the reactions depend on catalyst composition and concentration of surface hydrogen is discussed.

INTRODUCTION

Recently, Foger and Anderson (*1*) studied the reactions of a number of aliphatic hydrocarbons over a variety of dispersed iridium catalysts with $\bar{d}_{Ir}$ in the range ≤1 to 20 nm. Two basic hydrogenolysis modes were elucidated; reaction in a C_2-unit mode (ethane the archetypal hydrocarbon) with an activation energy in the region of 175 kJ mol^{-1}, and reaction in an iso-unit mode (neopentane the archetypal hydrocarbon) with an activation energy in the region of 235 kJ mol^{-1}. In each case, the activation energy and the frequency factor (expressed as rate per surface iridium atom) were independent of $\bar{d}_{Ir}$.

From these observations it was argued (*1*) that for neither of these reaction modes on iridium can the reaction site be of a type such that the site density depends on $\bar{d}_{Ir}$, and that all surface iridium atoms are equally effective, irrespective of surface geometry, although this need not necessarily imply that a reactive site is to be identified with a single surface iridium atom. Indeed, in recent work concerned with the skeletal isomerization of 2-methylpentane on iridium, Weisang and Gault (*2*) have suggested, using arguments of analogy and plausibility, that the reactive site consists of an adjacent pair of surface iridium atoms.

It is by no means clear if this suggestion should automatically be extended to include hydrogenolysis reactions per se, while it is also very desirable to attempt to obtain some independent evidence as to the nature of the reactive site. It is the purpose of this article to try to illuminate this question by the use of iridium–gold catalysts. To this end, we have examined the reactions of neopentane, neohexane, and *n*-butane over Ir–Au/aerosil catalysts for which the overall gold content varied in the range 0–86 mol%.

0021-9517/80/080448-16$02.00/0

EXPERIMENTAL

The reaction and adsorption measurements were made using the methods previously described (*1*). The reactions were carried out in a single-pass fixed bed reactor operating in a differential mode at low conversions (<10%). The weight of catalyst was 0.2–0.5 g, and prior to reaction the catalyst was reduced in a stream of hydrogen overnight at 620 K. Subsequently, the catalyst was cooled in a stream of hydrogen to reaction temperature, and the reactant mixture (normally hydrogen/hydrocarbon molar ratio 20/1) was passed over the catalyst at a total pressure of 101 kPa.

The catalysts were prepared by coimpregnation of the support (Degussa 200 aerosil,[1] 200 m^2 g^{-1}) with an aqueous solution containing chloriridic acid and chloroauric acid using the method of incipient wetness. The solvent was removed by slow evaporation under vigorous stirring, and the residue was dried at 380 K for several hours and subsequently reduced in a stream of hydrogen at 620 K overnight.

Hydrogen adsorption measurements were made by static volumetric adsorption methods, and the nature of the adsorbed hydrogen was also studied by a temperature-programmed desorption technique. The experimental procedures were the same as those previously described for use with the platinum–gold system (*3*).

TABLE 1

Details of Catalysts

Catalyst[a]	$\bar{d}$/nm[b]	Hydrogen adsorption/ molec H_2 (g metal)$^{-1}$ [c] (×10^{20})
Ir100, Au0;[d] 1.5 wt% metal	1.5 ± 0.2	12.0
Ir94, Au6; 1.3 wt% metal	3.0 ± 0.4	4.7
Ir81, Au19; 1.1 wt% metal	1.5 ± 0.2	8.9
Ir52, Au48; 0.8 wt% metal	1.5 ± 0.2	3.8
Ir14, Au86; 0.8 wt% metal	1.3 ± 0.2	1.0

[a] Overall metallic compositions given in mol%.

[b] Average metallic particle diameter by electron microscopy. The particles appear to be roughly spherical in the electron micrographs.

[c] "Saturated" hydrogen uptake measured at 293 K: for details see text.

[d] Data for this catalyst taken from Ref. (*1*).

The catalyst details are listed in Table 1, and this includes metallic particle size by electron microscopy, and hydrogen adsorption data. The catalysts were also examined by X-ray diffraction using a Siemens Model

TABLE 2

Reaction Rate Data

Hydrocarbon	Catalyst	Reaction temperature range (K)	Activation energy (kJ mol^{-1})	log(frequency factor) [frequency factor/molec s^{-1} Ir^{-1}(s)]
n-Butane	Ir100, Au0	433–493	170	17.1_0
	Ir94, Au6	463–493	168	16.5_8
	Ir81, Au19	453–485	171	16.6_2
	Ir52, Au48	463–503	170	16.0_1
	Ir14, Au86	493–521	166	15.3_0
Neohexane	Ir100, Au0	443–485	175	17.0_8
	Ir81, Au19	473–513	174	16.5_0
	Ir14, Au86	503–523	169	14.7_7
Neopentane	Ir100, Au0	493–523	240	21.8_2
	Ir94, Au6	514–543	238	21.2_6
	Ir81, Au19	511–533	237	21.1_3
	Ir52, Au48	523–558	249	21.1_1
	Ir14, Au86	523–553	246	21.1_2

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[1] Aerosil is a form of high-purity silica powder.

805 diffractometer, and these results are dealt with in a later section.

RESULTS

Hydrocarbon Reaction Data

Table 2 lists reaction conditions, activation energies, and frequency factors for the reaction of *n*-butane, neohexane, and neopentane, and Arrhenius plots for these reactions are shown in Figs. 1 and 2. For catalysts Ir100, Au0, Ir94, Au6, and Ir81, Au19 the reaction rates were strictly constant with time over the entire period of a run: with catalysts Ir52, Au48 and Ir14, Au86 there was some evidence for self-poisoning, and for these catalysts the initial reaction rates were used.

The initial product distributions obtained in these reactions are listed in Table 3. These initial distributions were, to better than 2% variation, independent of temperature over the reaction temperature range.

Partial pressures of hydrogen and hydrocarbon in the reactant stream were changed to measure the orders of the reaction (*n*, *m*) with respect to both reactants, according to

$$\text{rate} \propto P_{\text{HC}}^{\,n}\, P_{\text{H}_2}^{\,m} \qquad (1)$$

The results are summarized in Table 4 for the hydrocarbons *n*-butane and neopentane.

Hydrogen Adsorption and Temperature-Programmed Desorption

Hydrogen adsorption isotherms were measured in the pressure range 0.1–4 kPa at 293 K, by static volumetric measurement.

The nature of the isotherm varied with gold content, as is evident from the data shown in Fig. 3. In all cases, the isotherms showed an approximately linear region in the pressure range 0.5–4 kPa. However, as the gold content increased, the hydrogen uptake in the linear region increased more rapidly with increasing hydrogen pressure. This behavior is similar to that previously

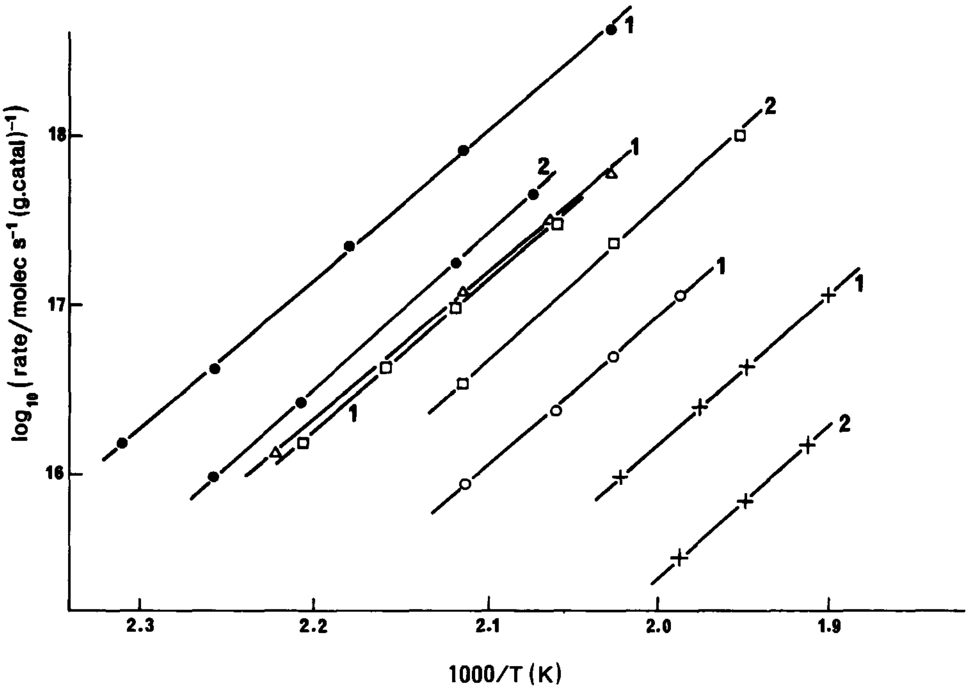


FIG. 1. Arrhenius plots of reaction rate data for *n*-butane and neohexane. ●, Ir100, Au0; △, Ir94, Au6; □, Ir81, Au19; ○, Ir52, Au48; +, Ir14, Au86 mol%. Curves 1 for *n*-butane, curves 2 for neohexane.

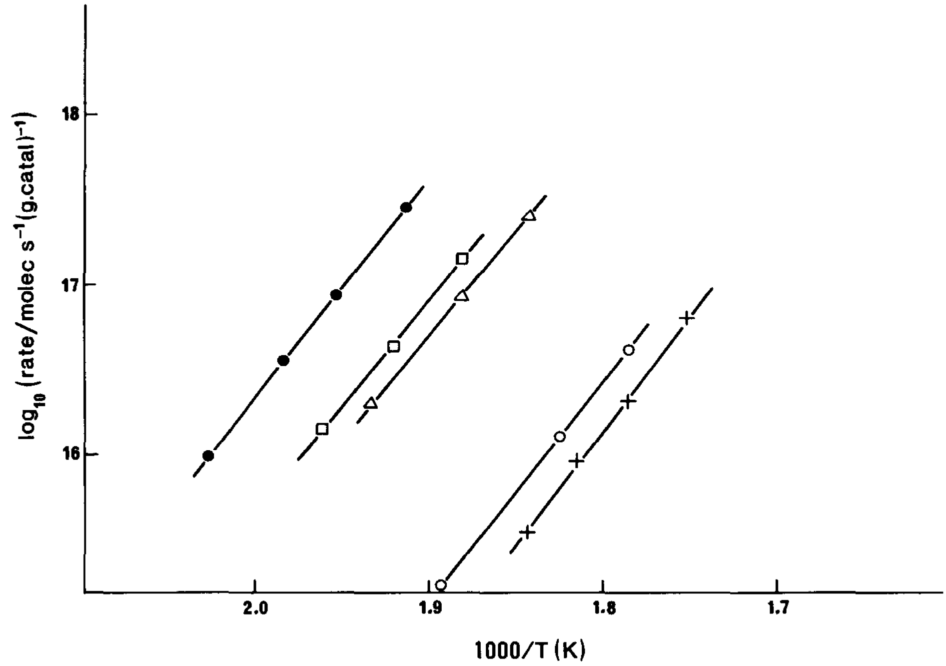


FIG. 2. Arrhenius plots of reaction rate data for neopentane. ●, Ir100, Au0; △, Ir94, Au6; □, Ir81, Au19; ○, Ir52, Au48; +, Ir14, Au86 mol%.

reported for hydrogen adsorption on dispersed platinum–gold catalysts (*3*).

We have estimated the "saturated" hydrogen adsorption by using the same method as previously described (*3*); that is, back-extrapolation of the linear part of the isotherm to zero pressure, and the hydrogen adsorption values so obtained are re-

TABLE 3

Distributions of Initial Products

Hydrocarbon	Catalyst	Initial product distribution (mol%)[a]					
		M	E	P	i-B	i-P	neo-P
n-Butane	Ir100, Au0	20.0	60.0	20.0	—	—	—
	Ir94, Au6	21.2	57.6	21.2	—	—	—
	Ir81, Au19	18.4	63.2	18.4	—	—	—
	Ir52, Au48	20.1	59.8	20.1	—	—	—
	Ir14, Au86	20.9	58.2	20.9	—	—	—
Neopentane	Ir100, Au0	58.1	8.7	2.5	30.7	—	—
	Ir94, Au6	55.6	10.8	3.6	26.7	3.5	—
	Ir81, Au19	56.3	9.8	3.0	27.0	3.9	—
	Ir52, Au48	55.1	9.1	4.1	25.6	6.2	—
	Ir14, Au86	54.4	10.4	2.8	26.9	5.9	—
Neohexane	Ir100, Au0	50	—	—	—	—	50
	Ir81, Au19	50	—	—	—	—	50
	Ir14, Au86	50	—	—	—	—	50

[a] M, Methane; E, ethane; P, propane; i-B, isobutane; i-P, ispentane; neo-P, neopentane.

TABLE 4

Kinetic Pressure Dependence Exponents

Hydrocarbon	Catalyst and reaction temperature	Pressure range (kPa)	Exponents in rate $\propto P_{HC}{}^{n}P_{H_2}{}^{m}$
n-Butane	Ir100, Au0; 463 K	P_{H_2}, 50–101 P_{HC}, 1.3–9	$n = 1.0$, $m = -2.9$
		P_{H_2}, 19–50 P_{HC}, 1.3–5.5	$n = 0.6_5$, $m = -1.5$
	Ir81, Au19; 463 K	P_{H_2}, 50–101 P_{HC}, 1.6–12	$n = 1.0$, $m = -2.8$
		P_{H_2}, 22–50 P_{HC}, 1.2–6	$n = 0.6_1$, $m = -1.4$
	Ir52, Au48; 473 K	P_{H_2}, 80–101 P_{HC}, 1.8–10	$n = 0.9$, $m = -2.7$
		P_{H_2}, 20–80 P_{HC}, 1.1–5	$n = 0.5_9$, $m = -1.5$
	Ir14, Au86; 503 K	P_{H_2}, 101 P_{HC}, 1.7–6.5	$n = 0.7_1$
		P_{H_2}, 20–90 P_{HC}, 1.2–5.5	$n = 0.5_8$, $m = -1.4$
Neopentane	Ir100, Au0; 523 K	P_{H_2}, 20–101 P_{HC}, 1.3–12	$n = 1.0$, $m = -2.9$
	Ir81, Au19; 523 K	P_{H_2}, 20–101 P_{HC}, 1.3–12	$n = 1.0$, $m = -2.9$
	Ir14, Au86; 553 K	P_{H_2}, 20–101 P_{HC}, 1.2–7	$n = 0.9_5$, $m = -2.4_5$

corded in Table 1. We have adopted this procedure in order to make an operational estimate of the total number of iridium atoms exposed in the catalyst surface, assuming that at "saturated" adsorption each surface iridium atom carries one adsorbed hydrogen atom. We justify this procedure by analogy with platinum–gold catalysts (*3*) where a similar assumption was internally self-consistent with independent estimates for $\bar{d}$ and surface composition. In the case of iridium–gold a similar check for internal self-consistency is not possible because X-ray diffraction data clearly show the presence of more than one metallic phase (cf. next section) and thus surface compositions cannot be estimated with any degree of confidence.

Temperature-programmed desorption measurements of adsorbed hydrogen were made using as sweep gas argon containing 0.1 vol% hydrogen and at a heating rate of 20 K min^{-1}. Before heating was commenced the sample was reduced in a hydrogen flow at 1 atm overnight at 620 K and then cooled in hydrogen at 293 K. Typical temperature-programmed desorption profiles are shown in Fig. 4.

X-Ray Diffraction

The low metallic content and very small metallic particle size of the catalysts resulted in very weak and broad diffraction lines. In no case could a line other than (111) be observed. The catalysts were always examined in the reduced state.

In the case of catalysts Ir100, Au0, Ir94, Au6, and Ir81, Au19, only a single line in the vicinity of iridium(111) was found. However, this was so broad that no information concerning metallic composition could be obtained, nor was it possible to say with any degree of confidence that only a single metallic phase was present.

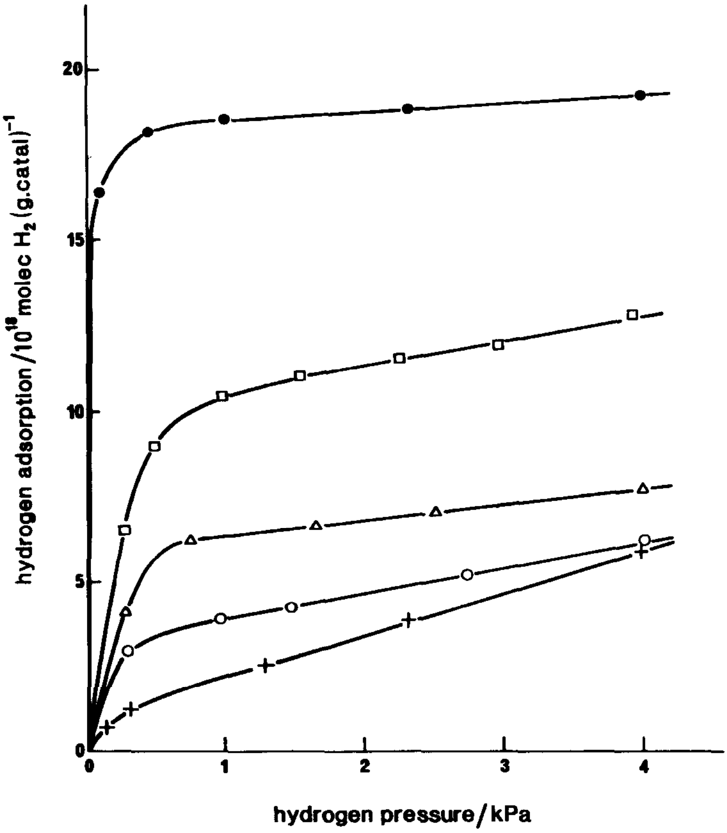


FIG. 3. Hydrogen adsorption isotherms on iridium–gold catalysts. ●, Ir100, Au0; △, Ir94, Au6; □, Ir81, Au19; ○, Ir52, Au48; +, Ir14, Au86 mol%. Temperature 293 K.

In the case of catalysts Ir52, Au48 and Ir14, Au86 two diffraction lines could be distinguished in the region of iridium(111). However, again these lines were so broad that no information concerning metallic composition could be obtained except to note that two metallic phases were obviously present.

DISCUSSION

Kinetic Parameters

The variation of the Arrhenius parameters with overall metallic composition is shown in Figs. 5 and 6. We have included in these data the estimated probable error on each point.

In the case of the activation energy (cf. Fig. 5), there is very little variation with metallic composition for any of the three reactant hydrocarbons. Neohexane and *n*-butane have the same activation energy and this is independent of metallic composition with a mean value of 170 ± 10 kJ mol^{-1}. In the case of neopentane the activation energy shows an apparent very small upward trend with increasing gold content. However, this change amounts to only about 4% over the entire composition range and is barely significant relative to the error estimates, and the neopentane activation energy can be taken as constant at 242 ± 15 kJ mol^{-1} for all catalysts.

In the case of the frequency factor data (cf. Fig. 6) the situation is quite different. With neohexane and *n*-butane, the frequency factors (*expressed in units of rate per surface iridium atom*) decrease with increasing gold content: over the entire metallic composition range the frequency

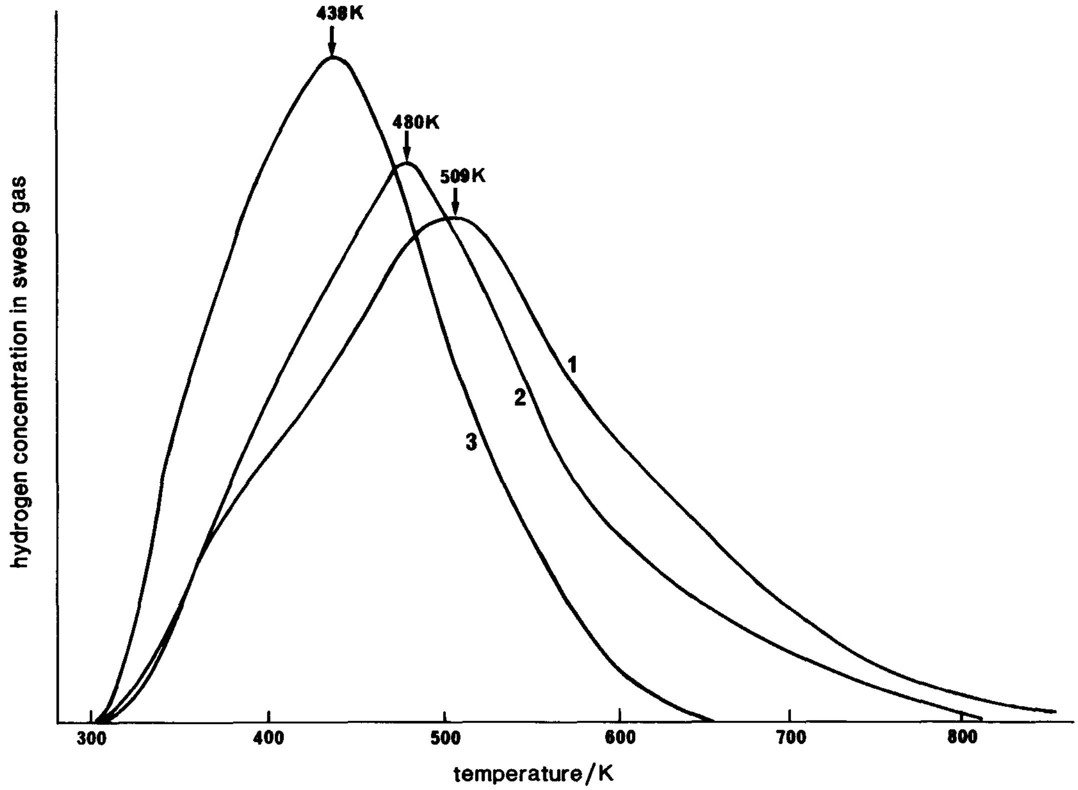


FIG. 4. Temperature-programmed desorption profiles of hydrogen from iridium-gold catalysts. Curve 1, Ir 100, Au0; curve 2, Ir94, Au6; curve 3, Ir81, Au19. Profiles normalized to equal areas.

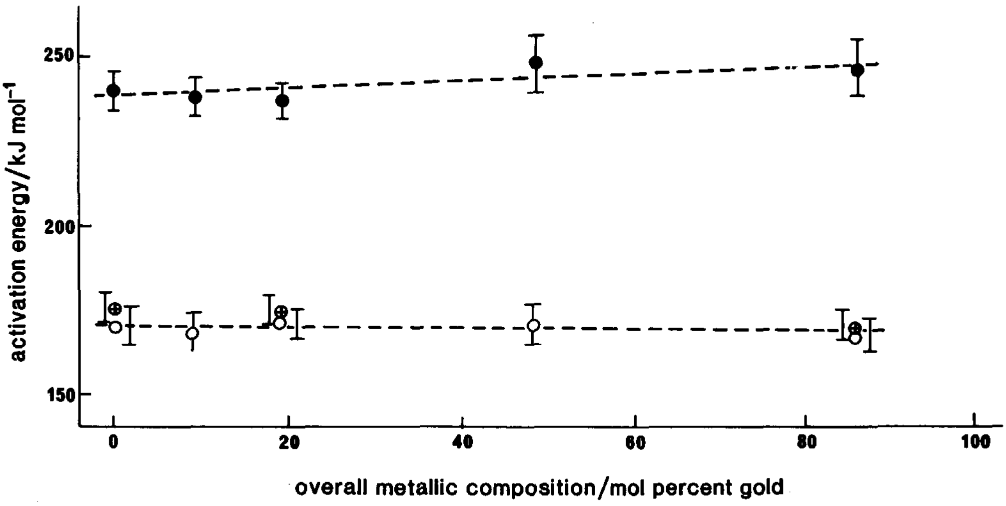


FIG. 5. Variation of activation energy with overall metallic composition. ●, Neopentane; ○, *n*-butane; ⊕, neohexane.

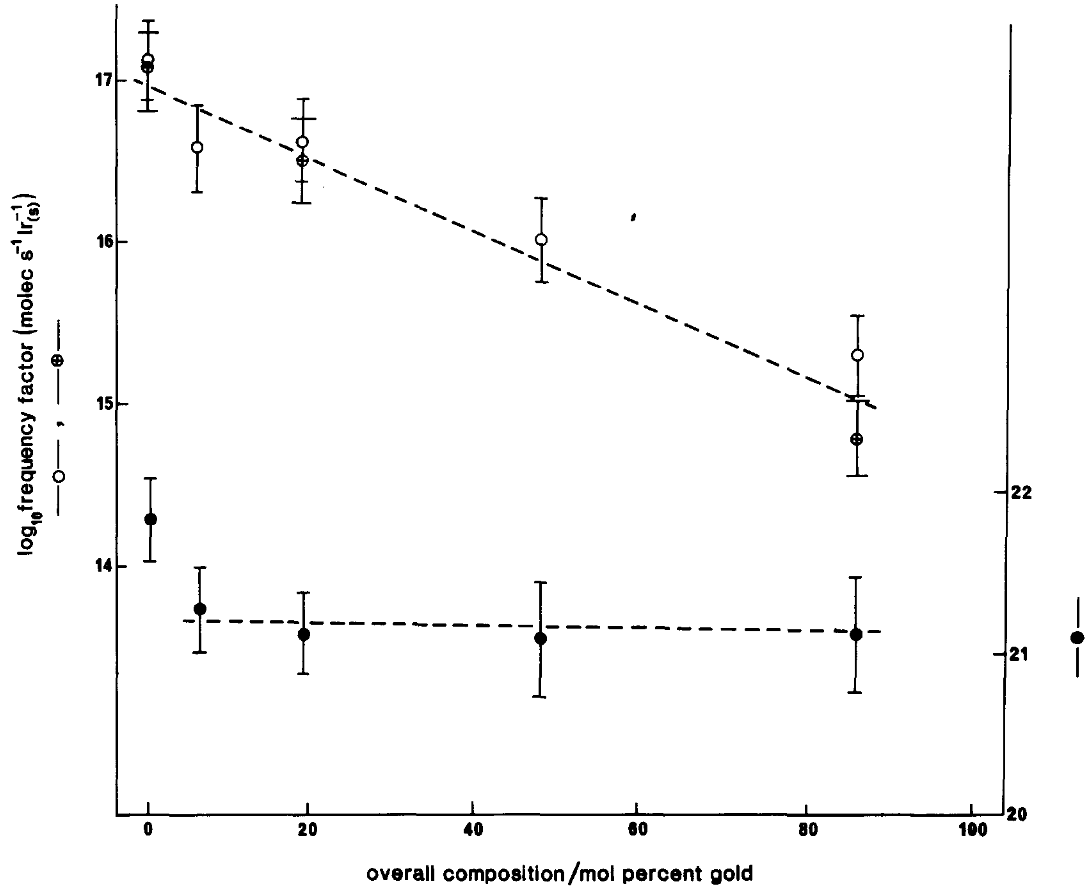


FIG. 6. Variation of frequency factor with overall metallic composition. ●, Neopentane; ○, *n*-butane; ⊕, neohexane.

factors decrease by a factor of about 10^2, and the plots of log (frequency factor) vs metallic composition for both these hydrocarbons fall on a common line. With neopentane the situation is again quite different. Over the composition range Ir94, Au6 to Ir14, Au86 the frequency factor is independent of metallic composition: on going from Ir94, Au6 to Ir100, Au0 there appears to be a small increase which is barely significant in relation to the error bars on the individual points. We sum up by saying that for neopentane the frequency factor is virtually independent of metallic composition.

The data in Table 4 show that with neopentane the pressure dependence exponents were constant over the whole metallic composition and pressure ranges studied ($P_{HC}^{1} P_{H_2}^{-3}$). Provided the hydrogen pressure was sufficiently high, similar behavior was found for *n*-butane (except at the composition Ir14, Au86 where a hydrocarbon exponent of 0.7 was observed even with a hydrogen pressure of 101 kPa). With *n*-butane at hydrogen pressures lower than 101 kPa, the pressure dependence exponents were changed ($P_{HC}^{0.6}$, $P_{H_2}^{-1.5}$): as the gold content increased, the critical hydrogen pressure separating the two pressure dependence regimes also increased, from about 50 kPa at Ir100, Au0 to >100 kPa at Ir14, Au86.

Product Distributions

It is evident from the data in Table 3 that over the entire metallic composition range, the initial product distributions are almost constant. The only change of any real significance is that on going from Ir100, Au0 to Ir94, Au6 with neopentane, the isomerization product isopentane appears (the proportion of isopentane increasing from zero to 3.5 mol%), while on going from Ir94, Au6 to Ir14, Au86 there is a further increase in the proportion of isopentane to 5.9 mol%. No evidence for isomerization was found with *n*-butane or neohexane with any of the present catalysts.

We ascribe the intervention of a small isomerization component from neopentane on iridium–gold catalysts to a reduction in the availability of adsorbed hydrogen, and this point is further discussed in a subsequent section.

With *n*-butane, the product distributions mean that the chance of breaking the central bond is three times greater than the chance of breaking an end bond.

Hydrogen Adsorption and TPD

The general character of the hydrogen adsorption isotherms (cf. Fig. 3) resembled that previously reported for dispersed platinum–gold catalysts (*3*). In particular, as with platinum–gold, the iridium–gold isotherms showed hydrogen uptakes that continued to increase with increasing hydrogen pressure above about 1 kPa so that these isotherms did not saturate in the same way as did isotherms for gold-free catalysts. The relative extent of this "suprasaturation" hydrogen uptake increased with increasing gold content, and we suggest that it owes its origin to a spillover process in a manner similar to that which operates with the platinum–gold system (*3*). Reference should be made to (*3*) for a more detailed discussion of this point.

The TPD profiles (cf. Fig. 4) showed two changes as the gold content of the catalysts increased: the profile maximum shifted to a lower temperature, and the high-temperature profile tail was severely truncated. Thus, going from Ir100, Au0 to Ir81, Au19 resulted in a shift in the profile maximum from 509 to 438 K, and the upper limit to the profile tail decreased from about 850 to 650 K. It thus seems clear that the addition of gold to iridium in these catalysts results in a significant reduction in the binding energy of adsorbed hydrogen, even at relatively low gold contents. This behavior is quite different from the platinum–gold system where, except possibly at quite high gold contents, the gold acts essentially as an inert diluent (*3*).

Reaction Mechanisms

A number of pieces of evidence lead to the conclusion that for our hydrocarbons, the basic reaction mechanisms are independent of the gold content of the catalysts. This evidence is: (i) the activation energies for the hydrocarbons are independent of gold content, (ii) the product distributions are independent of gold content, (iii) the kinetic pressure dependence exponents are independent of gold content (except for the change in critical hydrogen pressure separating the different kinetic regimes with *n*-butane).

Before discussing reaction mechanisms, we need to comment upon the way in which the metallic components may be disposed in these iridium–gold catalysts.

Iridium and gold are, in the bulk, of very limited miscibility. The solubility of iridium in liquid gold is <1 mol%, and that of gold in liquid iridium is <2 mol% (*4*). We also recall that our catalysts of compositions Ir52, Au48 and Ir14, Au86 mol% showed X-ray diffraction evidence for the coexistence of more than one phase.

Bearing in mind these facts together with our earlier comments concerning the ambiguous nature of the X-ray diffraction data for catalysts of compositions Ir94, Au6 and Ir81, Au19, we conclude that we can have no confidence that any of our iridium–gold catalysts contained a single metallic phase. This is sufficient to make any attempt at a quantitative evaluation of metallic surface composition virtually impossible. However, the problem is compounded by the fact that, in any given catalyst, the metallic particles are distributed in $\bar{d}$, but we have no information whether, given the coexistence of more than one metallic phase, a given phase exists preferentially in a particular fraction of the $\bar{d}$ distribution.

Nevertheless, there is internal evidence from the catalytic and hydrogen adsorption data which show that our catalysts do *not* merely consist of separate particles of pure iridium and pure gold. Our reasons for this conclusion are as follows.

If the iridium–gold catalysts consisted of pure iridium and pure gold particles, all hydrocarbon reactions would be characterized by frequency factors which, when expressed in units of rate per surface iridium atom, would change in the same manner with iridium–gold composition; for all hydrocarbons this frequency factor would be proportional to the surface area of the pure iridium phase. At this point it is important to recall that for none of these hydrocarbons are the activation energies or frequency factors (rate per surface iridium atom) dependent on $\bar{d}$.

It therefore follows that, given the different variation with metallic composition of the frequency factors for neopentane on the one hand, and *n*-butane or neohexane on the other hand, the surface upon which catalysis is occurring cannot be that of pure iridium, but the surface must contain iridium and gold atoms in a proportion that varies with the overall metallic composition. In coming to this conclusion, one should remember the evidence given previously for iridium–gold and pure iridium that the basic reaction mechanisms do not change with the introduction of gold for any of the hydrocarbons studied.

The above conclusion is supported by an examination of the hydrogen adsorption data. The first point to note is that the general character of the hydrogen adsorption isotherms (cf. Fig. 3) resembled that previously reported for dispersed platinum–gold (*3*), particularly in respect of the presence of a "suprasaturation" region which increased in extent with increasing gold content. In either case it is extremely difficult to see how such behavior could arise if the catalysts consisted of separate particles of pure gold, and pure iridium or pure platinum. Furthermore, since there is good evidence that the platinum–gold catalysts contained metallic particles with both platinum and gold atoms in the surface (*3*), the similarity in behavior strongly suggests that this is also true for iridium–gold.

The second point about hydrogen adsorption involves a comparison of our hydrogen adsorption data with what would be expected if the catalysts contained pure iridium and pure gold particles of mean diameter equal to $\bar{d}$ measured electron microscopically. For instance, for the Ir14, Au86 catalyst, the measured hydrogen uptake (saturated adsorption at 293 K, cf. Table 1) was 0.43×10^{14} molec H_2 cm^{-2}, whereas the value expected assuming particles of pure iridium and pure gold with $\bar{d} =$ 1.3 nm is 0.81×10^{14} molec H_2 cm^{-2}.

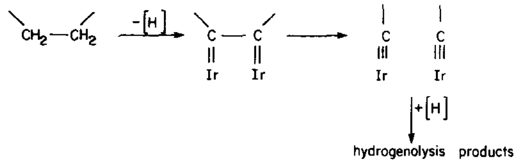
We shall thus discuss the hydrocarbon reactions on the basis that our iridium–gold catalysts presented metallic surfaces containing both iridium and gold atoms, and that the surface composition varied with the overall proportions of iridium and gold.

We have seen that for the reaction of neopentane, the frequency factor (rate per surface iridium atom) is nearly independent of overall gold content; that is, the frequency factor is nearly independent of the gold content of the active metallic surface. The most direct interpretation of this is to propose that for the reaction of neopentane the active site consists of a single iridium atom and that, irrespective of gold content, all surface iridium atoms are equally effective.

On the other hand, we have seen that for the reaction of *n*-butane or neohexane, the frequency factor (rate per surface iridium atom) falls by a factor of about 10^2 as the overall gold content increases from 0 to 86 mol%. The simplest interpretation of this is to propose that, as the gold content increases, the number of active sites per unit area decreases by a similar factor. The question is: what is the most probable active site which possesses this behavior. Since the activation energies and frequency factors for *n*-butane and neohexane on iridium are independent of $\bar{d}$ (*1*), it is reasonable to propose that this active site is not characterized by iridium atoms in special geometric locations in the surface. Accordingly, we propose that this active site consists of an ensemble containing more than one contiguous iridium atom, since the chance of obtaining such an ensemble in the surface falls with increasing surface gold concentration at a more rapid rate than does the total iridium concentration of the surface. Unfortunately, since we have no quantitative data for surface concentrations of gold and iridium, we are not able to estimate this ensemble size by using computer simulation techniques in a manner similar to that described previously for platinum–gold (*5*).

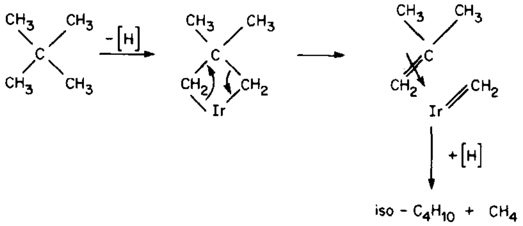
Nevertheless, on the basis of this interpretation, the general conclusion is clear: the active surface ensemble for the reaction of *n*-butane or neohexane is larger than that for neopentane. For the latter, a single surface iridium atom is the probable active site, while for the former, the active ensemble certainly contains two (and perhaps more than two) iridium atoms.

We showed previously (*1*) that for hydrogenolysis in the C_2-unit mode (that is, the hydrogenolysis mode for *n*-butane or for the ethyl group of neohexane), both carbon atoms between which the bond is to be broken must be secondary or primary, implying the necessity of forming at least carbon–iridium double bonds at each of these atoms. We thus have arrived at a mechanism for hydrogenolysis in the C_2-unit mode which is identical with part of the mechanism proposed independently by Weisang and Gault (*2*) for the isomerization of 2-methylpentane and for ring opening in methylcyclopentane. For example, bond rupture in a CH_2–CH_2-group is written:



(2)

In the case of hydrogenolysis in the iso-unit mode (that is, the hydrogenolysis mode for neopentane), we note that a number of mechanisms have been previously proposed for the reaction of neopentane at a single metal (platinum) atom (*6*–*9*). Although the situation is somewhat confused by the lack of hard evidence, on balance we consider that one of the processes recently suggested by Rooney (*9*) is the most probable for iridium, involving neopentane adsorption as a quasi-metallocyclobutane species, and the further transformation of this in a manner analogous to the established mechanism for olefin metathesis. The proposed quasi-metallocyclobutane species involving iridium seems reasonable in view of the fact that 3,3-dichloroplatinocyclobutane is a known compound (*10*), while an iridium metallocyclobutane intermediate is probable in the ring opening of cyclopropane with a catalyst consisting of an iridium (I) complex (*11*). We thus write the pathway for the hydrogenolysis of neopentane in the iso-unit mode as



(3)

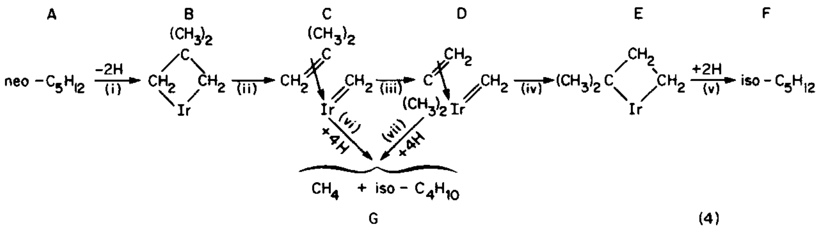
In the light of these conclusions we now construct a rather more general model for skeletal reactions on iridium which shows the relationship between hydrogenolysis and skeletal isomerization, and which indicates how the reaction selectivity is influenced by the composition of iridium–gold catalysts.

(i) *Iso-unit hydrogenolysis/bond-shift isomerization.* We deal first with hydrogenolysis in the iso-unit mode: the associated isomerization reaction (if any) is a bond-shift process, using the terminology accepted for reactions over platinum (cf. *12*).

There is evidence for isomerization by bond-shift in the following situations: neopentane on supported iridium–gold (this paper: 514–558 K; isomerization selectivity 9.7–16.5 mol% based on fraction of parent converted to isomer); neopentane on gold-free supported iridium of very low dispersion, $\bar{d} \geq 7$ nm (Ref. (*1*); 507–593 K; isomerization selectivity 24.4–25.0 mol%); isobutane on gold-free supported iridium (Ref. (*1*); 493–535 K; isomerization selectivity small); isobutane on gold-free iridium film (Ref. (*13*); 529–614 K; isomerization selectivity 4–8.5 mol%)[2]; isobutane on iridium–gold film (Ref. (*13*); Ir70; Au30 Mol%; 575 K; isomerization selectivity 35.5 mol%).[2]

In summary, we may distinguish two factors by which the bond-shift isomerization reaction component may be increased at the expense of iso-unit hydrogenolysis: one is the addition of gold to the catalyst, the second is by the use of gold-free iridium catalysts of very low dispersion. In the following discussion we construct a model to account for this behavior.

We refer to neopentane reactant to illustrate the main reaction features. In this case, and at least with supported catalysts where the effects of self-poisoning are very much less severe than with film catalysts, the reaction selectivity was little dependent on temperature, suggesting that both hydrogenolysis and isomerization pass via a common set of precussors. We propose that the generalized iso-unit hydrogenolysis/bond-shift isomerization reaction involving a single iridium atom active site, may be written



(4)

We would expect all steps in the pathway between the C_5 isomers [steps (i)–(v)] to be reversible but not necessarily in established equilibrium, and the steps involving the formation of the hydrogenolysis products [steps (vi) and (vii)] to be essentially irreversible.

In Reaction (4) we see that hydrogen reactant is involved in two different ways; the conversion of intermediates C and D to hydrogenolysis products (each needing 4 H), and the conversion of intermediate E to the C_5 isomer (needing 2 H). Overall, the isomerization process [A to F, Reaction (4)] does not result in the net consumption of hydrogen while for hydrogenolysis (A to G) there is a net consumption of hydrogen. Accordingly, one expects that if the concentration of reactive hydrogen is reduced, the effect will be to allow an increased fraction of the reaction to occur by isomerization.

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[2] With these systems the apparent isomerization selectivity fell sharply at higher reaction temperatures due to the effect of rapid secondary reactions.

Clearly the reactive hydrogen in Reaction (4) must be adsorbed hydrogen since it must be of a sort that the effective concentration is dependent on the nature of the catalyst.

From data in the present paper and in an earlier report (*1*), it follows that the concentration of adsorbed hydrogen present on iridium catalysts at reaction temperature (450–550 K) can be varied by the addition of gold to the iridium, and by changing the dispersion of gold-free iridium. The effect of gold is twofold. The "saturation" hydrogen adsorption per unit area of metal surface is reduced, and the binding energy for adsorbed hydrogen is also reduced. With gold-free iridium the binding energy for adsorbed hydrogen is higher for catalysts of very small metallic particle size (*1*).

The significance of these changes in hydrogen binding energy for the concentration of adsorbed hydrogen at reaction temperatures is demonstrated in Fig. 7. Here we have plotted, as a function of temperature (T), values for the ratio n_T/n_{295}, where n is the quantity of hydrogen desorbed in the TPD profile at temperatures above the specified temperature (TK or 295 K). Figure 7 presents data for, (i) Ir100, Au0; $\bar{d}$ = 1. 5 nm; cf. curve 1, Fig. 4, this paper; (ii) Ir81, Au19; d = 1. 5 nm; cf. curve 3, Fig. 4, this paper; (iii) Ir100, Au0; d = 7 nm; cf. Fig. 5, Ref. (*1*). The data in Fig. 7 cannot be used to make quantitative comparisons of hydrogen coverage under reaction conditions because the hydrogen pressures are considerably different in a reaction mixture and under TPD conditions. Nevertheless, a comparison at reaction temperatures (450–550 K) obviously shows that the concentra-

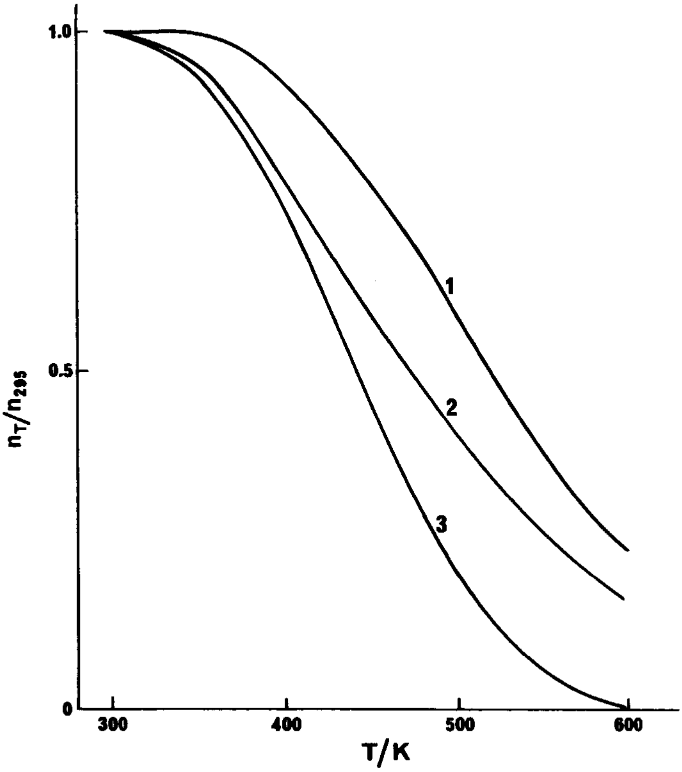
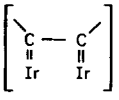
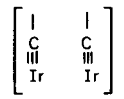
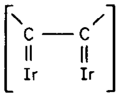
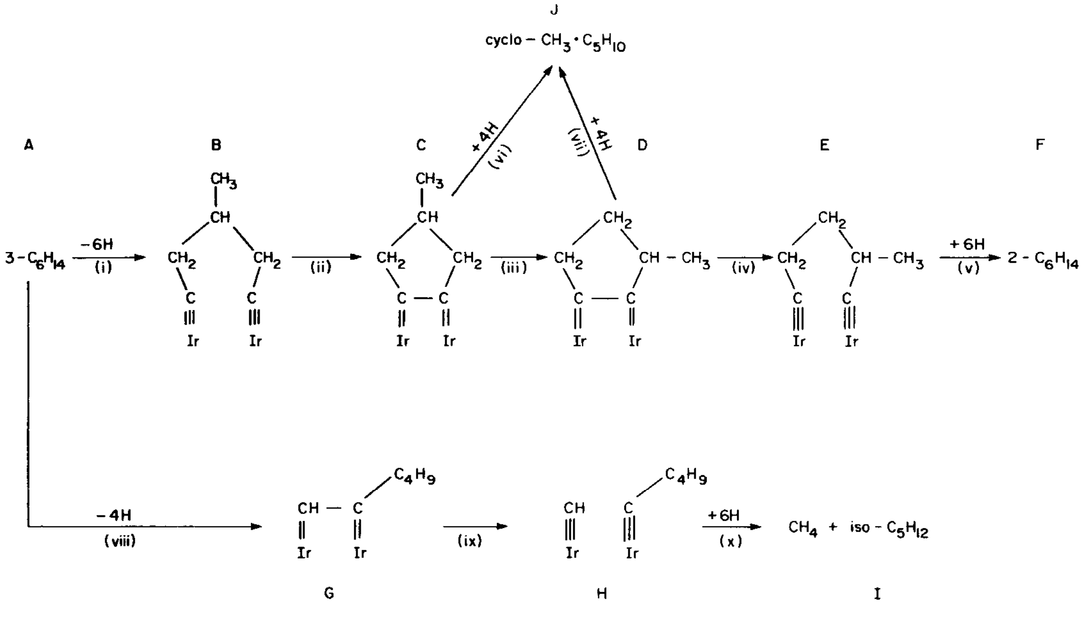


Fig. 7. Dependence of n_T/n_{295} on temperature (TK): n_T, quantity of hydrogen desorbed in TPD profile at temperatures above TK; n_{295}, quantity of hydrogen desorbed in TPD profile at temperatures above 295 K. Primary data from Fig. 4 and Ref. (*1*). Curve 1, iridium/aerosil, $\bar{d}$ = 1.5 nm; curve 2, iridium/aerosil, $\bar{d}$ = 7 nm; curve 3, Ir81, Au19/aerosil, $\bar{d}$ = 1.5 nm.

tion of adsorbed hydrogen falls in the sequence (Ir100, Au0, $\bar{d}$ = 1.5 nm) > (Ir100, Au0, $\bar{d}$ = 7 nm) > (Ir81, Au19, $\bar{d}$ = 1.5 nm), and this sequence corresponds with that for increasing isomerization selectivity.

(ii) *C_2-unit hydrogenolysis/carbocyclic isomerization.* We return to Reaction (2) responsible for hydrogenolysis in the C_2-unit mode. Under no circumstances can this reaction lead to isomerization by bond-shift (e.g., the conversion of neopentane to isopentane). However, as pointed out by Weisang and Gault (*2*), isomerization via a carbocyclic intermediate is readily formulated if

(a) interconversion between  and  is reversible and, (b) if in a carbon chain such as $-C_xH_2-C_yH_2-C_zH_2-$ the adsorption mode  can be propagated from the pair C_x–C_y to C_y–C_z. We illustrate these reactions with reference to 3-methylpentane reactant in Reaction (5), and we have included in this scheme the possibility of desorption of cyclic hydrocarbon from the carbocyclic intermediate.



In Reaction (5) all steps except (x) are probably reversible although not necessarily in established equilibrium.

Given a suitable reactant, a carbocyclic isomerization pathway resembling A to F, Reaction (5), could be written to involve an adsorbed intermediate of ring size other than C_5. However, there is evidence which suggests that, in this isomerization type of reaction, C_5 is overwhelmingly dominant. Thus, it has been shown (*13*) that the cyclization of *n*-pentane to cyclopentane was a major reaction over an iridium film catalyst at 521–556 K, while no cyclohexane was produced from *n*-hexane at 453–544 K (*14*).

The basic ideas shown in Reaction (5) account for all of the important experimental features: ring opening in methylcyclopentane to 2- and 3-methylpentane but not to *n*-hexane (*1*, *2*); the complete lack of any isomerization component with *n*-hexane reactant (*13*, *14*, *2*); and the positional isomerization observed with ^{13}C-labeled methylpentane reactant (*2*).

When gold is added to an iridium catalyst, it is useful to consider its effect on C_2-unit hydrogenolysis/carbocyclic isomerization in terms of two factors: a change in the active site concentration, and a change in the concentration of adsorbed hydrogen reactant.

We have already seen how, with an increasing surface concentration of gold, the concentration of sites for C_2-unit hydrogenolysis falls relative to the total surface concentration or iridium. We have interpreted this as being a consequence of the need for two adjacent iridium atoms for this reaction to occur. This model implies that, if the gold concentration is high enough, C_2-unit hydrogenolysis/carbocyclic isomerization should be quenched relative to iso-unit hydrogenolysis/bond-shift isomerization reaction which requires only a single iridium atom site. An example which probably illustrates this trend is provided by the reaction of *n*-butane. On gold-free iridium the reaction is entirely C_2-unit hydrogenolysis (450–500 K) (*1*); no isomerization is observed and, for this reactant, none would be possible via a C_5 carbocyclic mechanism. The present paper shows that this situation remains true for *highly dispersed supported* iridium–gold catalysts up to a composition Ir14, Au86. However, with an *evaporated film* catalyst of composition Ir14, Au86 Karpinski and Clarke (*13*) observed some isobutane reaction product at 691–721 K. Because of the very low surface/volume ratio in an evaporated film compared to a highly dispersed supported catalyst, it is very probably that, at a given overall composition, the surface of the former will be much richer in gold than the latter [this point is further discussed in Ref. (*3*) for the platinum–gold system] and, as a consequence, hydrogenolysis in the C_2-unit mode is quenched to a sufficient extent on the film catalyst for a small fraction of the reaction to become significant by iso-unit hydrogenolysis/bond-shift isomerization.

Karpinski and Clarke (*13*) also showed that, in the reaction of 3-methylpentane over iridium–gold film catalysts of composition in the range Ir100, Au0 to Ir19, Au81, an increasing gold content was accompanied by: a reduced selectivity for hydrogenolysis, an increased selectivity to methylcyclopentane and to benzene, while the fraction of the reaction yielding 2-methylcyclopentane and to benzene, while the fraction of the reaction yielding 2-methylpentane remained approximately constant. These observations are consistent with Reaction (5) and the reduced concentration of adsorbed hydrogen resulting from an increased gold content. The fact that methylcyclopentane and benzene production vary in like manner with changing gold content suggests that benzene is formed via ring enlargement of the adsorbed C_5 carbocyclic species.

(iii) *General remarks.* When invoking the concept of surface ensembles as active sites in a system like iridium–gold, the possible influence of adsorbed carbonaceous residues should not be forgotten. In general, one might expect the presence of such residues to generate larger amounts of smaller sized iridium ensembles than would be expected solely in terms of the proportions of iridium and gold in the surface. The proposed effect is due to steric blockage by the adsorbed residues. As pointed out in a previous section, self-poisoning appears to be kinetically most severe with catalysts of high gold content: it is therefore likely that this is also the composition regime where carbonaceous residues have the greatest effect on iridium ensembles.

Our discussion has so far assumed that

C_2-unit hydrogenolysis/carbocyclic isomerization and iso-unit hydrogenolysis/bond-shift isomerization are strictly alternative reaction types. However, it is obvious that the structure of the majority of hydrocarbons is such that a propensity exists for both reaction types to occur. C_2-unit hydrogenolysis/carbocyclic isomerization is intrinsically the more facile reaction type, but since the active sites for these two processes may be present in widely differing proportions, situations may easily exist where, at higher temperatures, both reaction types occur simultaneously to comparable extents.

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