Hydrogenation of Olefins on Platinum

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Hydrogenation of buta-1,3-diene was studied on the three low-index planes of platinum under quasi-atmospheric pressure and hydrogenation of 2-methyl-buta-1,3-diene was investigated on Pt(111) in the same conditions. Kinetic results and especially selectivity were analyzed and compared to each other. Special attention has been given to the adsorbed species and their relative abundance on the surface. A mechanism has been proposed which explains the variations observed in the studied systems. In no case is the reaction governed by the dissociation of hydrogen and the selectivity depends on the stability of the hydrocarbon species on the surface. © 1991 Academic Press, Inc.

INTRODUCTION

The hydrogenation of unsaturated hydrocarbons on platinum single crystals has been studied for several years in our laboratory. Many results have been obtained by varying the nature of the molecule, the crystalline orientation, and the experimental conditions; it is now possible to propose a reaction mechanism and to better understand which factors determine the activity and the selectivity of the reaction.

The aim of this paper is to make a synthesis of our results concerning the hydrogenation of ethene, buta-1,3-diene (butadiene), and 2-methyl-buta-1,3-diene (isoprene) on several surfaces of platinum. The originality of our study consists of three main points:

(i) reactions were achieved over well characterized surfaces thanks to standard UHV techniques;

(ii) hydrogenations were made in the presence of a hydrogen–deuterium equimolar mixture, the H_2–D_2 equilibration reaction being used as a surface probe for the dissociation of hydrogen;

(iii) an isolating valve located in our UHV system and connected to the gas reactor permitted reactions to be studied at quasi-atmo-

spheric pressure. The activity and the selectivity of the reactions are discussed when changing experimental conditions, temperature, and reactant pressures for several molecules, namely one olefine and two diolefines. Surface mechanisms are discussed and compared with models advanced by other authors and some more general concepts are put forward concerning these hydrogenation reactions on metals.

EXPERIMENTAL

All experiments were carried out in an ultrahigh vacuum system equipped with a retractable isolating cell connected to a reactor working in the 100 to 800-Torr pressure range. This UHV device was equipped with a CMA Auger (Riber O.P.C. 105), LEED optics (Varian), a quadrupole mass spectrometer (Leybold IQ 200), and an ion gun for cleaning the surface. During the catalytic reaction, the recirculation of gases was achieved by use of a pump with a constant flow rate of 3 liter min^{-1}. Preliminary experiments completed at various flow values have shown that, in our batch reactor, kinetics were not controlled by the gas flow rate. Conversion was monitored with a gas chromatograph (Intermast). Single crystals

356

of platinum (99.995% purity) were thin disks 0.5 mm thick and 1 cm^2 total area cut to within 1° of the desired orientation; the edges of the crystal were covered with a SiO_2–Al_2O_3 coating in order to avoid extra activity. Both crystal faces were cleaned by several cycles of ion bombardment, moderate heating treatment in the presence of oxygen (10^{-7} to 10^{-4} Torr) and high-temperature annealing to restore the surface. The purity and the crystallinity of the surface were checked by AES and LEED before each catalytic test. Research purity gases were used to prepare the reaction mixture, which was introduced onto the crystal heated at the desired temperature. The reaction temperature was controlled by using a chromel–alumel thermocouple spot welded to one face of the sample.

During the reaction, the hydrocarbon product formation was followed by gas chromatography. In order to study the initial stage of the reaction, the chromatogram was started at different times (0,1,2,3 . . . min) for several identical reactions; this procedure revealed no transitory or accommodation period. The H_2–D_2 reaction was simultaneously followed by mass spectrometry.

Once the reaction was achieved, i.e., conversion greater than 90% or 2-h maximum reaction time, gases were evacuated before cooling the sample to reduce additional hydrocarbon contamination of the surface during the cooling step. The reactor cell was then quickly evacuated by a turbomolecular pump. The sample was then reexposed to ultrahigh vacuum and the surface analyzed by LEED and AES.

RESULTS

The hydrogenations of butadiene (1–3) and isoprene (4) have been investigated on the three low-index planes in the following conditions:

$$100 \text{ Torr} < P_{tot} < 700 \text{ Torr}$$
$$10 < P_{H_2}/P_{HC} < 100$$
$$295 \text{ K} < T < 500 \text{ K}.$$

The H_2–D_2 equilibration had been previously investigated in the absence of hydrocarbon on platinum single crystals (5); H_2–D_2 reaction and hydrocarbon hydrogenation have now been investigated simultaneously and results are reported in the present paper. The hydrogenation of ethene was not studied in detail by us since many authors had already investigated and discussed this reaction (6), but we made some isolated experiments with C_2H_4 in order to check the agreement of our reaction rates with values from well established previous results.

In order to make the results clear, the activity and the selectivity of the studied reaction are presented and discussed separately. In the activity section, the influence of the structure for butadiene hydrogenation and the influence of the molecule for hydrogenation reactions on Pt(111) are successively presented. The selectivity section relates the influence of temperature and reactant pressures for the hydrogenation of butadiene on various planes of platinum and the influence of the geometry of the molecule comparing butadiene and isoprene on Pt(111).

ACTIVITY

The data considered in this section concern the turnover frequencies of the reactions at zero conversion, i.e., the initial rate of hydrocarbon conversion per surface platinum atom and per second.

(1) Activity in Butadiene Hydrogenation as a Function of the Structure

The initial reaction rates of butadiene hydrogenation as well as the simultaneous H_2–D_2 equilibration rate have been plotted in Fig. 1.

The initial activity increases with the roughness of the surface with a fivefold ratio between the (110) and (111) planes. The rate of the H_2–D_2 exchange is always more than one order of magnitude greater than the rate of hydrogenation. Activation energies do
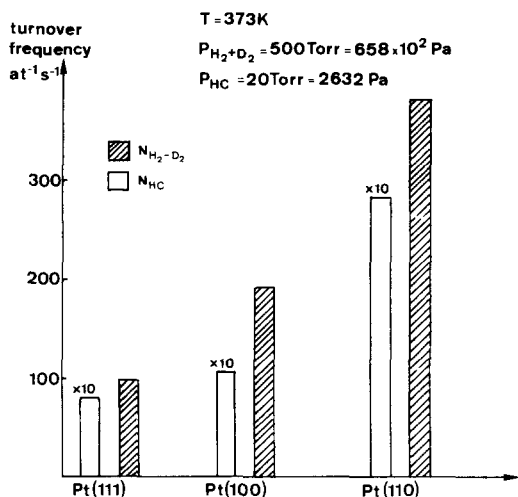
FIG. 1. Rate of butadiene hydrogenation on platinum as a function of the surface structure.

not significantly vary with the crystalline orientation:

	Pt(111)	Pt(100)	Pt(110)
$E_a(kJ \cdot mole^{-1})$	38	33	39

Under usual conditions, the Auger spectra after reaction indicate a carbon coverage close to the monolayer, roughly 2C atoms per platinum surface atom. At high temperature, above 500 K, the reaction is totally poisoned and the carbon coverage observed afterward is very high.

(2) Activity of Olefine Hydrogenation on Pt(111) as a Function of the Molecule

The initial activities have been plotted in Fig. 2 for C_2H_4, C_4H_6, and C_5H_8 hydrogenations on the dense (111) plane of platinum for reactions at $T = 373$ K.

The rate of initial conversion decreases considerably when the size of the molecule increases. It should be noted that the drop in activities is slightly more important when passing from C_4 to C_5 than from C_2 to C_4 hydrocarbons,

$$k_m C_4H_6/k_m C_5H_8 \ (= 6)$$
$$> k_m C_2H_4/k_m C_4H_6 \ (= 5),$$

k_m being the reaction rate in molecules per platinum atom per second.

In fact, since half of the initial amount of diolefine is directly twice hydrogenated, the rate of conversion of butadiene or isoprene is the rate of hydrogenation of two double bonds for half of the initial number of molecules. As a consequence, if the data of the diagram were increased by a factor 1.5 for C_4H_6 and C_5H_8, one obtains a transformed diagram (Fig. 3) which shows the rate of a double bond hydrogenation as a function of its surroundings.

This representation shows the relatively poor activity of a double bond of a C_4H_6 molecule and confirms the drastic effect of an additional CH_3 group on the molecule.

All the turnover frequencies are reported in Table 1. We should remark that our TOF values for C_4H_6 hydrogenation are hardly comparable with some recent work by Massardier et al. (7) since the experimental conditions were different. An extrapolation of
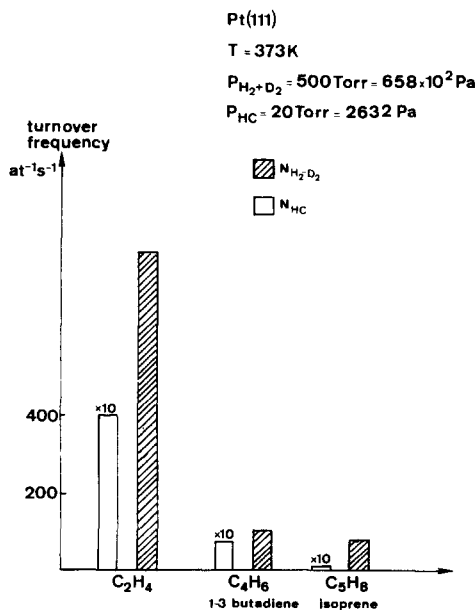

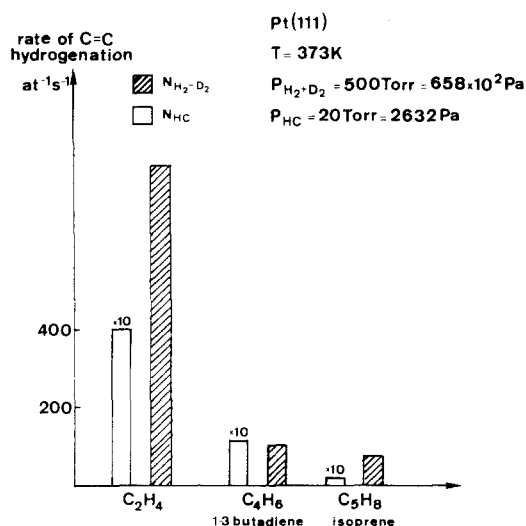FIG. 2. Rate of C_2H_4, C_4H_6, and C_5H_8 hydrogenation on Pt(111).

FIG. 3. Rate of C=C bond hydrogenation in C_2H_4, C_4H_6, and C_5H_8 on Pt(111).

their results to our chosen temperature and pressure conditions leads to very similar values.

SELECTIVITY

We next investigated the selectivity in olefine under stationary conditions of buta-

TABLE 1

Turnover Frequencies of Several Hydrogenation Reactions and of the H_2-D_2 Exchange on Platinum Single Crystals

Reaction[a]	TOF molecules (Pt atom^{-1}s^{-1})		
	Pt(111)	Pt(110)	Pt(100)
$H_2 + D_2$	8700	5.10^4	12600
$H_2C=CH_2 + H_2$	400		
$H_2 + D_2$	8400		
$H_2C=CH—CH=CH_2 + H_2$	80	280	110
$H_2 + D_2$	1000	4000	2000
$H_2C=C—CH=CH_2 + H_2$ 　　　$|$ 　　　CH_3	13		
$H_2 + D_2$	735		

[a] Experimental conditions: $T = 373$ K, $P_{H_2} + P_{D_2} = 500$ Torr, $P_{HC} = 20$ Torr.

diene or isoprene hydrogenation. As far as butadiene is concerned, we studied the variations in butene selectivity with experimental conditions at the origin of the reaction on the three low-index planes. We then compared the selectivity in olefines for the butadiene and for the isoprene hydrogenations, at the origin of the reaction.

In this paper, the selectivity is defined as the ratio [Σ butenes/Σ butenes + butane] as a percentage and the conversion is based on the total amount (%) of butadiene reacted.

(1) Selectivity in Butenes as a Function of Temperature

The observed variations of the butene formation at the origin of the reaction are collected in Fig. 4.

At 0% conversion, the temperature dependence of the selectivity in butenes is structure sensitive:

—on Pt(111), the selectivity is constant over the whole range of temperature;

—on Pt(110) a slight improvement of the butene selectivity occurs when the temperature increases;

—on Pt(100) a remarkable break in the butene formation appears at an intermediate value of the temperature: below 400 K it increases from 40 to 60% and then above 400 K it drops to 30%.

Note that around 400 K the selectivities of the three single crystals are identical.
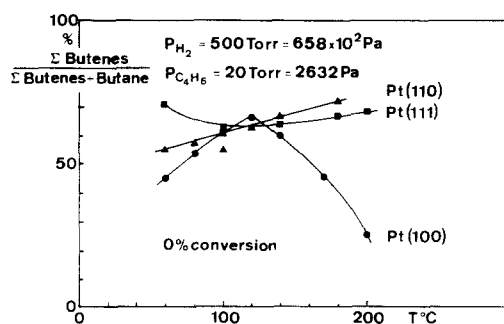
The selectivity is not significantly depen-

FIG. 4. Selectivity to butenes in C_4H_6 hydrogenation on platinum as a function of temperature.

dent on conversion provided the latter is below 60%. At high conversion, above 60%, the proportion of butenes drops, all of them being hydrogenated to butane at the end of the reaction.

(2) Selectivity in Butenes as a Function of Reactant Pressures

2a. Influence of P_{H_2}. In order to better understand the influence of P_{H_2} upon selectivity, we first report the values of α, the order of the reaction of butadiene conversion, measured at $T = 373$ K in the 50 to 800-Torr P_{H_2} range:

	Pt(111)	(100)	(110)
α, $P_{H_2} < 100$ Torr	1	0.5	2
α, $P_{H_2} > 100$ Torr	1	0.5	1

—At P_{H_2} above 100 Torr, the selectivity in butenes is constant when P_{H_2} varies and it is equal to 60% at the beginning of the reaction.

—At P_{H_2} lower than 100 Torr, Pt(110) exhibits a slight increase in butene selectivity when P_{H_2} decreases; the fraction of butenes reaches the 75% value for $P_{H_2} = 80$ Torr. These variations can be correlated to an increase of the order with respect to hydrogen. For both other orientations, no change of the selectivity could be detected.
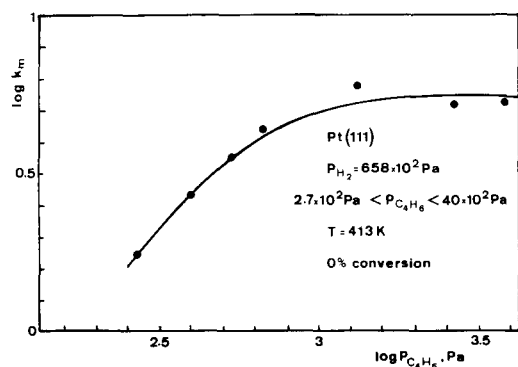

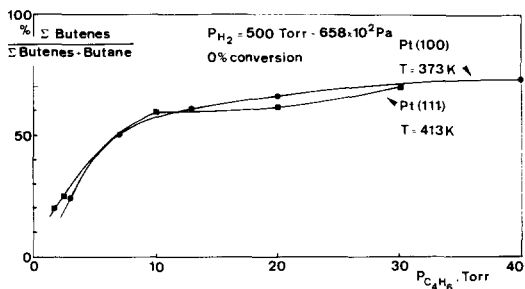FIG. 5. Rate of C_4H_6 hydrogenation on platinum as a function of $P_{C_4H_6}$.

FIG. 6. Selectivity in butenes in C_4H_6 hydrogenation as a function of $P_{C_4H_6}$ on Pt(111) and Pt(100).

2b. Influence of $P_{C_4H_6}$. Similarly to Section 2a, we report the values of β, the order of the reaction with respect to butadiene measured at $T = 373$ K in the 2- to 50-Torr $P_{C_4H_6}$ range (see Fig. 5).

	(111)	(100)	(110)
$\beta/P_{C_4H_6}$	1 to 0	0	0

The variations of the butene proportion in the initial stage of the reaction as a function of $P_{C_4H_6}$ are presented in Fig. 6 for Pt(111) and Pt(100). It keeps a constant value, equal to 60%, on Pt(110).

A correlation between the variation of the order and the change in selectivity is clear for the (111) orientation. The change in selectivity observed for the (100) orientation can be correlated to a change of the order of the second hydrogenation reaction (butene → butane) which becomes negative at a butadiene pressure lower than 20 Torr. No similar variation of the orders of either the first or the second hydrogenation reaction has been found for the (110) orientation. On this latter plane, the selectivity in butenes does not depend on $P_{C_4H_6}$.

(3) Selectivity in Olefines on Pt(111) as a Function of the Geometry of the Molecule

In the activity section, it was clear that with Pt(111) on passing from butadiene to isoprene, i.e., substituting a CH_3 group for
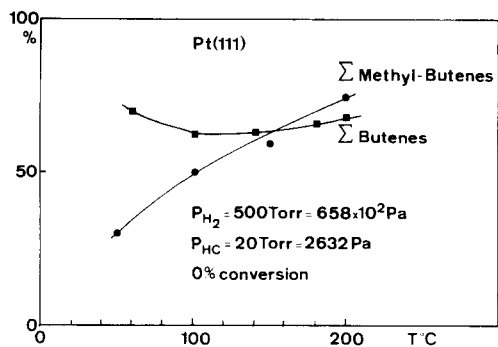
FIG. 7. Selectivity of the C_4H_6 and C_5H_8 hydrogenation reactions on Pt(111) as a function of temperature.
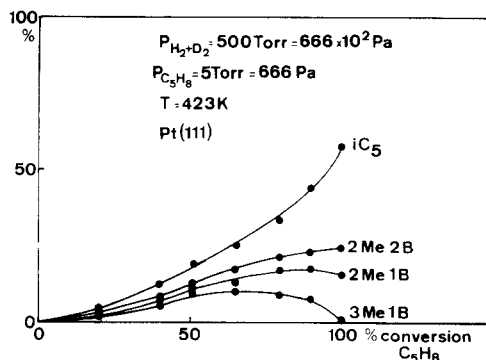

FIG. 8. C_5H_8 hydrogenation on Pt(111) 2Me2B = 2-methyl-2-butene, 2MeIB = 2-methyl-1-butene, iC_5 = isoprene, 3MeIB = 3-methyl-1-butene.

an H atom, the initial rate of conversion is reduced by a factor 6. On that same plane of platinum, the selectivity in olefines is also very dependent on the molecule, and it does not similarly change with temperature and reactant pressures for butadiene and isoprene.

3a. Selectivity in olefins as a function of temperature. The fraction of butenes formed at the origin of the reaction is independent of temperature while the fraction of methylbutenes increases with temperature (Fig. 7).

3b. Selectivity in olefine as a function of reactant pressures. Formation of both butenes and methylbutenes is independent of P_{H_2}. Differences have been observed when changing the initial pressure of diolefine: on Pt(111) selectivity to butenes improves when the initial $P_{C_4H_6}$ increases (Fig. 6) (cf. Section 2). As for the isoprene, selectivity to methylbutenes as well as the orders of the reaction are independent of $P_{C_5H_8}$.

3c. Selectivity in olefines as a function of conversion. No remarkable difference in olefine selectivity could be observed with butadiene or isoprene at low or intermediate conversions under intermediate conditions. The major difference appeared at high and total conversions with a much lower proportion of total hydrogenation for isoprene than for butadiene at equivalent conversion (Figs. 8 and 9); for example, at 100% conver-

sion and 100°C on Pt(111), 90% of butene but only 58% of isopentane are produced.

All these features make clear the influence of the geometry of the molecule on the reaction of hydrogenation.

DISCUSSION

The hydrogenation of diolefines over metal surfaces has attracted much interest during the last few years from the viewpoint of obtaining a better understanding of the nature of adsorbed reaction intermediates, of the reaction mechanisms, and of the factors governing the selectivity. It has already been proposed that the activity and the se-
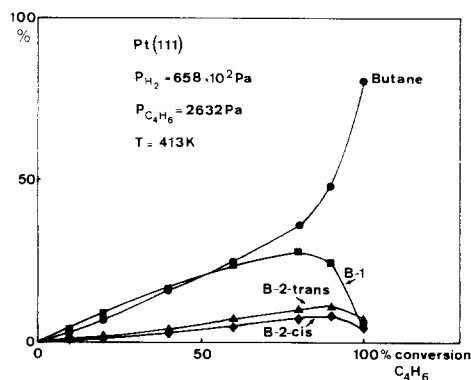

FIG. 9. C_4H_6 hydrogenation on Pt(111) B-1 = 1-butene, B-2-*trans* = *trans*-2-butene, B-2-*cis* = *cis*-2-butene.

lectivity of these reactions depend on the hydrocarbon coverage of the catalytic surface. The questions arising from catalytic experiments on model metal surfaces are: What are the species present on the surface during the reaction? Which are the most abundant species and which one governs the kinetics? Finally, are these studies representative of real catalytic challenges? An attempt is now made to answer these questions.

Activity in C_4H_6 Hydrogenation on Pt(111), Pt(100), and Pt(110)

The rate of butadiene hydrogenation, r, follows the order

$$r(111) < r(100) < r(110).$$

This increase in activities with the roughness of the surface has already been observed for the H_2–D_2 equilibration reaction.

From Fig. 1, the rate of the H_2–D_2 equilibration reaction, measured during the reaction of C_4H_6 hydrogenation, is more than one order of magnitude faster than the latter. Consequently, considering that the rate of H_2 dissociation is under stationary conditions, very close to that of the H_2–D_2 reaction, it is not the limiting step of the hydrogenation reaction.

Moreover, in the range of pressures 6 Torr

$\leq P_{C_4H_6} \leq 20$ Torr and 100 Torr $\leq P_{H_2} < 800$ Torr, the orders of the hydrogenation reaction with respect to butadiene are $\beta = 0$ on all surfaces, and with respect to hydrogen are $\alpha = 1$ on Pt(111),(110) and 0.5 on Pt(100), suggesting that the surface is saturated with hydrocarbon species and that the hydrogen coverage is low. The rate of butadiene hydrogenation would rather be limited by the amount of "active" dissociated hydrogen. Active hydrogen means hydrogen atoms adsorbed in the vicinity of hydrocarbon and available for the reaction of hydrogenation. The amount of that kind of hydrogen is clearly dependent on the site geometry and consequently on the crystalline orientation. As a matter of fact, the dissociation of hydrogen is known to be promoted by atoms in low coordination, e.g., edge and corner atoms, whose concentrations are in the order (110) > (100) > (111). Low coordination atoms may also be promoters for the activation of an unsaturated bond. On the three low-index planes considered the orders of the H_2–D_2 reaction measured in the presence of hydrocarbon are higher than on clean surface (5) in agreement with a decrease of the coverage in hydrogen. In accordance with the above discussion, we propose the following mechanism:

$$H_{2(g)} \rightleftharpoons 2H_{(ads)}$$
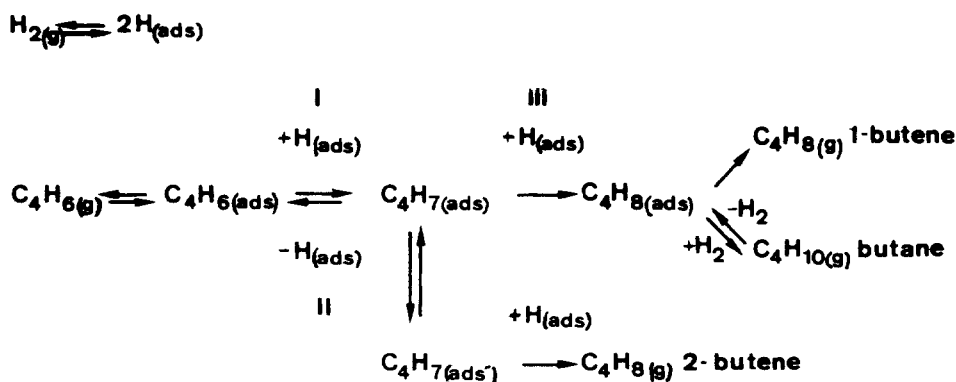
There should exist two configurations for the adsorbed C_4H_7 species, one leading to the 1-butene and the other to the 2-butene.

The rate, limited by reaction III, can be written

$$r = A\ [C_4H_7][H],$$

A being dependent on the temperature, and $[C_4H_7]$ and $[H]$ being the surface concentration of C_4H_7 and H, respectively.

The concentration in C_4H_7 is governed by reactions I, II, III,

$$[C_4H_7] = k_1\ [C_4H_6][H]/(k_2 + k_3\ [H]),$$

which for small values of $[H]$, such that $k_2 \gg k_3\ [H]$, simplifies to

$$[C_4H_7]/[C_4H_6][H] = k_1/k_2 = \text{constant}.$$

The rate determining step involves hydrogen and the most abundant hydrocarbon species, the concentrations of which accordingly appear in the rate constant expression. We attempt to explain the differences in the orders α by the following alternatives:

—*Either* the surface is mainly covered with C_4H_6 whatever the orientation and α changes because the coverage in active hydrogen is structure sensitive, being higher on (100) than on both (110) and (111) faces,

—*or* the nature of the most abundant surface species is itself structure dependent (it could be $C_4H_{6(ads)}$ on Pt(111) and Pt(110), and $C_4H_{7(ads)}$ on Pt(100)). The fact that the smallest value of the activation energy was measured for the (100) plane tends to indicate a correlation between the nature of the most abundant intermediate and the reaction order; a small order with respect to hydrogen would come with a more hydrogenated surface intermediate and a smaller activation energy. As a matter of fact, both propositions are correlated with one another through equilibrium II and one can see here the role of the particular configuration of the (100) plane which is the only surface having fourfold sites.

Since the first step of the mechanism is the adsorption of C_4H_6, we now attempt to correlate the effect of the structure observed in kinetics to experimental and theoretical studies dealing with adsorption of butadiene. The value of the Auger I_c/I_{Pt} peak-to-peak ratio after reaction, which is well reproducible on each plane, corresponds to the first plateau of the adsorption isotherm determined on Pt(111) and Pt(110), i.e., 1.5 C/Pt on Pt(111) (3) and 2C/Pt on Pt(110) (8). In agreement with the zero value of β/C_4H_6, we assume that under conditions of nonirreversible poisoning ($P_{H_2} > 100$ Torr, $T < 500$ K), the surface is covered with a monolayer of hydrocarbon C_4H_6 or C_4H_7. From the literature, two configurations can be considered for the C_4 hydrocarbon species, either standing up on the surface as "butylidyne" species bound by only one carbon atom as proposed by Godbey *et al.* (9) or flat di- or tetra-σ adsorbed species as suggested by Avery and Sheppard (10) from TDS and EELS evidence and confirmed by theoretical calculations of Maurice and Minot (11). In fact both the butylidyne and the "flat adsorbed" species could coexist on the surface, the latter being the catalytically active species. The concentration of butylidyne might be expected to be structure sensitive but it seems to us unlikely that these species would act as a cocatalyst or hydrogen transfer agent. It is more reasonable to think that in the presence of a large excess of hydrogen and whatever its orientation, the surface is mainly covered with flat adsorbed hydrocarbon molecules; the latter would leave a very small fraction of available sites for the dissociation of hydrogen. The observed activity of the H_2–D_2 exchange, which is, on average, 10 times lower than that observed on each plane in the absence of butadiene, directly gives an evaluation of the surface free of hydrocarbon and (or) of the defects in the adsorbed layer, namely one-tenth of the total active surface area. Our experimental results lead us to propose a mechanism involving flat adsorbed species and allow a correlation between kinetics and adsorption strength of

the main reaction intermediate. From the orders with respect to butadiene, it appears that, when $P_{C_4H_6}$ decreases from 50 to 3 Torr:

—on Pt(110), there is no influence on kinetics;

—on Pt(100), below $P_{C_4H_6} = 10$ Torr, the order of the reaction of butadiene hydrogenation is not affected but the order of the reaction of butane formation toward butadiene pressure becomes negative (this experimental feature indicates that butane principally comes from readsorption of butenes which is competitive with adsorption of butadiene);

—on Pt(111), butadiene is even more destabilized, the surface being no longer saturated for the conversion of butadiene (the order becomes positive) when $P_{C_4H_6}$ is below 10 Torr.

As a consequence, we propose that the reaction takes place between an active adsorbed species in a flat configuration with hydrogen dissociated on the fraction of the surface, which is left free.

Activity in C_2H_4, C_4H_6, C_5H_8 Hydrogenation on Pt(111)

The decreasing initial activity observed when passing from C_2H_4 to C_4H_6 and even more from C_4H_6 to C_5H_8 results from combined size and configuration effects.

It appears that the rate of H_2–D_2 exchange is not affected by ethene but decreases by a factor of 8 in the presence of butadiene and slightly more in the presence of isoprene. An explanation can be given by the occupancy of the surface. As a matter of fact numerous works have been devoted to C_2H_4 adsorption and in particular the coverage at saturation is still controversial: C/Pt maximum ratio is said to be 0.5 or 1 (12, 13, 14) and in any case much lower than the ratio reached after C_4H_6 or C_5H_8 adsorption. This rather low value of ethene coverage of the surface only slightly affects the rate of dissociation of hydrogen.

Comparing the rates of C_2H_4, C_4H_6 and C_5H_8 hydrogenation, one must consider the conjugated character of the C=C bond of C_4H_6 and C_5H_8 which is known to be involved in the adsorption and to react differently from the isolated C=C bond of C_2H_4.

Considering that the decrease of the rate of H_2–D_2 exchange is similar with butadiene and isoprene, the drastic difference in the hydrogenation rates of these two molecules must be due to the nature of the hydrocarbon–metal interactions. Recent work (15) has shown that on Pt(111) the first monolayer corresponds to C/Pt = 1.5 for butadiene and C/Pt = 1 for isoprene, respectively. This suggests that under our hydrogenation conditions, the number of molecules of hydrocarbon adsorbed on the surface and available for hydrogenation is much lower in the case of isoprene than in the case of butadiene. This is undoubtedly induced by the CH$_3$ group which has a steric effect and an electronic donor effect to the double bond in the α position and which strongly influences the adsorption as well as the reactivity of the molecule.

Selectivity in the C_4H_6 Hydrogenation on Pt(111), Pt(110), and Pt(100)

In previous papers, we have established that at low conversion the formation of butane proceeds in the main by hydrogenation of 1-butene and we proposed the following triangular reaction scheme:
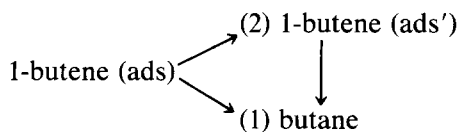
in which process 1 means an immediate second hydrogenation which does not require a readsorption of 1-butene, and is equivalent to a direct conversion of butadiene to butane, whereas process 2 results from desorption–readsorption of 1-butene before its hydrogenation; 1-butene (ads') represents a change of adsorption site of 1-butene.

This second hydrogenation scheme would be valid on the three considered surfaces,

with one or the other path being prevalent under particular conditions. The variations of the selectivity in butenes with the temperature (Fig. 4) can be explained by the above presented mechanism of second hydrogenation:

—An increase of the selectivity in butenes with temperature suggests that process 1 is predominant on the surface: butenes undergo a second hydrogenation, their desorption is partially activated by temperature, and is not compensated by readsorption. This would be the case of Pt(100) at $T <$ 120°C.

—A decrease of selectivity in butenes with temperature suggests that the formation of butane is promoted by the readsorption of butenes and this more easily at high temperature, when the surface is partially free of butadiene. This would be the case of Pt(100) at $T >$ 120°C. On Pt(110), the slight increase of butenes is in agreement with a strong adsorption of both butadiene and butenes. On Pt(111), the selectivity is almost constant with temperature, suggesting that desorption and readsorption of butenes compensate each other.

The influence of $P_{C_4H_6}$ on the selectivity can be simply correlated with the strength of adsorption of the hydrocarbon on the surface: on Pt(111) and Pt(100), the proportion of butenes increases with $P_{C_4H_6}$ because in the range of pressure, 3 Torr $< P_{C_4H_6} <$ 10 Torr, the coverage in butadiene varies as already seen in the above discussion of the reaction orders. On Pt(110), the selectivity does not change with $P_{C_4H_6}$, because, as indicated by constant and zero values of the orders, the surfaces remain saturated with butadiene.

The influence of P_{H_2} is opposite to that of $P_{C_4H_6}$. On Pt(111) and Pt(100), the selectivity does not change with P_{H_2}; let us note that the influence of P_{H_2} and the orders were studied at a value of T and $P_{C_4H_6}$ for which the selectivity is governed by process 1, i.e., without desorption–readsorption of butenes. The fact that neither the orders nor the selectivity change with P_{H_2} simply indi-

cates that both the reactions of first and second hydrogenation are identically affected by P_{H_2} and that the mechanism does not change. On Pt(110), the selectivity in butenes slightly increases when P_{H_2} decreases; this feature goes with an increase of the orders which means either a change of the most abundant intermediate species or a change of the coverage in hydrogen.

To sum up, when varying the reactant pressures, the surfaces which exhibit changes of selectivity are the ones for which reaction orders vary:

—Pt(110) with P_{H_2};
—Pt(111) and Pt(100) with $P_{C_4H_6}$.

These analogies clearly show that the selectivity in butenes is directly correlated with the nature of the species covering the surface. It appears that at constant P_{H_2} the selectivity in butene is related to the coverage in hydrocarbon; at constant $P_{C_4H_6}$ it is related to the capability of the surface to dissociate hydrogen. Note that the change in butene fractions are much less important with P_{H_2} on Pt(110) than with $P_{C_4H_6}$ on Pt(111) and Pt(100).

Selectivity of olefines in C_4H_6 and C_5H_8 Hydrogenation on Pt(111)

Experimental results show that on Pt(111) the selectivity in olefines, and in particular the influence of temperature and reactant pressures, depends on the geometry of the molecule. The fraction of methylbutenes increases with T but does not change with $P_{C_5H_8}$ when the fraction of butenes does not change with T but increases with $P_{C_4H_6}$. These points can be correlated with the relative positions of the adsorption isotherms of C_4H_6 and C_5H_8 on Pt(111). Some recent experiments (15) have shown that, in the 10^{-7} Torr range pressure, the surface becomes saturated with isoprene for a lower pressure than it does with butadiene. This leads us to suggest that below 10 Torr of hydrocarbon, the surface may no longer be saturated with C_4H_6 but, in the same conditions, is still saturated with C_4H_8. This explains the

respective influences of the pressures for butadiene and isoprene.

The influence of temperature is only observed for isoprene (Fig. 7) and is in agreement with the adsorption of methylbutenes being less strong than that of butenes. The desorption of the C_5H_8 species would be enhanced by an increase of temperature, thereby giving an improvement of the selectivity in olefines.

The most significant difference in the selectivities of butadiene and isoprene hydrogenations was observed at high conversion (Fig. 8) with a fraction of olefines much higher in the latter case than in the former. This is again proof of the weaker adsorption of methylbutenes compared to that of butenes.

CONCLUSION

This detailed study of the hydrogenation of both butadiene and isoprene has revealed a considerable structure sensitivity of the selectivity in olefines under certain conditions of temperature and pressure, and a remarkable correlation between variations of the reaction orders and changes in the selectivity. The main results can be summarized as follows:

—The reaction of butadiene hydrogenation is structure sensitive with an increase of the turnover frequency by a factor 5 from the denser to the rougher planes:

$$Pt(111) < Pt(100) < Pt(110)$$
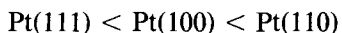
Concerning both butadiene and isoprene hydrogenation, the surface works as a *bifunctional catalyst*, hydrogenation and exchange seem not to occur upon the same kind of sites. Moreover:

—the catalytic surface works with a hydrocarbon layer present, the species not being identical on the three studied surfaces;

—the hydrocarbon layer does not prevent the dissociation of hydrogen but it induces both a geometrical blocking effect and an electronic effect (change of the orders of the H_2–D_2 exchange reaction);

—the rates of hydrogenation of both buta-

diene and isoprene are not controlled by the dissociation of hydrogen.

The influence of the reaction conditions, temperature and pressure, can cause a complete change of mechanism, passing from a "Somorjai type" mechanism involving carbon surface species at P_{H_2}/P_{HC} close to unity to a Langmuir–Hinshelwood type mechanism as proposed above for $P_{H_2}/P_{HC} > 10$ with the fraction of "active" dissociated hydrogen strongly depending on P_{H_2} and P_{HC}.

The selectivity seems to be essentially dependent on the strength of adsorption of the diolefine and olefine. Some ways of improving the selectivity, i.e., of destabilizing the olefine, appear to be either a modification of the surface by blocking some of the too reactive and adsorbing sites or by a modification of the molecule by a steric and electronic effect such as a CH_3 substituent. All these modifications tend to diminish the residence time of the once hydrogenated product. With a better understanding of the surface mechanism offered by very precise catalytic studies but also by theoretical model studies, one can expect to find a way to improve the selectivity of a simply hydrogenation reaction.

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