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Mechanism of Catalytic Hydrogenation of But-1-yne on Palladium

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The deuteration mechanism of but-1-yne on differently dispersed Pd/Al_2O_3 catalysts ($D = 26\%$, $>80\%$) was studied at 293 K. Experiments were performed by flowing a hydrocarbon square pulse at constant pressure (15 Torr) and a H_2–He carrier gas (37–708 Torr) onto the catalyst. Three stages were observed, namely (i) an initial stage with high activity and very low selectivity; the duration of this stage was proportional to the palladium weight and the number of hydrocarbon molecules which passed through the catalyst; (ii) a steady-state stage with constant activity and 98% but-1-ene selectivity; using microwave spectroscopy we found that in addition to the *cis* addition of two deuterium atoms, 10 to 20% of but-1-ene were produced by a different route; (iii) a final stage in which, when the hydrocarbon pressure decreased in the gas phase, an additional desorption peak was obtained consisting of C_4 hydrocarbons. It is proposed that the palladium surface during the steady state is covered by strongly but reversibly adsorbed but-1-yne molecules which act as a poison and are in equilibrium with the reactive chemisorbed but-1-yne molecules. The reactive molecules are described as vinylic adsorbed species in equilibrium with carbene and carbyne species. The first lead to a *cis* addition mechanism. The latter two lead to the *trans* addition and direct hydrogenation.

INTRODUCTION

The hydrogenation of acetylenic compounds has been found to proceed mainly by consecutive processes: the first hydrogenation step gives rise to an olefinic compound which is then hydrogenated further into a saturated one,

$$RC{\equiv}CR \overset{H_2}{\rightarrow} RHC{=}CHR \overset{H_2}{\rightarrow} RH_2C{-}CH_2R$$

From an industrial point of view, it is interesting that the reaction stops after the first hydrogenation step. For this purpose, palladium metal catalysts are usually chosen. Up to now, the reasons why such a metal is so selective in this reaction were unknown.

In this field of research many studies were devoted to hydrogenation of acetylene because of the commercial and fundamental importance of this reaction. The main interest was to optimize the catalyst and the experimental conditions to improve the semihydrogenation selectivity when traces of acetylene are present in a gas mixture containing a large amount of ethylene (*1–3*).

For basic research about the reaction mechanism, it is more interesting to study the hydrogenation of butyne in which different olefinic isomers can be formed (but-1-ene, but-2-ene). Meyer and Burwell (*4*) found that the deuteration of but-2-yne led to more than 99% of dideuterated (d_2)*cis*-but-2-ene. This complete stereospecificity of the reaction was explained by two successive addition steps of adsorbed deuterium atoms to the chemisorbed hydrocarbon; this mechanism is formally similar to the Horiuti–Polanyi mechanism proposed for olefin hydrogenation (*5*). For but-1-yne hydrogenation, the same mechanism was proposed; however, in this case it was shown that the acetylenic hydrogen takes part in the reaction (*6*) as in acetylene hydrogenation (*7*).

More recently, it was shown (*8, 9*) that,

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in addition to the successive hydrogenation steps which transforms acetylene into ethylene and then into ethane, a direct hydrogenation route of acetylene into ethane occurs. Since adsorbed acetylene was shown to exist on palladium as ethylidine species (*10–13*), it was proposed (*14, 15*) that these intermediates are involved in the direct hydrogenation of acetylene into ethane. Therefore, one can ask whether but-1-yne hydrogenation is a simple *cis* addition as Meyer and Burwell suggested or whether butylidine species are also involved in the reaction as ethylidine in acetylene hydrogenation.

On the other hand, in a previous paper (*16*), we have shown that but-1-yne is more strongly adsorbed on small palladium particles than on large ones and Sárkány *et al.* (*17*) suggested that different adsorbed species could exist on small palladium particles. To look further into the but-1-yne hydrogenation mechanism, we have studied the deuteration of but-1-yne using microwave spectroscopic analysis to determine precisely the position of deuterium tracer atoms in the reaction products. Palladium catalysts with different dispersions were used to examine the effect of particle size on the nature of the adsorbed species.

EXPERIMENTAL

Catalysts

Three palladium-on-alumina catalysts were studied:

Pd/Al_2O_3, 0.2% weight dispersion >80% (particle size <10 Å),

Pd/Al_2O_3, 0.45% weight dispersion = 97% (particle size <10 Å),

Pd/Al_2O_3, 0.45% weight dispersion = 26% (particle size = 40–60 Å).

The catalysts were prepared and characterized at the Institut Français du Pétrole, Rueil-Malmaison, as described elsewhere (*18*).

Catalytic Activation

Before each catalytic experiment the catalyst was activated with a flow of 5–95 H_2 (or D_2)–He at 573 K for 1 h. The reactor was then cooled to 293 K under H_2–He flow, and but-1-yne was introduced as described later. Between two catalytic runs on the same sample, an additional treatment of air flow at 573 K for 1 h was used before the H_2–He treatment. Under such conditions the catalytic results were quite reproducible.

Materials

The purification of but-1-yne (Air Liquide, 95%, purity) was made just before each run by distillation at 210 K. But-1-yne was then introduced into the reactor when the main impurity, acetylene, was less than 0.1%. A hydrogen (deuterium)–helium mixture from Air Liquide was used after purification on molecular sieves at 77 K.

Apparatus and Procedure

The catalytic reaction was carried out in an all-glass grease-free flow system, including a reactor operating under differential conditions. Just after the catalytic activation, a known quantity of but-1-yne under constant hydrocarbon pressure (15 Torr) was carried out along the catalyst by a 5–95 hydrogen (deuterium)–helium flow (745 Torr). The constancy of the hydrocarbon pressure and the time of reaction were determined by inserting two katharometers in the flow, upstream and downstream with respect to the reactor. The hydrocarbon flow rate could therefore be calculated.

Small amounts of products were drawn off the flow line at different times during the catalytic run and analyzed by gas–liquid chromatography on a 5-m-long, 3.175-mm-o.d. dimethylsulfolane column operating at 293 K with a flame ionization detector. When deuterium was used instead of hydrogen the hydrocarbon mixture was collected at 77 K and the different compounds were separated by gas–liquid chromatography on a 5-m-long, 6.35-mm-o.d. dimethylsulfolane column operating at 293 K and connected to a katharometer detector. Each hydrocarbon was analyzed by mass spectrometry (using a Type CH7 Varian

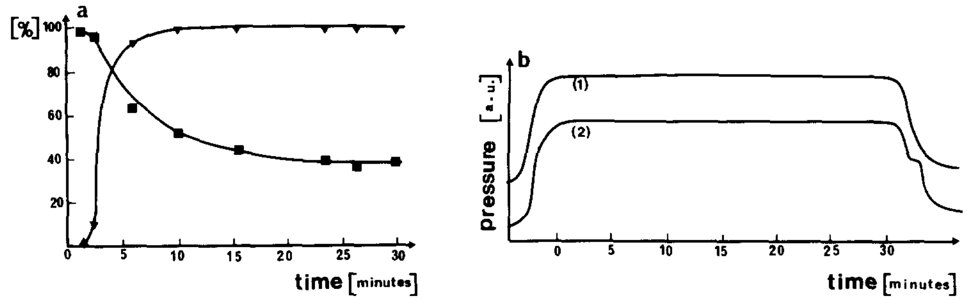


FIG. 1. But-1-yne hydrogenation on Pd/Al_2O_3, 0.2%, $D > 80\%$. (a) ▼, But-1-ene selectivity as a function of time (minutes); ■, but-1-yne conversion as a function of time (minutes). (b) Katharometer signals: hydrocarbon pressure (a.u.) as a function of time (minutes). (1) Upstream with respect to the reactor, (2) downstream with respect to the reactor.

spectrometer) and, in some cases, by microwave spectroscopy (using a 33.33-kHz Hewlett–Packard microwave spectrometer). The analysis procedures are described in detail elsewhere (*19*). The notation of the different deuterated but-1-enes is recalled in Scheme 1 (see next section).

RESULTS AND DISCUSSION

The part a of Fig. 1 shows the characteristic development of the total conversion and the but-1-ene selectivity as a function of time during one experiment where the contact time of the hydrocarbon on the catalyst is kept constant. The but-1-yne partial pressures recorded with two katharometers located upstream and downstream with respect to the reactor are given on the part b of the same figure. The conversion is defined as the percentage of but-1-yne molecules converted.

Whatever the catalyst used, the hydrogenation of but-1-yne showed three different phases:

—an initial phase where the catalytic activity was high and the but-1-ene selectivity was low; the activity then decreased and the selectivity increased.

—a stationary phase reached when the activity and the selectivity were constant.

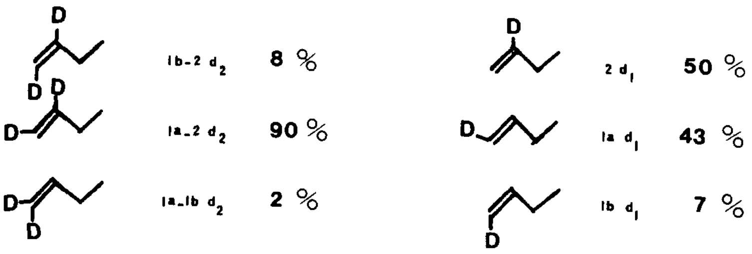
—a final phase observed when the partial hydrocarbon pressure decreased; a desorption peak was then recorded with the katharometer situated downstream with respect to the reactor.

We shall describe successively the stationary phase, the initial phase, and then the final phase.

A. Stationary Phase

During this phase, the conversion of but-1-yne was proportional to the contact time of the hydrocarbon with the catalyst. Up to a limiting conversion of but-1-yne, from which the but-1-ene readsorption occurred, but-1-yne was hydrogenated into but-1-ene (98%) and butane (2%). But-2-enes were also formed but in very small amounts ($\ll 0.01\%$). Such a high selectivity was observed to 40% but-1-yne conversion on large palladium particles and 70% on small particles. It must also be noted that at very high conversion, heavier hydrocarbons ($>C_5$) appear but they have not been identified. The detailed results concerning activities and selectivities during the stationary phase as a function of catalyst dispersion are published elsewhere (*16*).

Tracer studies by using deuterium gas instead of hydrogen gas were performed. The mass spectrometry results for all reaction products (butane, but-1-ene, but-1-yne) are given in Table 1, for the highly and poorly dispersed catalyst, respectively. The two catalysts gave similar results except for the mass spectrum of butane where the large



SCHEME 1

particles show a more important contribution of heavy species (d_6 to d_{10}). The mass distributions of but-1-ene and but-1-yne are similar to those previously obtained by Meyer and Burwell (*6*) and the same statistic formalism was used in order to recalculate the deuterium distributions in but-1-ene and butane. In addition, the location of deuterium in but-1-ene was studied by using microwave spectroscopy. The results are shown in Scheme 1. These molecules were formed directly because the same proportions of these different species were observed whatever the conversion.

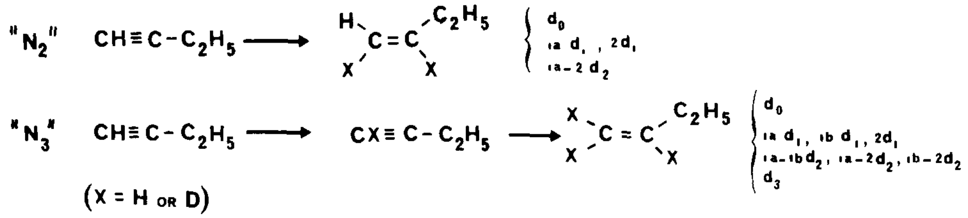
In the formalism proposed by Meyer and Burwell (*6*) a pool of hydrogen (H) and deuterium (D) atoms exists on the surface. This pool is not in equilibrium with the gas phase since no H_2 or HD molecules were found in the gas phase (this isotopic dilution on the surface mainly comes from the acetylenic hydrogen exchange in but-1-yne which occurs during the hydrogenation process giving d_3 but-1-ene).

From this H,D pool an adsorbed but-1-yne will pick up two or three atoms (D or H) which leads to the but-1-ene distribution (d_0, d_1, d_2, d_3). N_2 represents the proportion of the process in which only two C–H or/and C–D bonds have taken part while N_3 represents the proportion of the process involving the participation of three C–H and/or C–D bonds. In these "N_2" and "N_3" processes an additional distribution of D and H coming from the D/H pool will explain the deuterium distribution d_0, d_1, d_2,

TABLE 1

Reaction between But-1-yne and D_2

	Catalyst: 0.2% Pd/Al_2O_3, D > 80%							0.45% Pd/Al_2O_3, D = 26%						
	Butane 0.3%			But-1-ene 19.8%			But-1-yne 79.9%	Butane 0.1%			But-1-ene 9.3%			But-1-yne 90.6%
i	d_i Exp.	d_i Cal. (D/H = 10.2)	N_i	d_i Exp.	d_i Cal. (D/H = 8.1)	N_i	d_i Exp.	d_i Exp.	d_i Cal. (D/H = 12.1)	N_i	d_i Exp.	d_i Cal. (D/H = 12.0)	N_i	d_i Exp.
0	—	—		1.3	1.0		98.8	—	—		—	0.5		98.9
1	0.2	0.1		16.3	16.6		1.2	0.1	0.1		13.2	12.7		1.1
2	2.0	2.1		69.5	69.5	81.7		1.1	1.3		77.4	77.4	88.0	
3	14.9	14.9		12.9	12.9	18.3		11.9	11.5		9.4	9.4	12.0	
4	44.5	44.5	45.9					40.1	40.1	41.4				
5	27.3	27.3	40.8					25.2	25.2	34.3				
6	3.7	3.7	4.1					5.2	5.2	5.5				
7	2.4	2.4	3.4					3.9	3.9	4.4				
8	1.4	1.4	1.0					3.1	3.2	3.0				
9	1.9	1.9	0.5					4.2	4.3	—				
10	1.7	1.7	4.3					5.2	5.2	11.4				



SCHEME 2

d_3 but-1-ene as shown in Table 1. "N_2" is about 80 to 90%, "N_3" is 20 to 10% with D/H 10 ± 2. In the butane distribution, to take into account the spreading distribution found (d_1 to d_{10}), N_4 to N_{10} values must be calculated. However, N_4, N_5 are the most important (75 to 85%). It will be noted that the same D/H ratio was found in butane and but-1-ene distributions but the ratio N_5/N_4 in the butane distribution was much higher than N_3/N_2 in the but-1-ene distribution.

Meyer and Burwell (*6*) proposed, for the two processes "N_2" and "N_3", a *cis addition* mechanism of two D or H atoms to the C≡C bond. However, in the "N_3" process, the *cis* addition would occur on a molecule which would have previously exchanged its acetylenic hydrogen ($CD{\equiv}C{-}C_2H_5$). If these mechanisms are the right ones, we should therefore observe the same amount of the 1*b*—2d_2 and 1*a*—1*b*d_2 species and the same amount of 1*a*d_1 and 2d_1 (Scheme 2). Our results cannot be explained by this scheme: we observed four times more 1*b*—2d_2 species than 1*a*—1*b*d_2 species and slightly more 2d_1 than 1*a*d_1 species. In order to explain the excess of 1*b*—2d_2 species an additional reaction pathway must be found. In fact, this additional reaction would be a *trans* addition.

Several *trans* addition mechanisms can be proposed:

(i) a reaction involving surface steps, rejected because there was no difference in the *trans*/*cis* addition ratio when the catalyst dispersion was changed.

(ii) a radical mechanism, which would favor the polymerization. However, the quantity of hydrocarbons higher than C_4 is only appreciable at high conversion and in very small amounts.

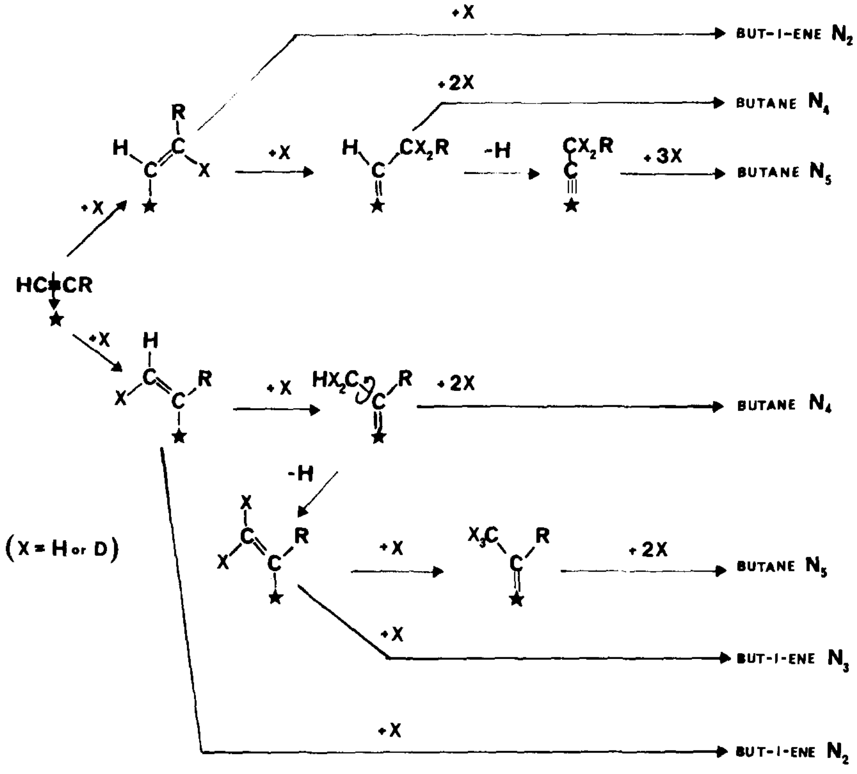
(iii) an Eley–Rideal mechanism, which should be sensitive to the hydrogen pressure. However, there was no significant difference in the ratio 1*b*—2d_2/1*a*-2d_2 when the hydrogen pressure was increased by a factor of 20.

Hence these *trans* addition processes which are "N_2" processes are inappropriate. Let us now introduce a single scheme which involves olefins, carbenes, and carbynes as adsorbed species (Scheme 3).

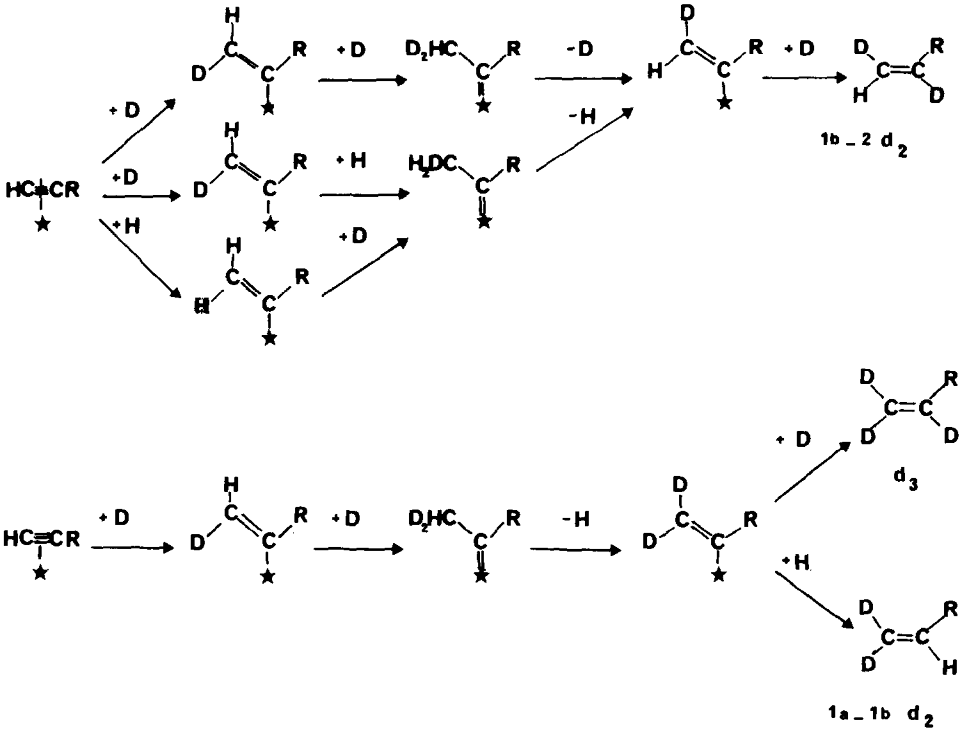
The but-1-yne adsorbs associatively on the catalyst and reacts with a chemisorbed hydrogen (or deuterium) to form an intermediate olefin adsorbed in a vinylic position. These intermediates can then desorb by a *cis* addition of another hydrogen (or deuterium) to form the but-1-ene ("N_2" mechanism). However, they can also turn into a primary or a secondary carbene.

With this secondary carbene intermediate a free rotation around the C_1–C_2 bond is possible. A further reversible step into vinylic species, following by desorption, gives rise to 1*b*—2d_2, 1*a*—1*b*d_2, and d_3 species ("N_3" mechanism) as shown in Scheme 4.

By a simple probability calculation, the ratio 1*b*—2d_2/1*a*–1*b*d_2 and d_3/1*b*–2d_2 should be respectively equal to $y + 2$ and $y/(y + 2)$ if y = D/H. The isotopic dilution (y) calculated from experimental deuterium mass distributions is 10 ± 2 (Table 1).



SCHEME 3



SCHEME 4

Therefore the ratios should be

$$[1b—2d_2]/[1a—1bd_2] = 12 \pm 2$$

and

$$d_3/[1b—2d_2] = 0.8 \pm 0.3.$$

However, the experimental values deviate from these values, but if one supposes an isotopic effect of 3.5 ± 0.5 in the (C–H)/(C–D) rupture the observed values ($[1b—2d_2]/[1a—1bd_2] = 4$, $d_3/[1b—2d_2] = 2.3$) are neatly explained. Such an isotopic effect value was already found by Flanagan and Rabinovitch (*20*) in a kinetic study of the exchange and isomerization of d_2 *trans*-ethylene on nickel.

The direct hydrogenation into butane (2%) can be explained by the same mechanism (Scheme 3) in which the carbene intermediates could be directly hydrogenated into butane. However, the exchange of acetylenic hydrogen is more important during the butane formation (butane-d_5) than during the but-1-ene one (butene-d_3). This is well explained by the formation of butylidine species obtained by dehydrogenation of the primary carbene. This type of direct hydrogenation with participation of carbyne species was already proposed by Moses *et al.* (*15*) for acetylene hydrogenation.

The presence of d_6 to d_{10} molecules in butane shows that the species first adsorbed on the C_1–C_2 bond are able to roll over the surface by breaking the C–H bonds of the ethyl group before desorption. In this sequence, one of the reaction intermediates should be a diadsorbed species. This latter intermediate needs at least two adjacent sites, so it explains the higher proportion of the heavier molecules obtained on large palladium particles.

This mechanism (Scheme 3) can also explain the formation of but-2-ene without any readsorption process. Indeed, the secondary carbene could form the secondary vinylic intermediate which leads to but-2-ene after desorption. The very small proportion of these isomers implies that the formation of the secondary vinylic intermediate is not favorable.

The fact that the same isotopic dilution was found in the calculated mass spectra might be an indication that only one type of site is involved in this mechanism for either butane or butene formation.

B. Initial Phase

This unsteady phase is characterized by an initial high activity which decreases and an initial low selectivity which increases until a steady state is reached. The duration of the initial phase is a reproducible parameter from one experiment to another. It is a function of the weight of the catalyst and the hydrocarbon flow. Figure 2 represents the experimental results obtained on the highly dispersed catalysts.

A linear relationship was found between the total quantity of hydrocarbon which passed through the catalyst during the initial period (duration of the initial period multiplied by the hydrocarbon flow rate) and the weight of the catalyst; moreover, this linear relationship was still operative with the amount of palladium. Two highly dispersed catalysts containing two different amounts of palladium were used and the ratio of the straight line slopes was found to be equal to the ratio of palladium contents.

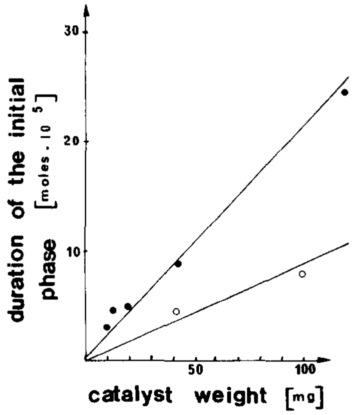


FIG. 2. Parameter related to the duration of the initial phase as a function of catalyst weight. ●, Pd/Al_2O_3, 0.2%, D > 80%; ○, Pd/Al_2O_3, 0.45%, D = 97%.

An attempt was made to correlate the duration of the initial phase with the number of surface palladium atoms by using catalysts with two different dispersions. However, the results were not significant due probably to an additional factor which is that different hydrogenation turnover numbers exist on small and large Pd particles (*16*).

In any case, on highly dispersed catalysts, it was found that the duration of the initial stage depends on the quantity of hydrocarbons which passes over the catalyst and on the content of palladium.

Two hypotheses can be presented to explain such phenomena. First, hydrogen atoms accumulated during the reduction treatment could be responsible for the great activity and the low selectivity of the initial phase. As soon as this hydrogen was consumed, the catalyst would become selective. As Konvalinka and Scholten (*21*) have shown that a helium flow at 300°C on the palladium catalyst eliminates all the absorbed and adsorbed hydrogen atoms, we applied this treatment before the catalytic experiment; however, under such conditions the same initial phase was observed. The second hypothesis, which is preferable, is that the catalyst became selective after some active sites were poisoned, reducing the activity and increasing the selectivity. In fact, this poisoning effect is a reversible process, because if another square hydrocarbon pulse was admitted to the same catalyst *without any treatment in between,* an initial period was also observed. Hence it is clear that the poison formed during the first contact time of the hydrocarbon with the catalyst desorbs at the end of the square pulse, when the hydrocarbon pressure drops on the catalyst releasing the quasi totality of the active sites. The results obtained in the final phase confirms this point of view.

A question which must be asked is that of the nature of the mechanism in the initial period. The deuterium tracer experiments will throw some light on this point. Thus, the experiment was performed under D_2–He carrier gas: the butane which is the only product formed in the very first period of the reaction was analyzed by mass spectrometry. The results are given in Table 2, as well as the spectra of butane obtained in the stationary phase at high but-1-yne conversion, and butane obtained from the but-1-ene deuteration experiment.

The butane which was formed in the first moment of the but-1-yne deuteration presents a spectrum where all the positions are exchanged with an important proportion of heavy species. The butane obtained at high but-1-ene conversion in the stationary phase is totally different. The distribution presents maxima for the species d_2, d_3, d_4 and the contribution of heavier species is quite low.

The mass spectra have been recalculated using the statistical procedure described by Philipson and Burwell (*22*). In this case the distribution of butane cannot be represented by only one set of N_i associated with one D/H ratio because one isotopic dilution cannot simultaneously accommodate rather large values of d_1, d_2, d_3 and substantial values for d_i where i is large.

With two sets of N_i (D/H = 11) and N'_4 (D/H = 1.4), respectively effective for 91 and 9%, the butane distribution (d_i) fits quite well. The butane distribution issuing from high butyne conversion during the stationary phase fits with 55% of the N_i set (D/H = 8) and 45% of N'_4 set (D/H = 1.1). These proportions are quite different from those calculated in the butane formed in the initial phase, while they are exactly the same as those calculated for the butane distribution coming from but-1-ene deuteration experiment as shown in the last part of Table 2.

Therefore, it is worthwhile to note that, by recalculating deuterium distributions using a statistical procedure, it is possible to distinguish between a process of readsorption of but-1-ene as it occurs at high but-1-yne conversion in the stationary phase and a direct hydrogenation process as it should occur at the initial contact time of the hy-

TABLE 2

Butane Distributions

	(a) Formed in initial phase in but-1-yne hydrogenation						(b) At high but-1-yne conversion in but-1-yne hydrogenation						(c) Formed in but-1-ene hydrogenation					
i	N_i (D/H = 11)	d_i	N_i' (D/H = 1.45)	d_i	d_i Calc.	d_i Exp.	N_i (D/H = 8)	d_i	N_i' (D/H = 1.10)	d_i	d_i Calc.	d_i Exp.	N_i (D/H = 20)	d_i	N_i' (D/H = 0.40)	d_i	d_i Calc.	d_i Exp.
0	—	—	—	0.2	0.2	—	—	—	—	2.3	2.3	2.7	—	—	—	23.0	23.0	23.0
1	—	—	—	1.4	1.4	1.7	—	0.1	—	10.1	10.2	10.2	—	1.3	—	18.4	19.7	19.8
2	—	0.3	—	3.1	3.4	3.1	—	0.7	—	16.6	17.3	16.6	12.9	13.4	45.1	3.7	17.1	17.0
3	—	2.8	—	3.0	5.8	7.4	—	4.3	—	12.2	16.5	17.3	12.6	12.6			12.6	12.6
4	7.9	10.2	8.9	1.1	11.3	10.0	9.9	11.6	44.5	3.3	14.9	14.4	9.4	9.2			9.2	9.2
5	12.5	12.6			12.6	12.6	11.3	11.8			11.8	11.8	6.7	6.5			6.5	6.5
6	10.0	11.0			11.0	11.0	10.3	10.3			10.3	10.3	5.0	4.7			4.7	4.7
7	11.5	10.5			10.5	10.5	9.2	8.3			8.3	8.3	3.4	3.2			3.2	3.2
8	7.1	10.3			10.3	10.3	8.1	5.5			5.5	5.5	2.5	2.2			2.2	2.2
9	0.8	16.1			16.1	16.1	5.1	2.4			2.4	2.4	1.6	1.3			1.3	1.3
10	41.3	17.3			17.3	17.3	1.6	0.5			0.5	0.5	0.8	0.5			0.5	0.5
$\sum_{i=0}^{10} d_i$		91.1		8.9				55.5		44.5				54.9		45.1		

drocarbon with the catalyst. Further analysis of the butane distribution during the initial phase shows a superposition of the direct hydrogenation process with highly multiple exchange and readsorption of but-1-ene due to the very high but-1-yne conversion.

At the beginning of the reaction, on clean catalyst, several adjacent sites exist on the surface even for highly dispersed catalyst and the multiple exchange occurs by formation of polyadsorbed molecules. The number of free adjacent sites decreases by poisoning due to more strongly adsorbed but-1-yne molecules leading to a conversion drop and the disappearance of highly multiple exchange. This poisoning reaction does not take place instantaneously because it proceeds layer by layer of the catalytic bed creating a gradient of pressure all along the catalytic bed and therefore a gradient of hydrogenation rates because of the negative order related to the hydrocarbon pressure (*16*). These gradients change with the site poisoning. The reaction reaches the stationary phase when these gradients disappear.

C. Final Phase

This phase appears at the end of the hydrocarbon square pulse, when the hydrocarbon pressure drops in the gas phase, while H_2/He carrier gas flows continuously over the catalyst at atmospheric pressure.

During this transient regime, the catalytic activity is then greater and the but-1-ene selectivity is lower as expected from the negative order related to the hydrocarbon pressure in but-1-yne hydrogenation rate. However, an additional desorption peak was recorded on the katharometer situated downstream from the reactor (Fig. 1). This peak appeared clearly on the chart when the catalyst consisted of small palladium particles, whereas with large particles under the same experimental conditions it could not be detected. The products which desorb are C_4 molecules (but-1-yne, but-1-ene, but-2-ene, butane).

The presence of this additional desorption peak is good evidence for more strongly adsorbed but-1-yne which accumulates in the initial phase, acts as poison and gives rise to a highly selective catalyst.

Such strongly adsorbed species (but-1-yne)$_{aa}$ should be in equilibrium with the reactive weakly adsorbed species (but-1-yne)$_a$,

$$\begin{tikzcd} & \text{but-1-yne} \arrow[d, shift left] & \\ (\text{but-1-yne})_{aa} \arrow[r, shift left, "k'"] & (\text{but-1-yne})_{a} \arrow[l, shift left] \arrow[u, shift left] \arrow[r] & \text{but-1-ene and butane} \end{tikzcd}$$

A similar scheme was proposed both in other model reactions (*23*) and in the hydrogenation reaction of but-1-yne in the liquid phase on Pt, Pd, and Rh (*24*). In this latter case the surcomplexation constant k' was calculated. It was found that k' varies with the metal dispersion and the nature of metal. In accordance with these results, we can therefore propose that, on small Pd particles, the surcomplexation constant is greater and the hydrocarbon limit pressure, from which the desorption occurs, is smaller. Therefore the desorption peak appears on the downslope or tail of the hydrocarbon pressure signal. On large particles the surcomplexation constant is small and the desorption occurs at a pressure too close to the constant pressure used in the stationary phase to be detected on the chart.

CONCLUSION

As often occurs in heterogeneous catalysis, reactive species and poisons coexist on the surface. Usually, in hydrogenation reaction, poisons are considered as being irreversibly adsorbed (*25, 13*). The aim of our work was not to identify their nature; however, these poisons exist in our experiments too, since it is necessary to regenerate the catalyst between two runs. These species could be either the carbyne species which hydrogenates very slowly as Beebe and Yates (*13*) proposed or the heavier hydrocarbons detected in some cases, as already suggested in acetylene hydrogenation (*25, 15*).

However, this present work underlines the presence of reversibly chemisorbed but-1-yne molecules which act as a poison. They are in equilibrium with the but-1-yne reactive species. The poison site could be one palladium atom surrounded by several but-1-yne molecules preventing the hydrogen accessibility and the hydrogenation reaction. When the but-1-yne hydrocarbon pressure decreases, this poison site turns into a reactive site by losing one but-1-yne molecule and then creating a vacancy available to a hydrogen atom.

The reactive species during the steady state of the reaction could be described as a but-1-yne molecule chemisorbed on one palladium atom. This but-1-yne molecule reacts with a hydrogen atom to turn into a vinylic adsorbed species and further carbene and carbyne species.

The deuteration mechanism on palladium during the steady state is, for 80% of the reaction, a *cis* addition mechanism. The 20% loss of selectivity comes from the formation of carbene and carbyne species. As was proposed by van Broekhoven and Ponec (*26*), the palladium is not prone to form such species by comparison with platinum, for example. This could be the reason why palladium is such a selective catalyst in the hydrogenation reaction.

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