JOURNAL OF CATALYSIS 5, 65–73 (1965)

# The Hydrogenation of Acetylene

## II. The Reaction of Acetylene with Hydrogen Catalyzed by Alumina-Supported Palladium

G. C. BOND* AND P. B. WELLS

*From the Department of Chemistry, The University, Hull, England*

Received March 2, 1965; revised May 4, 1965

Kinetics and product analyses are reported for the hydrogenation of acetylene catalyzed by palladium-alumina between 0° and 30°C. Four types of behavior have been distinguished: (*i*) Equimolar mixtures of hydrogen and acetylene, or hydrogen-deficient mixtures, produced ethylene very selectively throughout the reaction (ethane yields 2% to 7%). (*ii*) Reactions involving an initial hydrogen:acetylene ratio of 2:1 maintained their initial selectivity until complete acetylene removal, after which rapid ethane formation occurred. (*iii*) When the initial hydrogen:acetylene ratio exceeded 2:1 the reaction commenced selectively but became nonselective before the acetylene had disappeared. (*iv*) When a sufficiently high initial hydrogen pressure was employed the reactions were completely nonselective. Within the range of conditions in which the reaction was highly selective, the selectivity decreased slightly with increasing conversion, increasing hydrogen pressure, and decreasing acetylene pressure. When high initial hydrogen:acetylene ratios were employed, added ethylene hastened the onset of nonselective conditions, but when the initial hydrogen:acetylene ratio was 2:1 or lower added ethylene had no such effect. The composition of the $C_4$ hydrocarbons produced from acetylene is reported and their mode of formation is discussed. The proposed mechanism for acetylene hydrogenation is an extension of that proposed in Part I for the simpler platinum-catalyzed reaction.

### INTRODUCTION

The selective hydrogenation of acetylene catalyzed by palladium has been studied by several workers (*1–6*) and is the subject of many patents. Preliminary accounts of this study in the context of other related work have appeared in this journal (*7*), and elsewhere (*3*, *8–10*). It is generally agreed that palladium is active for acetylene hydrogenation at room temperature and that, during the initial stages of reaction, it catalyzes the formation of ethylene in preference to ethane, while at the same time possessing extremely high activity for the hydrogenation of ethylene. Some mechanistic implications of this selective behavior have been discussed (*2*, *7–10*), but the causes underlying sudden changes from selective to nonselective behavior [a characteristic peculiar to palladium (*3*)] and the effect of initially added ethylene upon the reaction have not been understood.

In this study, we have attempted to achieve a deeper understanding of the reaction mechanism by obtaining the dependencies of selectivity upon all experimental variables and examining the complex effects of initially added ethylene. Further, we have compared the behavior of palladium with that of platinum which was reported in Part I of this series (*11*).

### EXPERIMENTAL

The three catalyst samples used in the present work were taken from the same stock

---

* Present address: Johnson, Matthey & Company Ltd., Exhibition Grounds, Wembley, Middlesex, England.

whose preparation has been described previously (*2*). The reduced metal was supported on 8–16 mesh α alumina at a concentration of 5 molar %. Each sample was again reduced in 100 mm of hydrogen for 1 hr at 200° before use.

The apparatus, materials, experimental procedure, and analytical techniques were described fully in Part I; the following is a summary. Catalysts weighed 0.3 g and were contained in an 80-ml reaction vessel which was attached to a conventional high-vacuum system. Pressures were measured using a mercury manometer which, because of the potency of mercury as a poison for palladium (*12*), was isolated from the system by a tap except for the time required to take readings. Product compositions were estimated by gas-liquid chromatography: a stationary phase of silver nitrate in benzyl cyanide supported on firebrick (30% wt/wt) contained in a 16-ft column was used to estimate ethylene and ethane; $C_4$ products were analyzed using a 20-ft column containing 30% wt/wt hexane-2,5-dione on firebrick. Both columns were operated at room temperature, with nitrogen or hydrogen as carrier gas.

## Results

### *Kinetics*

**Pressure against time curves.** For reactions in which the initial reactant pressures were equal, the rate decreased continuously; the order was 0.5 ± 0.1 in total reactant pressure. When the initial hydrogen:acetylene ratio was 2:1, curve (a) of Fig. 1 was obtained; this consisted of a zero order region (AB) followed first by a slow acceleration (BC) and then by a very rapid acceleration (at C) after which the rate decreased to zero as the reactants were exhausted. As the initial hydrogen:acetylene ratio was further increased region BC contracted, so that at 20°, for example, it had virtually vanished when the reactant ratio was 3.5:1 [see curves (b) and (c), Fig. 1]. When the hydrogen:

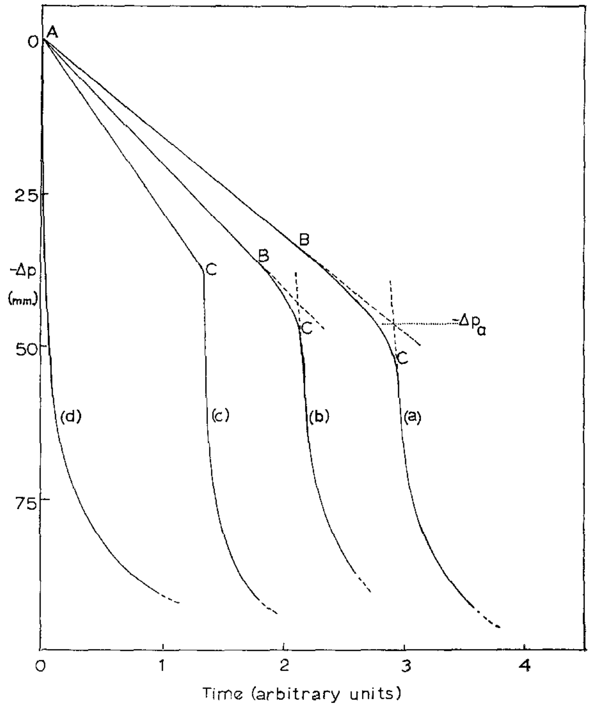


Fig. 1. The forms of the pressure fall, $-\Delta p$, against time curves obtained at 19°C when using an excess of hydrogen. Initial acetylene pressure, 50 mm throughout. Initial hydrogen pressure, (a) 100 mm; (b) 130 mm; (c) 175 mm; (d) 500 mm.

acetylene ratio was increased sufficiently, region AB also disappeared so that the reaction exhibited only the rapid rate region [see curve (d), Fig. 1].

In Part I of this series the term "acceleration point" (symbol $-\Delta p_a$) was defined as shown in Fig. 1 for curve (a); for curve (c) the acceleration point is coincidental with the point C. The value of $-\Delta p_a$ varied with experimental conditions as shown below.

TABLE 1

ORDER OF REACTION IN ACETYLENE BY THE INITIAL RATE METHOD

| Temperature (°C) | Mean hydrogen pressure (mm) | Range of acetylene pressures (mm) | Observed order (±0.03) |
|---|---|---|---|
| 0° | 205 | 50 to 150 | −0.55 |
| 19° | 50 | 20 to 200 | −0.55 |
| 19° | 205 | 50 to 300 | −0.67 |

TABLE 2

VARIATION OF THE ACCELERATION POINT, $-\Delta p_a$, WITH INITIAL HYDROGEN PRESSURE AT 0° AND AT 20°[a]

| Initial hydrogen pressure (mm) | 100 | 150 | 200 | 210 | 243 | 300 | 395 | 495 |
|---|---|---|---|---|---|---|---|---|
| $-\Delta p_a$ at 0° (mm) | 46.8 | — | — | 39.0 | — | 32.5 | 23.3 | 13.8 |
| $-\Delta p_a$ at 20° (mm) | 44.2 | 40.2 | 34.0 | — | 28.7 | — | — | — |

[a] Initial acetylene pressure, 50 mm.

The total pressure fall for the complete reaction of a 1:1 mixture of acetylene and hydrogen exceeded that expected, the excess being attributable to a secondary reaction in which acetylene was converted to $C_4$ hydrocarbons.

**Orders of reaction by the initial rate method.** Orders in hydrogen of 1.0 were obtained at 0°, 20°, and 30°, and a value of 1.4 was recorded at 125°. Orders in acetylene were negative; the degree of negativity increased with increasing initial hydrogen pressure and with increasing temperature, as shown in Table 1.

**Activation energy.** An activation energy of 11.0 ± 0.5 kcal mole$^{-1}$ was obtained from activity measurements at 0°, 20°, and 30°.

**The dependence of acceleration point upon experimental variables.** The acceleration point decreased with increasing initial hydrogen pressure and with increasing temperature (see Table 2). Initially added ethylene also affected the acceleration point; reactions accelerated earlier the higher the initial pressure of ethylene and the effect of a given pressure of ethylene was greater the higher the initial hydrogen pressure (see Fig. 2). Initial rates were depressed by about

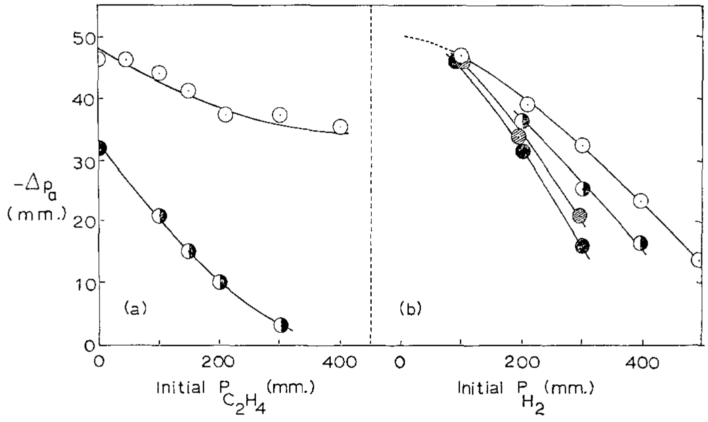


FIG. 2. (a) The variation at 19°C of the acceleration point, $-\Delta p_a$, with the initially added pressure of ethylene; initial acetylene pressure, 50 mm; initial hydrogen pressures, 100 mm (open circles) and 200 mm (half-filled circles). (b) The variation at 0°C of the acceleration point, $-\Delta p_a$, with initial hydrogen pressure; initial acetylene pressure, 50 mm; pressures of initially added ethylene: 0 mm, open circles; 100 mm, half-filled circles; 200 mm, hatched circles; 303 mm, filled circles.

10% when ethylene was added initially, but the extent of this depression was independent of the pressure of ethylene over the pressure range 50 to 400 mm.

### *The Effect of Experimental Variables upon Selectivity*

Selectivity is defined as $P_{C_2H_4}/(P_{C_2H_4} + P_{C_2H_6})$.

**The dependence of selectivity upon pressure fall.** A reaction of equimolar quantities of acetylene and hydrogen at 0° gave a constant selectivity of 0.975 ± 0.002 throughout the reaction. For reactions that showed an acceleration point, the selectivity was very high and independent of conversion until the *fast* acceleration commenced [i.e., points C on curves (a) and (b), Fig. 1] as shown in Table 3. As soon as the reaction accelerated rapidly, ethane was formed rapidly and the selectivity fell precipitously. In reactions represented by curve (d), Fig. 1, rates were too fast for analyses to be carried out at low conversions; however, ethane was assumed to be the major initial product because this curve corresponds to the situation in which regions AB and BC of curves (a) and (b) are absent. Further, the rates of these reactions were so fast as necessarily to be diffusion-controlled, and on this basis alone ethane is expected as the major initial product.

TABLE 3

MEASUREMENTS OF SELECTIVITY AS A FUNCTION OF PERCENTAGE CONVERSION[a]

| | | | | | |
|---|---|---|---|---|---|
| | Series 1: Initial hydrogen pressure = 163 ± 2 mm<br>$-\Delta p_a = 37.0$ mm | | | | |
| Pressure fall (mm) | 11.0 | 20.0 | 25.0 | 33.0 | 35.0 |
| Selectivity (±0.002) | 0.975 | 0.980 | 0.969 | 0.978 | 0.970 |
| | Series 2: Initial hydrogen pressure = 153 ± 3 mm<br>$-\Delta p_a = 37.5$ mm | | | | |
| Pressure fall (mm) | 12.4 | 19.0 | 25.0 | 36.1 | |
| Selectivity (±0.002) | 0.967 | 0.963 | 0.966 | 0.960 | |

[a] Temperature 20°. Initial acetylene pressure, 50mm. Series 1 and 2 represent results obtained from two catalyst samples.

**Dependence of selectivity upon hydrogen and acetylene pressures and upon temperature.** Selectivities decreased with increasing initial hydrogen pressure at 0°, 20°, and 30° as shown in Table 4. When the initial hydrogen pressure exceeded a critical value (about 300 mm at 0°, 200 mm at 20°, and 150 mm at 30°) the selectivity fell more steeply. Thus a temperature variation of 30° does not significantly effect the initial selectivity, but increasing temperature progressively restricts the range of conditions under which highly selective hydrogenation takes place.

TABLE 4

VARIATION OF SELECTIVITY WITH INITIAL HYDROGEN PRESSURE AND WITH TEMPERATURE[a]

| Initial hydrogen pressure (mm) | Selectivity at 0° | Selectivity at 20° | Selectivity at 30° |
|---|---|---|---|
| 30 | — | — | 0.977 |
| 50 | 0.977 | 0.978 | 0.978 |
| 76 | 0.976 | — | 0.976 |
| 100 | 0.974 | 0.970 | 0.968 |
| 128 | — | — | 0.964 |
| 150 | 0.972 | 0.962 | 0.962 |
| 176 | — | — | 0.931 |
| 200 | 0.970 | 0.962 | — |
| 250 | 0.972 | 0.931 | — |
| 300 | 0.964 | — | — |
| 345 | 0.960 | — | — |
| 395 | 0.948 | — | — |
| 500 | 0.913 | — | — |

[a] Initial acetylene pressure, 50 mm. Pressure fall before extraction for analysis, 25 mm.

The selectivity increased with increasing acetylene pressure at 0°. When the initial hydrogen pressure was maintained constant at 205 mm, selectivities of 0.926, 0.953, 0.960, and 0.962 were recorded when the initial acetylene pressures were 20, 50, 100, and 150 mm, respectively.

### *The Formation of $C_4$ Hydrocarbons*

Analyses of reactions carried out at 16°, using 165 mm of acetylene and 160 mm of hydrogen, showed that $C_4$ hydrocarbons accounted for 23% of the total reaction product after 90% reaction. Thus, of the acetylene that reacted, 37% was consumed in this side reaction; this compares with a figure of 28% obtained for the platinum-catalyzed reaction at 136° (*11*). The $C_4$ yield had the composition: 1,3-butadiene, 4%; 1-butene, 54%; *trans*-2-butene, 24%; *cis*-2-butene, 14%; *n*-butane, 4%. Trace quantities of hexenes were also produced. Similar products were reported recently by Kabe and Yasumori (*6*).

### *Phase Change in the Palladium-Hydrogen System*

When catalyst samples were heated slowly *in vacuo* or in hydrogen from 20° to 140°, hydrogen was evolved over the temperature interval 92° to 97°, and on cooling hysteresis was observed, the hydrogen being reabsorbed between 69° and 72°. This showed unequivocally that the palladium was present as the hydrogen-rich $\beta$ phase during the experiments at 0°, 20°, and 30° whereas it was present as the hydrogen-depleted $\alpha$ phase during the single initial rate order measurement at 125°.

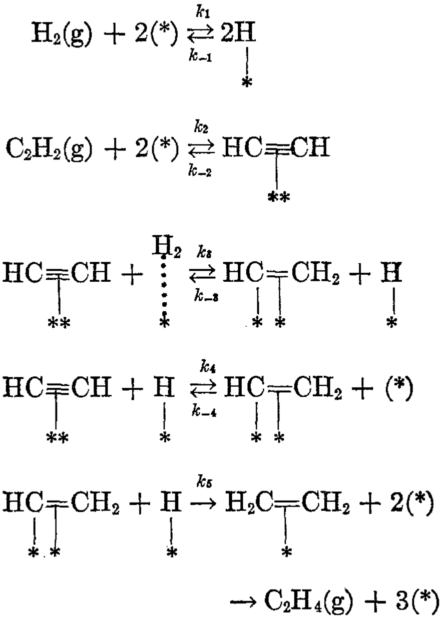
## DISCUSSION

The results described above show certain similarities to those reported in Part I for the platinum-catalyzed reaction (*11*). Over both metals, (*i*) ethylene is formed as the major initial product, (*ii*) the initial rate orders are positive in hydrogen and negative in acetylene, and (*iii*) the formation of $C_4$ hydrocarbons accompanies simple hydrogenation. However, detailed comparisons of the results reveal important differences in the kinetics of the two reactions, in the effects of initially added ethylene, and in the activities of the two metals.

### *Kinetics*

**Orders of reaction by the initial rate method.** The negative order in acetylene indicates strong adsorption and high surface coverage of this reactant. Possible origins of the negativity were discussed in Part I and are equally relevant here. In contrast, hydrogen was comparatively weakly adsorbed.

The following elementary steps were proposed in Part I and are relevant again:



$$H_2(g) + 2(*) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\underset{*}{\underset{|}{H}} \quad (1)$$

$$C_2H_2(g) + 2(*) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{**}{\underset{|}{HC{\equiv}CH}} \quad (2)$$

$$\underset{**}{\underset{|}{HC{\equiv}CH}} + \overset{H_2}{\underset{*}{\vdots}} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \underset{*\,*}{\underset{|\;|}{HC{=}CH_2}} + \underset{*}{\underset{|}{H}} \quad (3)$$

$$\underset{**}{\underset{|}{HC{\equiv}CH}} + \underset{*}{\underset{|}{H}} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \underset{*\,*}{\underset{|\;|}{HC{=}CH_2}} + (*) \quad (4)$$

$$\underset{*\,*}{\underset{|\;|}{HC{=}CH_2}} + \underset{*}{\underset{|}{H}} \overset{k_5}{\rightarrow} \underset{*}{\underset{|}{H_2C{=}CH_2}} + 2(*) \rightarrow C_2H_4(g) + 3(*) \quad (5)$$

The rate of ethylene formation, $r$, is then given by

$$r = \frac{k_5(k_3[*]\theta_{C_2H_2}P_{H_2} + k_4\theta_{C_2H_2}\theta_H)\theta_H}{k_{-3}\theta_H + k_{-4}[*] + k_5\theta_H}$$

In Part IV of this series it will be shown that deuterium adsorption on palladium in the presence of acetylene is irreversible (i.e., $k_{-1}\theta_H{}^2 = k_{-3}\theta_{C_2H_2}\theta_H = 0$) and that $k_5\theta_H/k_{-4}[*] \sim 2$. Thus, by analogy with the platinum-catalyzed reaction, we should expect $\theta_H \propto p_{H_2}$ and the order in hydrogen to be intermediate between 1.0 and 2.0. The order was 1.4, in agreement with this expectation, when the palladium was in the hydrogen-depleted $\alpha$ state at 125°. However, when the metal was in the hydrogen-rich $\beta$ state at 0°, 20°, and 30°, the order was exactly unity. We conclude from this that step (3) does not occur to a significant extent, and that on palladium the surface coverage of hydrogen atoms is proportional to some *fractional* power of the hydrogen pressure, possibily due to the unknown influence of dissolved hydrogen.

**Pressure fall against time curves.** The curves obeyed the rate expression $-d(P_{C_2H_2})/dt = k(P_{H_2})^{1.0}(P_{C_2H_2})^{-0.6}$ when the initial hydrogen:acetylene ratio was 2.0 or less. Thus, when this ratio was unity the order of the reaction was about one-half and when the ratio was 2.0 [see Fig. 1 curve (a)] the removal of acetylene (region ABC) showed a zero order period followed by a mild acceleration. The selectivity was constant throughout region ABC, thus confirming that the mild acceleration was due to acetylene removal and not to ethylene readsorption and hydrogenation to ethane. After complete acetylene removal, ethylene was rapidly hydrogenated to ethane.

When the initial hydrogen:acetylene ratio was 3.5:1 or greater the pressure fall against time curves were not of the form expected from the general rate expression because the mild acceleration region had disappeared and rapid ethylene hydrogenation occurred *in the presence of acetylene.* Only 70% of the acetylene was hydrogenated selectively in the reaction represented by curve (c) in Fig. 1. Curve (b) shows behavior intermediate between that shown in (a) and (c). No selective hydrogenation took place at all when $P_{H_2}/P_{C_2H_2} = 10.0:1$ initially at 19° [see curve (d), Fig. 1]. Thus, when $P_{H_2}/P_{C_2H_2} > 2.0$ initially, the acceleration points denote the critical conditions under which selective formation of ethylene breaks down before the complete removal of acetylene. This behavior contrasts sharply with that of platinum, which showed type (a) curves for all degrees of hydrogen excess and which did not exhibit a breakdown of selectivity before complete acetylene removal. The reasons for the "premature breakdown" of selective behavior over palladium will be discussed further below.

**Selectivity.** Ethylene was the major initial product when selective hydrogenation conditions obtained but small quantities of ethane were also produced, showing that complete hydrogenation of some acetylene during one residence of the hydrocarbon unit on the surface was possible.

The fundamental contribution of thermodynamic and mechanistic factors to the determination of selective hydrogenation conditions has been discussed fully in Part I (*11*) and that discussion applies *mutatis mutandis* to the present reaction.

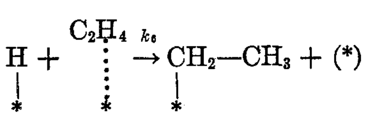
We will now examine the reason for the higher selectivity shown by palladium, compared to platinum, and enquire into the factors which cause "premature breakdown" of selectivity over palladium.

In Part I we proposed that a metal's inherent activity for acetylene hydrogenation is one factor which governs the selectivity which it affords in acetylene hydrogenation. Now, Beeck (*13*) and Schuit and van Reijen (*14*) agree that, for films and silica-supported metals respectively, palladium is more active for ethylene hydrogenation than platinum by a factor of 5, approximately. Consequently some other feature of the mechanism must account for the observation that the selectivity exhibited by palladium is much higher than that of platinum (e.g., $S_{Pd} \sim 0.95$ at 30°; $S_{Pt} \sim 0.68$ at 41°).

The critical feature is the relation between the chance of ethylene desorption and the chance of its hydrogenation to form an ethyl group. The former chance will depend upon the strength of ethylene adsorption and upon the effect of acetylene in the gas phase, which may displace ethylene from the surface since it is potentially a stronger adsorbate; this is a manifestation of the thermodynamic factor governing selectivity. The chance of ethyl formation will depend upon the availability of adsorbed hydrogen, i.e., upon $\theta_H$. Our studies of the ethylene–deuterium reaction, using palladium-alumina (*15*a) and platinum-alumina (*15*b) from the same stocks, have shown that the relative chance of ethylene desorption from palladium is greater than that from platinum by a factor of 12 under similar pressure conditions at 25°C. Unfortunately, this factor cannot be applied quantitatively to the fate of ethylene during acetylene hydrogenation, since the surface coverage of hydrogen atoms must be expected to vary from metal to metal for a given reaction. However, it is reasonable to suppose that this relatively higher chance of olefin desorption from palladium is the feature responsible for its more highly selective nature.

Palladium is more selective than platinum for the hydrogenation of propyne (*16*), 2-butyne (*17*, *18*), allene (*7*), 1,3-butadiene (*19*), and other diunsaturated hydrocarbons (*7*). This is not surprising since the relative strengths of adsorption of alkene on palladium and platinum are not likely to be greatly modified by substitution of the alkene. (This is supported by the observation that the stabilities of platinum-alkene $\pi$ complexes exceed those of the analogous palladium complexes irrespective of the alkene involved.)

**The premature breakdown of selective hydrogenation.** The premature breakdown of selectivity occurred earlier in the reaction, (*i*) the higher the initial hydrogen pressure; (*ii*) the higher the temperature; and (*iii*) the higher the pressure of ethylene in the gas phase. Also the acceleration point was sharper the larger the initial excess of hydrogen. Two problems accompany these phenomena: first, how does ethylene enter the reactive layer at the surface in the presence of acetylene which is more strongly adsorbed, and secondly, why is the acceleration point so sharp? The first problem is acute, since the independence of selectivity upon conversion before the acceleration point (see Table 3) shows that ethylene returned to the gas phase cannot compete with acetylene for the surface, and acts merely as a diluent. Consequently, it is most unlikely that ethylene adsorbs as such even at the point of premature breakdown of selectivity, and we suggest its conversion to ethyl occurs by its direct interaction, from the van der Waals layer, with adsorbed hydrogen, thus



$$\underset{\substack{|\\ *}}{\mathrm{H}} + \overset{\mathrm{C_2H_4}}{\underset{*}{\vdots}} \xrightarrow{k_6} \underset{\substack{|\\ *}}{\mathrm{CH_2}}\text{—}\mathrm{CH_3} + (*) \qquad (6)$$

According to step (6), rapid ethane formation ensues when the surface concentration of hydrogen atoms is sufficiently high for that step, and the hydrogenation of ethyl, to become noticeable. As reactions having initial hydrogen:acetylene ratios greater than 2.0 proceed, the instantaneous hydrogen:acetylene ratio increases and this causes an increase in the surface coverage of hydrogen atoms. Consequently, at a given temperature, the higher the initial hydrogen: acetylene ratio the earlier in the reaction will the critical ratio be achieved, and hence the earlier will the premature breakdown of selectivity occur, in agreement with the results (see Table 2). In the limit when the hydrogen:acetylene ratio was sufficiently high (e.g., 15:1 at 20°) the required hydrogen atom coverage was achieved initially and the entire reaction was nonselective. Moreover, the higher the initial hydrogen: acetylene ratio, the more rapidly does the instantaneous ratio increase during reaction, and hence the more abrupt does the acceleration point appear to be [compare curves (b) and (c) in Fig. 1].

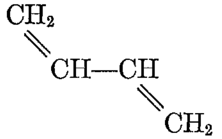
In acetylene hydrogenation, the surface coverage of hydrogen atoms may reasonably increase as the temperature is raised. If this is the case, then the temperature dependence of $-\Delta p_a$ is immediately understood, since, for two reactions conducted at different temperatures but having the same initial hydrogen:acetylene ratio, the critical hydrogen atom concentration for step (6) (and hence $-\Delta p_a$) will be achieved earlier in the reaction at the higher temperature. This concurs with the results shown in Table 2.

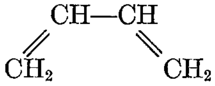
The complex effects of initially added ethylene are also simply interpreted by this mechanism. The effect of initially added ethylene upon $-\Delta p_a$ (see Fig. 2) was very small when the initial hydrogen:acetylene ratio was 2.0 because the required hydrogen coverage was only achieved when acetylene removal was virtually complete. However, when the required hydrogen atom coverage was achieved in the presence of acetylene, the acceleration point was approximately first order in ethylene, as expected from step (6).

**The formation of $C_4$ hydrocarbons.** The Sheridan mechanism for acetylene polymerization [see Part I and ref. (*20*)] envisages that a free radical form of the adsorbed vinyl group initiates the process and, according to this mechanism, the adsorbed 1,3-butadiene formed after hydrogen acquisition is a necessary precursor of

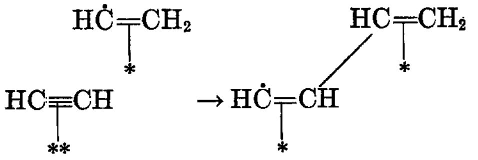
$$\dot{C}H\text{—}CH_2(ads) \xrightarrow{+C_2H_2(ads)} \dot{C}H\text{—}C_3H_4(ads) \xrightarrow{+H} C_4H_6(ads) \xrightarrow{+2H} C_4H_8 \quad (7)$$

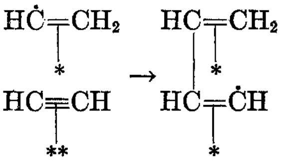
the butenes. In Part I we showed that the distribution of butenes obtained from acetylene was the same as that obtained from 1,3-butadiene hydrogenation over platinum catalyst from the same batch; a similar comparison of the behavior of palladium reveals a more complex situation. The ratio of 1-butene:2-butene is indeed the same (60%:40% at 16°) from both acetylene dimerization and 1,3-butadiene hydrogenation (*19, 20*), but the *trans*:*cis* ratio in the 2-butene is 1.8 in the former reaction and 12.0 or greater in the latter. Valuable information on the mechanism can be gleaned here. In palladium-catalyzed 1,3-butadiene hydrogenation (*19*) we have shown (*i*) that the *trans*:*cis* ratio in the 2-butene is a measure of the relative abundances of conformations (I) and (II) of adsorbed 1,3-butadiene;


(I)


(II)

(*ii*) that the 2-butene is formed wholly by 1:4 addition of hydrogen; and (*iii*) that conformations (I) and (II) are virtually noninterconvertible when adsorbed. Thus the *trans*:*cis* ratio of 1.8 observed in the 2-butene formed from acetylene shows that the steric situation in the $C_4$-forming step is nearly twice as likely to be that shown in A as that shown in B, below. This confirms our previously expressed contention that staggered packing is


(A)


(B)

the most favored steric arrangement for acetylene molecules adsorbed on palladium (*12*).

Further, the importance of steric situation (A) rules out an alternative mechanism in which two adsorbed acetylene molecules interact to form adsorbed cyclobutadiene, which then undergoes ring fission and hydrogen atom addition to give 1,3-butadiene adsorbed in conformation (II). Such a mechanism would give 2-butene wholly in the *cis* configuration, which is not the observed result.

**Activity of the catalyst.** Three-tenths of a gram of the palladium catalyst was as active at 0° as the same weight of the platinum catalyst at 120°, i.e., the palladium catalyst was more active by a factor of about 200. Thus, either the strengths of adsorption of the adsorbed species on the palladium surface were nearer to the critical values for optimum catalytic activity than was the case on the platinum surface, or the availability of adsorbed hydrogen was greater on palladium than on platinum. An adsorbed hydrogen availability effect could arise because the hydrogen-rich $\beta$ phase of palladium was used at 0°, 20°, and 30° and equilibrium exists between adsorbed and absorbed hydrogen in this system. However, if this is so, the situation is complex because ethane and ethylene were formed from acetylene only when gaseous hydrogen was present as a reactant. A recent report of the hydrogenation of acetylene at palladium and platinum electrodes (*21*) has shown that hydrogen adsorbed in palladium is effective for the reduction of acetylene dissolved in acidic or alkaline aqueous solutions; in this study also the hydrogenation activity of palladium at room temperature greatly exceeded that of platinum.

## ACKNOWLEDGMENTS

The authors wish to acknowledge their gratitude to Imperial Chemical Industries (Billingham Division) for a grant (to P.B.W.) and for the loan of apparatus.

## REFERENCES

1. Sheridan, J., *J. Chem. Soc.*, p. 470 (1945).
2. Bond, G. C., Dowden, D. A., and Mackenzie, N., *Trans. Faraday Soc.* **54,** 1537 (1958).
3. Bond, G. C., Newham, J., and Wells, P. B., *Actes Congr. Intern. Catalyse, 2$^e$, Paris, 1960* **1,** 1177 (Editions Technip, Paris, 1961).
4. Grignon-Dumoulin, A., and Thonon, C., *Rev. Inst. Franc. Pétrole et Ann. Conmustibles Liquides* **14,** 214 (1959).
5. Shcheglow, N. I., and Sokolskii, D. V., *Tr. Inst. Khim. Nauk, Akad. Nauk Kaz., S.S.R.* **2,** 150 (1958).
6. Kabe, Y., and Yasumori, I., *J. Chem. Soc. Japan* **85,** 410 (1964).
7. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Catalysis* **1,** 74 (1962).
8. Wells, P. B., *Platinum Metals Rev.* **7,** 18 (1963).
9. Wells, P. B., *Chem. and Ind.*, p. 1742 (1964).
10. Bond, G. C., and Wells, P. B., *Advan. Catalysis* **15,** 92 (1964).
11. Bond, G. C., and Wells, P. B., *J. Catalysis* **4,** 211 (1965).
12. Bond, G. C., and Wells, P. B., *Actes Congr. Intern. Catalyse, 2$^e$, Paris, 1960,* **1,** 1159 (Editions Technip, Paris, 1961).
13. Beeck, O., *Discussions Faraday Soc.* **8,** 118 (1950).
14. Schuit, G. C. A., and van Reijen, L. L., *Advan. Catalysis* **10,** 242 (1958).
15. (a) Bond, G. C., Phillipson, J. J., Wells, P. B., and Winterbottom, J. M., *Trans. Faraday Soc.*, in press; (b) *ibid.* **60,** 1847 (1964).
16. Bond, G. C., and Sheridan, J., *Trans. Faraday Soc.* **48,** 651, 658 (1952).
17. Phillipson, J. J., Wells, P. B., and Gray, D. W., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* **2,** 1250 (1965).
18. Meyer, E. F., and Burwell, R. L., *J. Am. Chem. Soc.* **85,** 2877 (1963).
19. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Chem. Soc.*, p. 3218 (1965); Leszczynski, Z., and Wells, P. B., *Przemysl Chem.* **43,** 508 (1964); Young, W. G., Meier, R. L., Vinograd, J., Bollinger, H., Kaplan, L., and Linden, S. L., *J. Am. Chem. Soc.* **69,** 2046 (1947).
20. Sheridan, J., *J. Chem. Soc.*, p. 133 (1945).
21. Burke, L. D., Lewis, F. A., and Kemball, C., *Trans. Faraday Soc.* **60,** 919 (1964).