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Catalytic Dehydrogenation of Propane to Propene over Platinum and Platinum–Gold Alloys

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The rates of dehydrogenation of propane to propene over platinum and very dilute platinum-in-gold alloys have been measured. In the composition range of 0.5–14.0 atom% platinum, the rates per unit surface area of the alloy powders vary linearly with the bulk platinum concentration in the alloys. From this it is concluded that only one platinum atom is involved in the rate-determining step.

For both platinum and the alloys, activation energies of some 29 ± 2 kcal/mole were measured. The reaction rate order in hydrogen, however, is different. It is proposed that propane dehydrogenation over platinum and over the alloys occurs via the same reaction mechanism, namely, dissociative chemisorption of propane on a single platinum atom to which two adsorption sites are associated, one of which carries a hydrogen atom. The subsequent conversion of the propyl radical into π-bonded propene via β-hydrogen elimination appears to be rate determining. The last step, desorption of π-bonded propene, has a comparatively low activation energy. The difference in negative reaction order, with respect to hydrogen, between platinum and its diluted alloys reflects a lower steady-state θ_H on Pt atoms surrounded by Au atoms vis-à-vis Pt atoms on a Pt surface.

INTRODUCTION

The mechanism of the catalytic dehydrogenation of paraffins over transition metals such as platinum is still a matter of controversy. This also applies to related reactions on which much more fundamental work has been done, such as paraffin/deuterium exchange, olefin hydrogenation, and isomerization of double bonds in olefins. In the older literature the emphasis was on α,β-diadsorbed alkyl radicals, supposedly bonded to two adjacent metal atoms of the catalyst (*1*). Later, the emphasis shifted to π-olefinic and π-allylic intermediates, which may coordinate to one single atom on the surface of the metal catalyst (*2*). For the hydrogenation of olefins it has recently been suggested that the actual hydrogen transfer takes place between an adsorbed species C_xH_y and adsorbate olefin, thus linking hydrogenation with self-hydrogenation (*3*).

Information about the number of catalyst atoms involved in the rate-determining step of a given reaction may come from experiments in which the catalytically active metal is diluted in a catalytically inactive one. Provided that the two metals mix, the average size of surface-exposed "ensembles" of contiguous active atoms will decrease upon dilution. When reactions differ from one another with regard to the number of contiguous active atoms engaged simultaneously in the rate-determining step, dilution may lead to a change in catalytic selectivity. This is what has been observed in a number of recent studies of hydrocarbon conversions over group VIII

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transition metals diluted in a group Ib matrix [Refs. (*4*, *5*) and, for reviews, Ref. (*6*)]. The information is qualitative in nature as long as the data are confined to selectivities, but when reaction rates per unit alloy surface area can be measured, quantitative information may also result. Thus, in a recent study of ethane hydrogenolysis over Cu–Ni alloys it was concluded that the pre-exponential factor in the rate of hydrogenolysis (per unit alloy surface area) decreases quadratically with decreasing nickel concentration. This indicates that ensembles of two contiguous nickel atoms participate in the rate-determining step (*7*). Although some restrictions and assumptions are involved [cf. the discussion in Ref. (*7*) and in the present paper], the overall approach seems to be sound. Therefore, we selected the "quantitative dilution method" for studying the catalytic dehydrogenation of paraffins.

In order to minimize collective phenomena we chose a series of alloys in which not only the surface concentration, but also the bulk concentration, of the active metal is low. Furthermore, we aimed to collect rate data pertaining to alloy surfaces that are substantially free of irreversibly adsorbed carbonaceous residues. To this end we used an appreciable hydrogen pressure and a high hydrogen-to-hydrocarbon ratio. With these precautions we measured initial rates of propane dehydrogenation over a series of highly diluted platinum-in-gold alloys. In order to be able to interpret the results we subjected the same alloys to additional catalytic tests including *n*-hexane isomerization, hexene-1 double-bond isomerization, and hydrogen and CO chemisorption.

TABLE 1

Physical Properties of Platinum–Gold Alloy Powders

Alloy composition (atom% of platinum)	BET surface area (m^2/g)	Number of constituent phases as determined by XRD
0.0	0.016	1
0.5	0.017	1
1.0	0.023	1
2.5	0.024	1
7.0	0.14	1
18.7	0.58	2[b]
100.0	0.17	1
100.0[a]	—	—

[a] Platinum wire; diameter, 0.2 mm.

[b] 95% weight has the composition 14 ± 1 atom% Pt–Au; 5% weight has the composition 96 ± 1 atom% Pt–Au.

EXPERIMENTAL

Catalyst Preparation and Characterization

Platinum–gold alloy powders were prepared following the method of Kulifay (*8*), i.e., platinum and gold present in *aqua regia* solutions were reduced by hydrazine dissolved in water. In the Kulifay (*8*) synthesis, which also has a purifying effect, since noble metals are preferentially reduced/precipitated, we used metals of 99.99% purity (Drijfhout) and reagents of a.r. grade (Merck). After filtering, washing, and drying, the precipitates were sintered in hydrogen for 16 hr at 420°C and, then, were characterized by BET-N_2 adsorption, X-ray diffraction analysis (XRD), and electron microprobe analysis (Table 1).

Sintering temperatures well above 420°C resulted in an unacceptable loss of (BET) surface area, especially with the preparations containing $\leqslant 7\%$ Pt. The temperature during the activity test runs, therefore, was limited to $T \leqslant 410°C$. The absence of appreciable sintering during the catalytic test was verified with BET measurements on the spent catalysts.

Electron microprobe analyses revealed that the spatial variation in platinum content of the alloy powders is well below 10% (spatial resolution $\approx 10^4$ Å). According to XRD [(111) and (422) diffractions], the ~18% Pt–Au alloy contains a platinum-rich phase (97% Pt) in addition to a goldrich one (14% Pt). This is in agreement with the existence of a miscibility gap in the Pt–Au system, extending at 300°C from approximately 14 to 97% Pt by weight (*9*). Actually, the overall composition, i.e., ~18% Pt, resulted from an error during the preparation which was aimed at producing a 14% alloy. The other alloys showed only one phase in XDR. Lattice constants were observed to be approximately 0.1% below the value calculated from the linear interpolation between the values for pure platinum and pure gold [(422) diffractions].

Test Procedures

The catalyst powders were tested in a microflow reactor system as particles of 0.05–0.08 mm. The (variable) amount of catalyst powder was supplemented with sufficient inert diluent, either SiC or α-Al_2O_3 to obtain a catalyst bed with an approximately constant volume (~1 cm^3). All experiments were conducted under plug-flow conditions. Neither the comparisons of the catalytic activity of highly porous platinum powder with that of massive wire nor the experiments in which both the amount of catalyst and the gas flow were varied proportionally disclosed any evidence of distortion of the kinetic data by either intra- or interparticle diffusion.

The reactor used in the catalytic tests was made of gold-coated stainless steel. Conditions could be monitored and regulated with an accuracy well within 0.2°C (temperature) and 5% (pressure and flow).

Feedstocks included *n*-hexane as well as propane and hexene-1. The *n*-hexane was purified by distillation and percolation over SiO_2 and was deoxygenated prior to use. Propane was purified *in situ* by passing it in succession through a high- and a low-temperature Pt/SiO_2 catalyst bed located upstream of the microreactor. Hydrogen was purified by diffusion through a palladium thimble.

TABLE 2

Examples of Catalyst Decline[a]

Time lapse after cut-in of hydrocarbon feed (min)	Conversions[b]		
	$C_3^=/C_3$ ($H_2/C_3 = 50$; $T = 360°C$)	$C_3^=/C_3$ ($H_2/C_3 = 1$; $T = 360°C$)	$2MP/nC_6$ ($H_2/nC_6 = 80$; $T = 390°C$)
2	≡1.00	≡1.00	≡1.00
17	0.97	0.95	0.72
32	1.07	0.88	0.61
47	1.01	0.79	0.55
62	1.02	0.72	0.53
α_0[c]	0.98 ± 0.05	1.03 ± 0.03	0.92 ± 0.08

[a] Catalyst: platinum powder; total pressure, 2 bar.

[b] Basis: conversion after 2 min ≡ 1.00.

[c] α_0 = initial activity calculated from a least-squares fit of the data tabulated with the decline model: $\alpha(t) = \alpha(o) \exp[-\beta \times t]$.

Prior to catalytic testing the catalysts were subjected to an *in situ* cleaning procedure, comprising oxidation (1 bar O_2, $T = 220°C$, $t = 1$ hr) and reduction (2 bar H_2, $T = 400°C$, $t \geqslant 6$ hr). To obtain a constant initial activity it sometimes proved necessary to repeat the oxidation/reduction cycle several times. During the oxidation step the temperature had to be limited to 220°C, because, at higher temperatures, oxygen induced dehydrogenation activity of the reactor walls. The catalytic tests were carried out at higher temperatures ($T = 360$–$390°C$) and, therefore, might give rise to further segregation of bulk impurities. However, when we subjected a few selected samples to an external burn-off with oxygen (1 bar O_2, $T = 420°C$, $t = 24$ hr), no significant increase in catalytic activity was observed.

The first product analysis by on-line glc was usually made 120 sec after cut-in of hydrocarbon into the hydrogen feed, and subsequent analyses were performed with 15-min time intervals. From the resultant activity decline curves, the initial activity was determined by extrapolation toward $t = 0$. All numbers for catalyst activities in this paper (turnover numbers) pertain to these initial activities. In all experiments, the decline in catalyst activity was found to be very smooth, from which we conclude

TABLE 3

Turnover Numbers for the Production of Propene from Propane, Measured at Standardized Conditions[a]

Bulk platinum content of the Pt–Au alloy (atom% of Pt)	Turnover numbers	
	(moles of propene/sec/m^2 of alloy surface area)	(molecules of propene/sec/surface-exposed Pt atoms)
0.0	⩽0.07 × 10^{-9}	—
0.5	0.42 × 10^{-9}	5.0 × 10^{-3}
1.0	0.85 × 10^{-9}	5.1 × 10^{-3}
2.5	2.7 × 10^{-9}	6.5 × 10^{-3}
7.0	4.7 × 10^{-9}	4.0 × 10^{-3}
14.0[c]	13.8 × 10^{-9}	5.9 × 10^{-3}
100.0	580 × 10^{-9}	35 × 10^{-3}

[a] Standard conditions: $T = 360.0°C$; $P_{H_2} = 2.00$ bar; $P_{C_3} = 0.040$ bar; flow rate = 50 Nl/hr; catalyst weight variable: 0.5 mg (100% Pt) up to 7000 mg (0.5% Pt in Au).

[b] Calculated assuming that $x_{Pt}^{surface}/x_{Pt}^{bulk} \equiv 1$.

that the initial activities are a valid representation of the steady state. Typical examples are given in Table 2.

We measured the rate of dehydrogenation of propane at constant temperature, pressure, and flow with a variable amount of catalyst. In the absence of the catalyst (but with the diluent present) the oxidation/reduction procedure resulted in propane conversions $\leqslant 1 \times 10^{-6}$. Our catalytic conversions, expressed as the propene/propane ratio, usually were in the range between 5×10^{-6} and 5×10^{-5}. This range is well above the baseline of the empty reactor and sufficiently below the equilibrium value, which, at $P_{H_2} = 2$ bar and $T = 360°C$, is approximately 2×10^{-4}. Under the conditions chosen, conversions are thus approximately proportional to rates, as was confirmed by the good linearity for the relation between conversion and catalyst weight at constant flow. From this we conclude that our data pertain to catalytic dehydrogenations measured in the kinetic region. However, when we compare experiments with different reactor fillings, the data on initial activities are found to scatter considerably ($\sigma \approx 50\%$). The precision of the data obtained with one particular reactor filling is better than 10%. To our mind, the relatively large scatter of data with different reactor fillings may well be due to a varying degree of initial surface cleanliness of the catalyst. Consequently, our values for the activation energies and reaction rate orders (stemming from experiments on one reactor loading) are probably accurate within 10% (Table 4), but values for turnover numbers (Table 3, Fig. 1) can only be accurate within a factor of 2.

TABLE 4

Activation Energies and Reaction Orders for the Dehydrogenation of Propane to Propene over Platinum and Platinum Gold Alloys

Parameter	Pt	Pt–Au
Reaction order in propane	+1.00 ± 0.02	+0.98 ± 0.01
Reaction order in hydrogen	−1.1 ± 0.1	−0.49 ± 0.06
Activation energy (kcal/mole)	30.5 ± 1.8	27.1 ± 1.1

RESULTS

Propane Dehydrogenation

The rates of dehydrogenation of propane to propene, obtained under identical test conditions for all catalysts, are given in

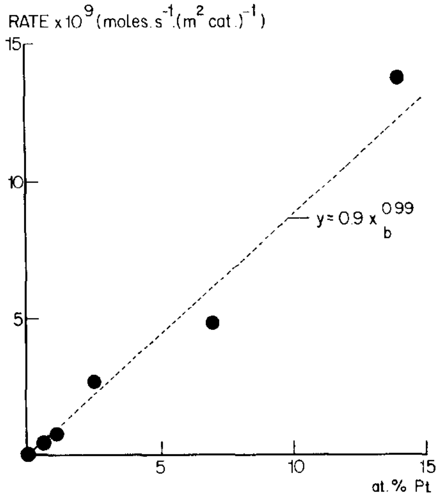


FIG. 1. Rates for propene production over Pt–Au alloys with varying bulk platinum content (cf. data of Table 3).

Table 3 and Fig. 1. They are presented as turnover numbers, i.e., moles of propene produced per second per square meter of catalyst surface. As discussed in the experimental section, the turnover numbers are inaccurate up to at least 50% relative. Nevertheless, the relation between them and the bulk platinum content, x_b, is found to be close to linear. When fitting a power curve, $R(x_b) = \alpha x_b^{\beta}$ moles per second per square meter of alloy surface area, to the data in Table 3 (Fig. 1), we obtain a least-squares regression coefficient of $\beta = 0.99$ for $0 \leqslant x_b \leqslant 0.15$.

Table 4 summarizes the activation energies and the orders of the reaction rates in propane and hydrogen. Because the variations in these values within the alloy series are insignificant relative to the measurement precision (10%), the data obtained on the individual alloys have been averaged.

n-Hexane Isomerization

With n-hexane as the feed, catalytic conversions over platinum and various alloys were measured at $T = 390°C$, $P_{H_2} = 2$ bar, and $H_2/nC_6 = 300$ moles/mole. The rate of the catalytic isomerization of n-hexane to 2-methylpentane (2MP) increases with increasing bulk platinum content, x_b, of the Pt–Au alloys, and, compared to the rate of propane dehydrogenation, it does so much faster (Table 5). When fitting a power curve, $R = \alpha x_b^{\beta}$ moles per second per square meter of alloy surface, to the isomerization data, we obtain $\beta \approx 3$. If macroscopic segregation of unalloyed platinum on the surface of the alloy catalysts took place we would rather expect a linear relation between rate and alloy composition (*10*). Thus, formation of a platinum phase seems to be absent in our alloy powders.

TABLE 5

Rate of Propane Dehydrogenation Relative to n-Hexane Isomerization versus Alloy Composition[a]

Catalyst	Rate ($C_3 \rightarrow C_3^{=}$)/ rate ($nC_6 \rightarrow 2MP$)
100% Pt	1.3×10^2
14% Pt–Au	5.5×10^5
7% Pt–Au	2.5×10^6
1.5% Pt–Au	$\geqslant 1.2 \times 10^7$

[a] $T = 360°C$; $P_{H_2} = 2$ bar; $H_2/C_3 = 50$; $H_2/nC_6 = 80$.

Hydrogenation and Double-Bond Isomerization of Hexene-1

For an olefin such as hexene-1 the kinetics change rapidly in the temperature range of 100–200°C. The activation energies drop sharply with increasing temperature (Table 6), even becoming negative at

TABLE 6

Activation Energies for Double-Bond Isomerization (E_1) and Hydrogenation (E_2) of Hexene-1 over Pt

Temperature range (°C)	E_1 (kcal/mole)	E_2 (kcal/mole)
80–100	19[a]	14
100–140	9	9
140–190	5	3

[a] Conditions: $H_2/nC_6^{=} = 300$; $P_{H_2} = 2$ bar. Rate ($T = 100°C$) $\approx k \times P_{nC_6^{=}}^{0.0}$.

$T \geqslant 200°C$. This has previously been observed for other olefins (*11, 12*). The activation energy for double-bond isomerization of hexene-1 approaches 20 kcal/mole when the rate approaches zero reaction order in hexene-1.

Chemisorption Experiments

When alloying platinum with gold we observe a decrease in hydrogen chemisorption, which is much more pronounced than the decrease in CO chemisorption (Table 7). Irreversible chemisorption of hydrogen on 14% Pt–Au is nondetectable, even when the temperature during hydrogen exposure is raised from 273 to 400 K. This indicates that "dilution" of surface-exposed platinum atoms with gold substantially reduces their ability to dissociate and/or chemisorb hydrogen. Surprisingly, Pt–Au films do not show this behavior (*13*), but Pt–Sn powders do (*14*).

Surface Composition

CO chemisorption indicates that the surface of the Pt–Au alloy powders is substantially enriched in gold (Table 7): $x^{\mathrm{Pt}}_{\mathrm{surface}}/x^{\mathrm{Pt}}_{\mathrm{bulk}} \approx \frac{1}{3}$. A modest surface enrichment in the component with the lowest heat of sublimation has also been observed for Ni–Au and Pd–Au by measurements of inelastic ion scattering (*15*). We found this method to be inapplicable to Pt–Au (mass differences too small, even when using Kr^+ ions). Auger (AES) measurements on 14% Pt–Au (*15*) and CO chemisorption on various Pt–Au alloy films (*16*) did not indicate a surface segregation of gold. Therefore, a definitive value for $x^{\mathrm{Pt}}_{\mathrm{surface}}/x^{\mathrm{Pt}}_{\mathrm{bulk}}$ cannot be given, but it seems safe to assume that $\frac{1}{3} \leqslant x^{\mathrm{Pt}}_{\mathrm{surface}}/x^{\mathrm{Pt}}_{\mathrm{bulk}} \leqslant 1$.

TABLE 7

Irreversibly Chemisorbed CO and H_2[a]

	Sample	
	100% Pt	14% Pt–Au
CO-ad (molecules/m^2)	8.6×10^{18}	4.3×10^{17}
H_2-ad (molecules/m^2)	4.8×10^{18}	$<2 \times 10^{16}$
H_2-ad[b] (molecules/m^2)		$<2 \times 10^{16}$
CO-ad/H_2-ad	1.8	>20

[a] Exposure at 0.1 Torr for 10 min at $T = 273$ K; removal of reversibly adsorbed species by 10 min of evacuation at $T = 273$ K.

[b] Exposure at 0.1 Torr for 10 min at $T = 400$ K.

DISCUSSION

Catalytic Dehydrogenation: Intrinsic Activity of Platinum Ensembles of Different size

Dilution of catalytically active platinum atoms in a matrix of catalytically inactive gold atoms has been employed as a means of studying the intrinsic activity of ensembles of contiguous platinum atoms of different size. To what extent the resultant rates per unit surface area can be interpreted depends on two conditions. (i) The intrinsic activity of ensembles of any given size must be sufficiently constant despite the variation in alloy composition; and (ii) the variation in distribution of active atoms over ensembles of different size with the variation in alloy composition must be sufficiently large. Before interpreting the rate data for the dilution series 0.5–14% Pt in gold, we will discuss to what extent these conditions have been met.

The intrinsic activity of an ensemble of a given size or geometry will depend on its coordination in both the surface and subsurface planes. It may, in addition, be influenced by collective (band structure) phenomena. As a result, intrinsic activities may well vary with the overall alloy composition. On the other hand, the platinum in the present alloy series occurs in a highly dilute form. With increasing dilution, the individual platinum ensembles will become more and more isolated from each other, and, therefore, we know that in the limit of very high dilution, their intrinsic activity must become constant. Thus, in view of the highly diluted nature of the present alloys, the assumption of approximately constant intrinsic activity is probably justified.

The variation in distribution of active atoms over ensembles of different size with the alloy composition can be calculated from elementary statistics, when we assume the atoms to be noninteracting. The results depend on the coordination number; for systems exhibiting six coordinations the results have been listed in Table 8. It follows that, for a concentration of the minority component in the range 0.5–14 atom%, the fraction of minority atoms present in clusters, i.e., ${}_6F_{>1}$, varies drastically (Table 8):

$$Q \equiv ({}_6F_{>1}{}^{14\%})/({}_6F_{>1}{}^{0.5\%}) \geqslant 20.$$

In an estimate of the value of Q for platinum–gold alloys, three effects are relevant: (i) the occurrence of four coordination besides six coordination; (ii) surface enrichment of the alloy in gold; and (iii) clustering of platinum (and gold) due to the endothermicity of the alloy.

Effects i and ii increase Q further toward its limiting value (i.e., 28), whereas effect iii decreases the value of Q. When we calculate a dimerization constant at 360°C corresponding to an endothermicity of some 0.4 kcal/mole (*9*) and neglect effects i and ii, we obtain a lower limit for Q:

$$Q \equiv (F_{>1}{}^{14\%\ \mathrm{Pt-Au}})/(F_{>1}{}^{0.5\%\ \mathrm{Pt-Au}}) \geqslant 12.$$

Thus, when we decrease the bulk platinum concentration from 14% down to 0.5% Pt, we decrease the fraction of surface-exposed platinum atoms having at least one platinum atom as nearest neighbor, i.e., $F_{>1}$, by at least one order of magnitude. If the dehydrogenation reaction requires two or more contiguous platinum atoms, and if the intrinsic activity of these ensembles does not increase by at least one order of magnitude, a decrease in dehydrogenation rate (turnover number) per platinum atom surface exposed upon dilution must be expected.

TABLE 8

Distribution of Solute Atoms in Systems Featuring Six Coordination

x_s	${}_6F_1{}^a$	${}_6F_2$	${}_6F_3$	${}_6F_{>1}$	${}_6F_{>2}$
0.14	0.405	0.251	0.062	0.595	0.344
0.07	0.647	0.235	0.064	0.353	0.118
0.025	0.859	0.122	0.019	0.141	0.019
0.010	0.941	0.055	0.0040	0.059	0.0040
0.005	0.970	0.029	0.0011	0.030	0.0011

[a] ${}_6F_{(>)i} \equiv$ Fraction of all surface-exposed atoms of the solute present in the surface in an atomic fraction x_s, in a cluster of size $(>)i$.

The rate of dehydrogenation of propane over the alloys can be represented by (cf. Fig. 1 and Table 3)

$$R = a(x_b)^{1.0}\ \mathrm{mol/sec/m^2},$$

in which x_b corresponds to the bulk platinum concentration in the alloy. For our highly diluted alloys the extent of surface enrichment, i.e., x_b/x_s, will hardly depend on the bulk platinum content, x_b; thus, it follows that

$$R = b(x_s)^{1.0}\ \mathrm{mol/sec/m^2},$$

in which x_s corresponds to the surface platinum concentration in the alloy. As the rates are expressed per unit (BET) surface area of the alloys, this means that the turnover numbers per surface-exposed platinum atom (TON) vary with R/x_s, and, thus,

$$\mathrm{TON} = C(0.5\% \leqslant x_{\mathrm{Pt}}^{\mathrm{bulk}} \leqslant 14\%),$$

i.e., the turnover numbers per platinum atom exposed at the surface are independent of both x_s and x_b.

Whereas the turnover numbers (and activation energies!) appear to be independent of alloy composition, the fraction of platinum atoms present in ensembles, i.e., $F_{>1}$, varies significantly. Therefore, we conclude that ensembles and isolated platinum atoms have, within the measurement precision, the same intrinsic activity per platinum atom. This important outcome shows that the rate-determining step in the catalytic dehydrogenation of propane over platinum–gold alloys *involves one platinum atom only.*

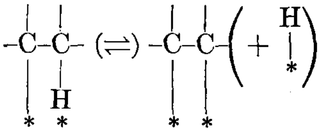
Reaction Mechanism

Five results derived from the present work are of possible relevance to the reaction mechanism. (A) The activation energies for propene dehydrogenation over Pt and dilute Pt–Au alloys are equal within the experimental error. (B) The order in hydrogen of the dehydrogenation rate is −1.0 over Pt and −0.5 over the dilute Pt–Au alloys. (C) The rate-determining step with the dilute alloys involves one Pt atom only. (D) The activation energy for propane dehydrogenation (29 kcal/mole) is distinctly higher than that for hexene-1 double-bond isomerization in the region of zero reaction order (19 kcal/mole). (E) The steady-state coverage, with hydrogen (at $P = 0.1$ Torr H_2 and $T \geqslant 120°C$), of platinum atoms on platinum–gold surfaces is very low and considerably below that of platinum atoms on platinum surfaces.

On the analogy of the numerous reaction mechanisms proposed so far for, *inter alia,* olefin- and alkane–deuterium exchange and olefin hydrogenation (*17, 18*), the overall dehydrogenation reaction probably involves three major steps: (i) cleavage of the first C–H bond in a dissociative adsorption step, resulting in an adsorbed alkyl group; (ii) cleavage of the second C–H bond, resulting in a π- or σ-bonded olefin; (iii) desorption of the olefin.

In regard to the question which is the rate-determining step, step iii has to be discarded in view of our result D, and (i), in view of the general observation that the activation energy for alkane–deuterium exchange over group VIII transition metals is low [10 kcal/mole for platinum (*17*)]. For the further discussion we thus assume that step ii is the rate-determining step, namely, conversion of the adsorbed alkyl species into adsorbed olefin.

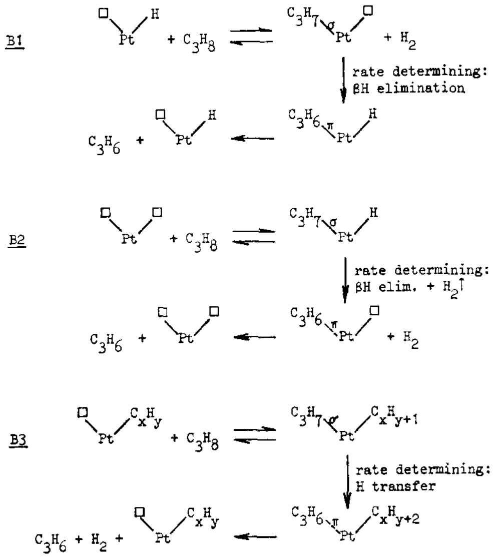
According to the classical Horiuti–Polanyi mechanism (*1*), several sites are required for the conversion of adsorbed alkyl species into adsorbed olefin, and at least two of these sites are associated with a pair of *adjacent* metal atoms.



$$\underset{*\quad\;\;*}{-\overset{|}{C}-\overset{|}{\underset{H}{C}}-}\;(\rightleftharpoons)\;\underset{*\quad *}{-\overset{|}{C}-\overset{|}{C}-}\left(+\;\underset{*}{\overset{H}{|}}\right)$$

For the dilute alloys this can be either a Pt–Au atom pair of a Pt–Pt pair. The former possibility would be very difficult to reconcile with our result A. Other reasons to reject it are found in results obtained by Van Schaik *et al.* (*19*) and de Jongste *et al.* (*20*) on Pt–Au and Pt–Cu alloys. These authors conclude that Pt–Au pairs, unlike Pt–Cu pairs, are unable to act as dual ensembles for paraffin chemisorption. The possibility that a pair of adjacent Pt atoms is required obviously conflicts with our result C. Therefore, we propose that the two sites required for the conversion of the adsorbed alkyl species into adsorbed olefin *are located on one and the same Pt atom.* The utilization of two ligand sites on the same transition metal atom is not unusual in homogeneous catalysis; in heterogeneous catalysis, it has been proposed by Cossee (*21*), for Ziegler–Natta polymerization, and by Takeuchi *et al.* (*22*), for olefin hydrogenation and exchange of isotopes between protonated and deuterated paraffins over sulfided nickel catalysts with perfectly isolated nickel atoms in the surface.

Three possible reaction modes can be visualized to account for the role played by such geminal-site pairs in the dehydrogenation of a paraffin such as propane.



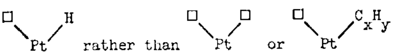
The third of these modes adapts a recent suggestion by Thomson and Webb (*3*) for the mechanism of olefin hydrogenation to the present case of paraffin dehydrogenation.

A further distinction between these three modes can be made on the basis of the observed reaction orders in hydrogen (−0.5 for the alloys; −1.0 for platinum; cf. Table 4), i.e., result B. When we assume all the adsorption/desorption equilibria preceding the rate-determining step to be established, we calculate for rate $\alpha P_{H_2}^{n}$, the following values of n.

	$\theta_{Pt-H} \ll 1$	$\theta_{Pt-H} \approx 1$
Mechanism B1	$-\frac{1}{2}$	-1
Mechanism B2	0	$-\frac{1}{2}$
Mechanism B3	0	$-\frac{1}{2}$.

From our results E and B, we then conclude that for the alloys mechanism B1 is to be preferred to the two other mechanisms discussed.

As far as platinum itself is concerned, we cannot exclude the possibility that our results have been distorted by the rapid formation of a carbonaceous overlayer in the period preceding the first measurement of catalytic performance. The chances of such distortion are slim, however, considering the measurement conditions (high hydrogen pressure, low hydrocarbon pressure) and the observation that the dehydrogenation rate is first order in propane over a propane pressure range as wide as 4×10^{-3} bar $\leqslant P_{C_3} \leqslant 0.5$ bar (P_{H_2} = C = 2 bar). From the combined results (E, B) and A, therefore, we conclude that mechanism B1 is also the preferred one for platinum itself. The finding that the turnover number per surface-exposed platinum is higher for platinum itself than for the alloys (by a factor of 2–7; cf. Table 3 and the data on surface composition of the alloys) is consistent with this conclusion, because with



as the catalytic site, a higher surface coverage with adsorbed hydrogen implies a higher turnover number.

Apart from result E, which is the outcome of chemisorption measurements, there is also evidence from alkane-deuterium exchange (*23*) and from calculations (*24*) suggesting that alloy surfaces might well be comparatively deficient in hydrogen.

CONCLUSIONS

(i) Considering the dehydrogenation reaction, the intrinsic activity of the platinum atoms forming part of the surface of a dilute platinum-in-gold alloy is essentially independent of the extent of dilution (0.5 atom% $\leqslant x_b^{Pt} \leqslant$ 14 atom%).

(ii) All rate data, i.e., those obtained on the alloys and on platinum itself, can be accounted for by the same mechanism. This mechanism has as the rate-determining step the conversion of propyl radicals to π-bonded propene, using two adsorption sites located on one platinum atom. The differences between platinum itself and its alloys, manifest in the turnover numbers and the order of the reaction rate in hydrogen, derive according to the proposed mechanism from a difference in surface coverage with hydrogen, the alloy surfaces being comparatively deficient in hydrogen. Evidence to this effect is provided by chemisorption experiments.

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