JOURNAL OF CATALYSIS 5, 419–427 (1966)

The Hydrogenation of Acetylene

III. The Reaction of Acetylene with Hydrogen Catalyzed by Alumina-Supported Rhodium and Iridium

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

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

Received September 6, 1965

The hydrogenation of acetylene catalyzed by rhodium-alumina (18–150°) and iridium-alumina (45–185°) is described. Reactions were approximately first order in hydrogen, and zero (Rh) or negative (Ir) order in acetylene. Under comparable conditions, rhodium was always the more selective catalyst for the production of ethylene, although the selectivity was dependent upon all experimental variables. Over both metals, ethylene formation diminished as conversion and initial hydrogen pressure were increased, and as initial acetylene pressure and temperature were decreased. Olefin was hydrogenated slowly in the presence of acetylene and extremely rapidly in its absence. C_4 products formed from acetylene are reported. The results are interpreted in terms of the mechanism and concepts discussed in Parts I and II of this series, and the characteristics of Rh, Ir, Pd, and Pt as catalysts for this reaction are compared.

INTRODUCTION

The rhodium- and iridium-catalyzed hydrogenation of acetylene has been studied briefly by Sheridan and Reid (*1*), who found both metals to be active when supported on pumice. They observed that ethylene formed about 58% of the C_2 yield over rhodium at 88° and about 30% over iridium at 175°. Thus, both metals were less selective for ethylene formation than platinum-pumice at 57° or palladium-pumice at 36°, which had been observed to give 66% and 92% ethylene, respectively (*2*, *3*).

Bond, Dowden, and Mackenzie have shown that rhodium is also active when supported on α alumina (*4*) and that at 133°C about 92% of the C_2 yield is ethylene. Indeed, rhodium at this temperature was more selective for the formation of ethylene than platinum-alumina at 105°C, which afforded 75–85% of the C_2 yield as ethylene. Thus, the relative selectivities reported for rhodium and platinum by these two groups of workers do not agree.

In the present study we have examined the rhodium- and iridium-catalyzed hydrogenation of acetylene in greater detail, using alumina-supported metal catalysts. This paper is complementary to our studies of the platinum- and palladium-catalyzed reactions which were reported in Parts I (*5*) and II (*6*) of this series, respectively. Preliminary reports of this and other related work have appeared (*7–11*).

Here we report (i) the kinetics of the reaction, (ii) the yields of ethylene and ethane over a wide range of conditions, (iii) the effect of initially added olefin upon the reaction, and (iv) the C_4 products formed.

EXPERIMENTAL

Six samples of rhodium catalyst (designated Rh I-VI) and two samples of iridium catalyst (Ir-I and Ir-II) were used. The catalysts consisted of the reduced metal supported on α alumina (8–16 mesh) at a concentration of 5 molar %. These were prepared by impregnating the alumina with

---

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

the appropriate quantity of a solution of ammonium chlororhodate or ammonium chloroiridate, drying, and reducing in a stream of hydrogen at 400°. About 10 g of each catalyst was prepared in this way. Each sample used for experimentation weighed about 0.3 g and was reduced again in 100 mm hydrogen for 1 hr at 200°C before use.

The apparatus, materials (except argon), and experimental techniques were described in detail in Part I (*5*). Argon (British Oxygen Company) was dried before use. The following is a brief summary of the experimental details. The catalyst sample rested on the bottom of an 80-ml Pyrex reaction vessel which could be evacuated by conventional rotary and mercury diffusion pumps. Reactants were added in the order acetylene, ethylene or 1-butene where appropriate, and lastly hydrogen. Pressure changes were observed using a mercury manometer, and products were analyzed by gas-liquid chromatography.

RESULTS

In this paper the symbolism $(P_X)_0$ will be used to denote the pressure of reactant X in the reaction vessel at the beginning of the reaction.

Activity of Catalysts

The activities of freshly reduced rhodium and iridium catalysts fell to, respectively, 30% and 10% of their initial values during the first ten experiments. Thereafter, constant activity was achieved except that the use of high partial pressures of hydrogen tended to activate catalysts reversibly and, over rhodium only, the selectivity was temporarily increased, while high partial pressures of acetylene often poisoned activity and depressed selectivity irreversibly. This latter effect was so severe in the case of rhodium, that experimentation was mostly confined to conditions in which the initial hydrogen : acetylene ratio was 2 : 1 or greater.

Kinetics

Pressure fall against time curves. Figure 1 shows that reactions which employed an excess of hydrogen exhibited two stages; an acceleration point, $-\Delta p_a$, denotes the end of the first stage and the beginning of the second. Over fresh rhodium catalyst the rate at any instant during the first stage, r, obeyed the expression $r = k(P_{H_2})_i^{1.5}$ where $(P_{H_2})_i$ is the hydrogen pressure remaining at that instant. Over well-used catalysts the exponent in this expression was about unity. Linear function plots could not be obtained for the first stage of iridium-catalyzed reactions; the order apparently changed as the reaction proceeded.

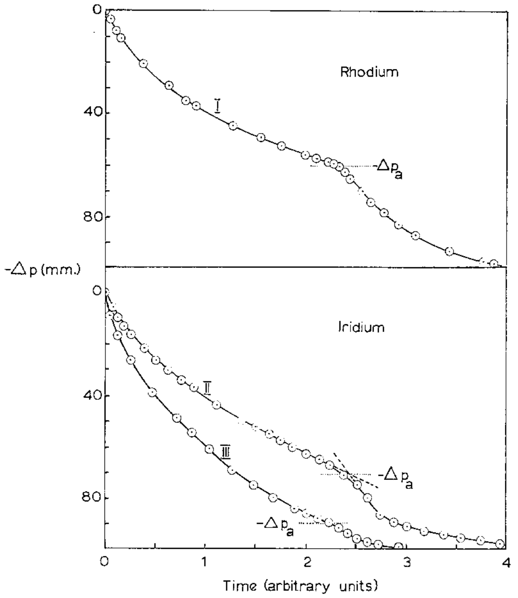


FIG. 1. Typical pressure fall, $-\Delta p$, against time curves for the complete hydrogenation of 50 mm acetylene. Curve I, Rh-IV at 131°C, $(P_{H_2})_0 = 105$ mm; II, Ir-I at 133°C, $(P_{H_2})_0 = 235$ mm; III, Ir-II at 62°C, $(P_{H_2})_0 = 200$ mm.

Values of $-\Delta p_a/(P_{C_2H_2})_0$ were 1.1 to 1.3 for all rhodium catalysts, 1.4 to 1.6 for Ir-I, and 1.75 to 1.85 for Ir-II. The acceleration points exhibited by iridium-catalyzed reactions were frequently so ill-defined that the dependence of $-\Delta p_a$ upon experimental variables was not measured. However, over rhodium, $-\Delta p_a$ could be assigned a numerical value with an average uncertainty of ±1.0 mm. Its value was independent of temperature over the range 117° to 165° (Rh-II) but it decreased slightly with increasing initial hydrogen pressure [Rh-IV at 131°, $(P_{C_2H_2})_0 = 50$ mm].

$(P_{H_2})_0$(mm)	104	206	302	400	450
$-\Delta P_a$(mm)	61	61	60	56	54

Over Rh-VI at 139°, using initial acetylene and hydrogen pressures of 50 and 200 mm, respectively, 2.5 mm of acetylene remained at the acceleration point and the rate of acetylene removal did not increase as the rate of pressure fall accelerated.

Over both metals, conversion to paraffin was complete at the end of the second stage of the reaction.

Orders of reaction by the initial rate method. Using fresh rhodium catalysts (Rh-I and II) the order in hydrogen by the initial rate method was 1.5 ± 0.1 but this value decreased to 1.0 ± 0.1 after about 50 reactions. At 172°C, the order in acetylene was zero for a 15-fold change of acetylene pressure (Rh-V).

Initial rates, r_0, using iridium obeyed the expression $r_0 = k(P_{C_2H_2})_0^{-0.4}(P_{H_2})_0^{1.0}$. The order in hydrogen was measured at 130° and 184° (Ir-I) and the acetylene order at 132° (Ir-I) and 106° (Ir-II).

Activation energies. The values obtained are shown in Table 1.

TABLE 1
ACTIVATION ENERGIES FOR ACETYLENE HYDROGENATION MEASURED USING CATALYSTS RH-IV, IR-I, AND IR-II

Catalyst	Activation energy (kcal mole^{-1})	Temperature range (°C)
Rh-IV	9.0 ± 0.5	117 − 165
Ir-I (fresh)	7.7 ± 1.0	115 − 180
Ir-I (well-used)	7.5 ± 0.5	115 − 180
Ir-II	16.9 ± 0.5	90 − 130

The Effect of Experimental Variables upon Selectivity

Selectivity is defined as $P_{C_2H_4}/(P_{C_2H_4} + P_{C_2H_6})$. Selectivity decreased slowly through the first stage of the reaction over both metals and it decreased more rapidly as the acceleration point was approached (see Fig. 2). Selectivity also decreased with increasing initial hydrogen pressure (see Fig. 3). All curves are convex with respect to the origin initially; some remain so (Ir-I), but others (Rh-II and Ir-II) later become concave, the point of inflection occurring when the initial hydrogen : acetylene ratio is about 5.5:1.

Results obtained using Rh-III show that selectivity increased with increasing temperature over the range 18° to 116°C [$(P_{C_2H_2})_0 = 50$ mm; $(P_{H_2})_0 = 220$ mm]. Temperature dependencies for some other catalyst samples can be derived by interpolation in Fig. 3.

Temperature(°C)	18	32	94	116
Selectivity	0.566	0.645	0.745	0.817

The Effect of Initially Added Olefins upon the Reactions

Rhodium. When ethylene was initially added to the reaction mixture the acceleration point was delayed (see Table 2) and was less sharp although the point of inflection which preceded it was not effected. This delay in the acceleration point shows that ethylene competed successfully with acetylene for the surface. Complete analysis of reaction mixtures showed that selectivity was depressed throughout the reaction by approximately 0.2 units when $(P_{C_2H_4})_0 = 100$ mm and by about 0.3 units when $(P_{C_2H_4})_0 = 200$ mm. The acceleration point remained insensitive to changes in the initial hydrogen pressure when ethylene was initially added (see Table 2).

TABLE 2
THE EFFECT OF INITIALLY ADDED ETHYLENE UPON THE ACCELERATION POINT, $-\Delta p_a$ USING CATALYST RH-IV AT 130°C[a]

Initial hydrogen pressure (mm)	Initial ethylene pressure (mm)	$-\Delta p_a$ (mm)
205	0	61
305	0	60
217	105	70
300	105	70
414	105	70
210	200	76
324	200	77

[a] Initial acetylene pressure, 50 mm.

The effect of the initial addition of 1-butene to the reaction was also studied. In the following results allowance has been made for butenes and butane produced from

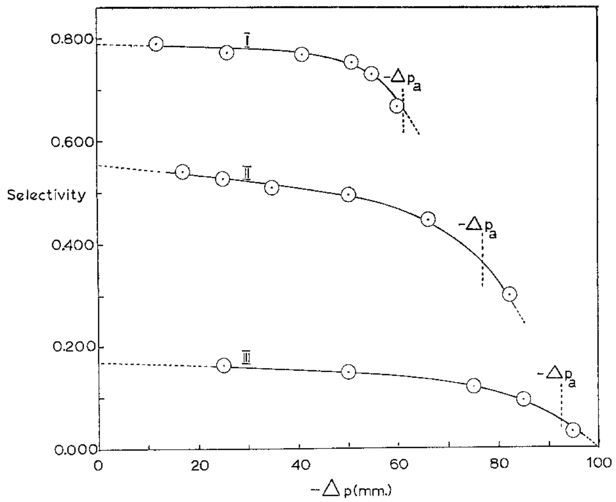


FIG. 2. The dependence of selectivity upon pressure fall, $-\Delta p$, during the hydrogenation of 50 mm acetylene. The acceleration point, where ~95% of the acetylene has been hydrogenated, is denoted by $-\Delta p_a$. Curve I, Rh-IV at 131°C, $(P_{H_2})_0$ = 200 mm; II, Ir-I at 112°, $(P_{H_2})_0$ = 260 mm; III, Ir-II at 46.5°C, $(P_{H_2})_0$ = 200 mm.

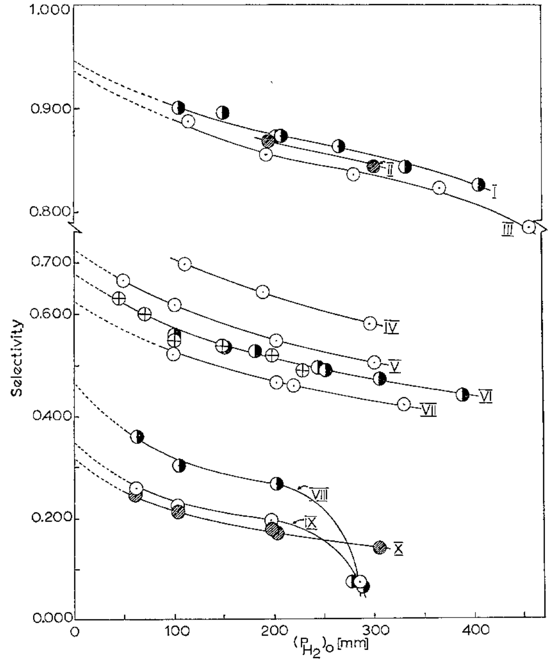


FIG. 3. The variation of selectivity with initial hydrogen pressure, $(P_{H_2})_0$, at various temperatures. $(P_{C_2H_2})_0$ = 50 mm throughout. Analyses were made after $-\Delta p$ = 25 mm (Ir) or 35 mm (Rh). Curve I, Rh-II at 152°; II, Rh-II at 132°; III, Rh-II at 115°; IV, Ir-I at 184°; V, Ir-I at 151°; VI, Ir-I at 133° (half-filled circles denote normal sequence of addition of reactants, crossed circles denote reverse sequence of addition of reactants); VII, Ir-I at 115°; VIII, Ir-II at 115°; IX, Ir-II at 81°; X, Ir-II at 62°.

acetylene (see below). Table 3 shows that 1-butene competed successfully with acetylene for the rhodium surface and that it underwent isomerization to 2-butene and hydrogenation to *n*-butane. The depression of selectivity, $S - S^*$ [where $S^* = P_{C_2H_4}/(P_{C_2H_4} + P_{C_2H_6} + P_{C_4H_{10}})$] caused by the addition of 1-butene was about 25% of that caused by the initial addition of the same pressure of ethylene. However, the initial rate of 1-butene hydrogenation was 25% that of ethylene hydrogenation [at 140°; $(P_{H_2})_0$ = 100 mm in each case] and thus we conclude that ethylene and 2-butene competed equally effectively with acetylene for the surface. Table 3 also shows that acetylene modified the reaction of 1-butene in that it increased both the 2-butene:butane and the *cis*-2-butene:*trans*-2-butene ratios.

The initial addition of 250 mm of 1-butene decreased the rate of reaction of 25 mm of acetylene with 100 mm of hydrogen by 50% and delayed the acceleration point slightly.

Iridium. When acetylene and ethylene were co-hydrogenated the rate of ethylene removal frequently exceeded the rate of its production. The yields of ethane produced were measured relative to the nonreacting gas argon, which was also added at known pressure to the initial reactant mixture.The results in Table 4 show that 100 mm of initially added ethylene caused a consider-

TABLE 3

Some Characteristics of the Hydrogenation of Acetylene, 1-Butene, and Acetylene + 1-Butene Mixtures over Rh-VI at 140°C

Initial hydrogen pressure (mm)	Initial acetylene pressure (mm)	Initial 1-butene pressure (mm)	Pressure fall before extraction (mm)	S	S^{*a}	$P_{\text{Butane}}/P_{\text{2-Butene}}$	*cis*-2-Butene/*trans*-2-Butene
100	25	0	16	0.882	—	—	—
100	0	250	10	—	—	0.6	1.0
100	25	250	16	0.884	0.803	0.4	1.2
200	25	250	24	0.857	0.752	0.6	1.2
200	50	100	16	0.843	0.792	0.3	1.3

[a] $S^* = P_{C_2H_4}/(P_{C_2H} + P_{C_2H_6} + P_{C_4H_{10}})$.

TABLE 4

The Variation of the Ethane Yield with Pressure Fall in the Absence and Presence of Initially Added Ethylene Using Ir-II at 85°C[a]

Pressure fall (mm)	Ethane yield (mm)		
	$(P_{C_2H_4})_0 = 0$ mm	$(P_{C_2H_4})_0 = 100$ mm	$(P_{C_2H_4})_0 = 200$ mm
5.5	2.6	3.4	3.5
10.0	4.3	5.9	—
15.5	6.9	9.2	9.8
20.0	9.3	11.5	12.9

[a] $(P_{C_2H_2})_0 = 50$ mm; $(P_{H_2})_0 = 100$ mm.

able increase in the ethane yield, but a further 100 mm had little additional effect.

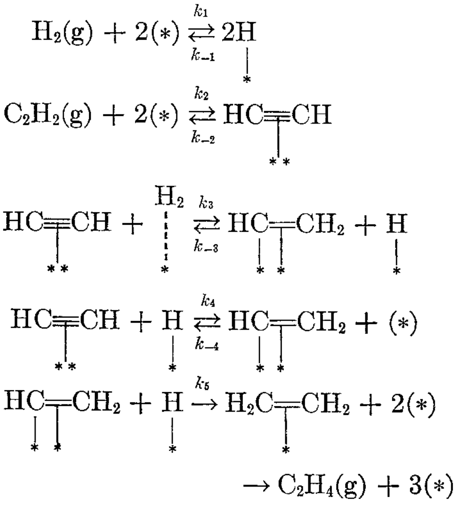
The Formation of C_4 *Hydrocarbons*

Although production of ethylene and ethane was the major process taking place in our experiments, production of higher molecular weight hydrocarbons consumed some 12% to 15% of the acetylene. The C_4 hydrocarbons produced are shown in Table 5 and these were accompanied by traces of propene, propane, and C_6 hydrocarbons. 1,3-Butadiene, which was formed when we hydrogenated acetylene over platinum (*5*) and palladium (*6*), was absent when using rhodium and iridium. Isobutene was only observed when using rhodium.

DISCUSSION

The zero order in acetylene measured over rhodium shows that this reactant was very strongly adsorbed, that it achieved maximum surface coverage, and that in consequence hydrogen was adsorbed noncompetitively at sites which were geometrically precluded for acetylene adsorption. Over iridium the order in acetylene was negative (as was the case over palladium and platinum), which indicates that acetylene and hydrogen competed for adsorption sites on the surface. A full discussion of negative orders in acetylene was given in Part I (*5*).

Over both metals the hydrogen order was unity or greater, indicating comparatively weak adsorption of this reactant, and this is interpretable in terms of the mechanism put forward in Part I



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

$$C_2H_2(g) + 2(*) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{**}{HC{=}CH} \qquad (2)$$

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

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

$$\underset{*\,*}{HC{=}CH_2} + \underset{*}{H} \xrightarrow{k_5} \underset{*\qquad *}{H_2C{=}CH_2} + 2(*) \rightarrow C_2H_4(g) + 3(*) \qquad (5)$$

The rate of ethylene formation, r, is given by the expression

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

In Part IV, where the reaction of acetylene with deuterium catalyzed by the same

TABLE 5

C_4 PRODUCTS OBTAINED WHEN 155 MM ACETYLENE AND 145 MM HYDROGEN REACTED TO COMPLETION AT 135°C OVER RH-IV AND IR-II

Catalyst	1-Butene (%)	*cis*-2-Butene (%)	*trans*-2-Butene (%)	Isobutene (%)	$\frac{C_4H_8}{C_4H_8 + C_4H_{10}}$	$\frac{C_2H_4}{C_2H_4 + C_2H_6}$
Rh-IV	46	37	8	9	0.93	0.89
Ir-II	64	33	3	—	0.55	0.30

rhodium and iridium catalysts will be described, it will be shown that hydrogen atoms are removed from the surface as rapidly by recombination [step (−1)] as by the hydrogenation process [steps (4) and (5)]. Further, it will be shown that $(k_{-3}\theta_H + k_{-4}[*])/k_5\theta_H$ takes values from 3 to 10 over these metals.

Because step (−1) is important, the relation $\theta_H \propto P_{H_2}$ [which was justified in Part I for the platinum-catalyzed reaction where step (−1) was very slow] may no longer be valid. As an alternative one may consider using the Langmuir expression for the competitive adsorption of hydrogen and acetylene,

$$\theta_H = b_H^{1/2}P_{H_2}^{1/2}/(1 + b_H^{1/2}P_{H_2}^{1/2} + b_C P_{C_2H_2})$$

where $b_H = k_1/k_{-1}$ and $b_C = k_2/k_{-2}$; this would approximate to $\theta_H \propto P_{H_2}^{1/2}/P_{C_2H_2}$ for the situation at the iridium surface where acetylene adsorption is strong and hydrogen adsorption is weak but competitive with acetylene. At the rhodium surface, adsorption of reactants does not appear to be competitive, and so the Langmuir expression above would be appropriately modified by putting $b_C = 0$. Unfortunately, Langmuir expressions cannot be rigorously true, because they require the rate of removal of hydrogen atoms by the hydrogenation process to be very small compared to their rate of recombination. Thus, the operative relation must lie between these two alternatives, i.e., $\theta_H \propto P_{H_2}^{1/n}$ where $2 > n > 1$.

A prediction of the hydrogen order from the rate expression can be made if we know the relative importance of steps (3) and (4), but it is difficult to see how this information can be obtained from studies of acetylene hydrogenation. However, our study of the reaction of dimethylacetylene with deuterium, using the same rhodium and iridium catalysts (*12*), has shown conclusively that the process analogous to step (3) does not occur. Consequently we feel justified in disregarding step (3) and writing the rate equation in the form,

$$r = k_4k_5\theta_{C_2H_2}\theta_H^2/k_{-4}[*]$$

Thus, as $n \rightarrow 2$, the reaction will tend to first order in hydrogen, which was observed experimentally, and the order will exceed unity if $n < 2$. The reduction of the hydrogen order from 1.5 to 1.0 as the rhodium catalysts were used was probably caused by a change in the relative importance of steps (−1), and (4), and (5) as the active surface aged.

Pressure Fall against Time Curves

Over rhodium, the curves were of the form expected from the equation $-d(P_{C_2H_2})/dt = kP^0_{C_2H_2}P_{H_2}^{1.0}$. The surface was mostly covered with adsorbed acetylene until the acceleration point occurred, and the rate decreased during the first stage as the concentration of adsorbed hydrogen diminished. The declining rate of acetylene removal contrasts with the accelerating rate of removal observed using platinum and palladium, where orders in acetylene were negative. At the acceleration point, the instantaneous value of $P_{C_2H_4}/P_{C_2H_2}$ had risen to approximately 20, which is about the same as that found using platinum (*5*) and the residual pressure of acetylene (2–3 mm) was no longer able to prevent ethylene readsorption and hydrogenation.

The orders observed using iridium are very similar to those reported in Part II for palladium (*6*). However, palladium gave mostly ethylene as the initial product, whereas iridium gave mostly ethane. Iridium's low selectivity declined throughout the reaction (see Fig. 2) and acetylene remained in the system until the reaction was nearly complete. This has two consequences. First the expected acceleration in the rate of acetylene removal, if it occurred, took place late in the reaction and was masked by the readsorption and hydrogenation of ethylene. Secondly, readsorption of ethylene was probably responsible for the apparent change in order of the pressure–time curve during the first stage of the reaction.

Selectivity

This part of the discussion has two objectives: (i) to rationalize the dependence of selectivity upon experimental variables for each metal, and (ii) to examine the reasons why the selectivities afforded by rhodium and iridium differ from each other and from their Group VIII neighbors, palladium and platinum.

Selectivity decreased with increasing initial hydrogen pressure (see Fig. 3) and this behavior is common to all metals so far studied. Since the concentration of adsorbed hydrogen increases with increasing hydrogen pressure, the probability that adsorbed ethylene formed in step (5) will hydrogenate rather than desorb is also increased. The same effect is responsible, in part, for the decrease of selectivity with pressure fall (see Fig. 2); for reactions having an initial excess of hydrogen the instantaneous value of $P_{H_2}/P_{C_2H_2}$ increases throughout the first stage of the reaction, this causes an increase in θ_H, and selectivity falls accordingly. However, a second factor also contributes. The considerable depression of selectivity by initially added olefin shows that ethylene produced by acetylene hydrogenation is able to compete with acetylene for the surface and undergo hydrogenation throughout the reaction. This is supported by the observation that the rate of selectivity fall with pressure fall [i.e., $dS/d(-\Delta p)$ in Fig. 2] is greater for rhodium and iridium than for palladium and platinum where added olefin has but little effect upon selectivity (*5*, *6*).

Selectivity increased with increasing temperature over both rhodium and iridium, and similar behavior was reported for platinum (*5*). Approximate values of the selectivity as hydrogen pressure is reduced to zero, S_0, are obtained by the extrapolations shown in Fig. 3. From these values, the difference between the activation energies of ethylene desorption and ethylene hydrogenation, $(E_d - E_h)$ can, in principle, be calculated because $(1 - S_0)/S_0 = k_h/k_d$, where k_h and k_d are the velocity constants for ethylene hydrogenation and ethylene desorption respectively. S_0 values are only sufficient in the case of Ir-I, for which we calculate $(E_d - E_h) = 5.7 \pm 1.0$ kcal mole^{-1}. This is in satisfactory agreement with the value of 5.9 ± 0.5 kcal mole^{-1} that we obtained for the difference between the activation energies of ethylene exchange and ethylene hydrogenation during our study of the ethylene–deuterium reaction over iridium catalyst from the same batch (*13*). The agreement is meaningful because the activation energy for ethylene exchange is closely related to that for ethylene desorption; it differs only inasmuch as the desorption of ethylene-d_0 (whose concentration was small) was not observable in the ethylene–deuterium reaction.

The selectivity exhibited by a given metal arises from the simultaneous operation of mechanistic and thermodynamic factors [see Part I (*5*) for detailed discussion]. Thus, a catalyst will be highly selective for ethylene formation (i) if its activity for ethylene hydrogenation is low and (ii) if the difference between the free energies of adsorption of acetylene and ethylene is large, so that acetylene effectively displaces ethylene from the surface before it reacts further. Schuit and van Reijen (*14*) have reported that the specific activity of rhodium-silica exceeded that of iridium-silica by a factor of 100. However, the reverse appeared to be the case with our catalysts. The ethylene hydrogenation activity of our rhodium-alumina was less than that of our iridium-alumina and the ratio (ethylene hydrogenation activity) : (acetylene hydrogenation activity) was greater for our iridium catalysts than for the rhodium catalysts. Thus, on the basis of this consideration alone, we expect rhodium to be more selective for ethylene formation than iridium. Furthermore, the effect of initially added ethylene was greater over iridium than over rhodium and, as we noted above, $dS/d(-\Delta p)$ was greater over iridium than over rhodium. From this we conclude that the thermodynamic factor operated less powerfully in the iridium-catalyzed reactions than in those catalyzed by rhodium. Thus, rhodium is expected to be more selective than iridium on both counts, and this accords with the experimental observations.

Iridium is also less selective than rhodium, palladium, or platinum in the hydrogenation of allene (*8*), 1,3-butadiene (*8*, *15*), 1,3-pentadiene, 1-pentyne, 2-pentyne (*16*), and 2-butyne (*12*), although for the last-mentioned molecule the selectivity was high (0.96). Thus poor selectivity in the hydrogenation of diunsaturated hydrocarbons is a fairly general feature of the catalytic chemistry of iridium. In contrast, rhodium is as selective or more selective than platinum, but less selective than palladium in the reactions listed above.

We now consider the higher selectivity afforded by Ir-I compared to Ir-II. Two further samples of iridium catalyst behaved as Ir-II over the range 40° to 100°C and we are certain that our results for Ir-II represent the normal behavior of this metal. It was suggested above that the hydrogen coverage during reaction was lower on the surface of Ir-I than on Ir-II. Such a difference would lead us to expect a higher selectivity of Ir-I than of Ir-II, as observed, because the ethylene hydrogenation rate would thereby be diminished. However, the origin of this difference of behavior is obscure, and a hydrogen coverage effect does not furnish an explanation of the high activation energy recorded for Ir-II (see Table 1).

The Formation of C_4 Hydrocarbons

Less acetylene was converted to C_4 hydrocarbons over rhodium and iridium (12–15%) than over platinum (28%) and palladium (37%). The Sheridan mechanism for polymerization, which was discussed in Parts I and II (*5*, *6*) envisages adsorbed 1,3-butadiene as the precursor of the C_4 olefins and butane. This was justified by our results for platinum and palladium because (i) 1,3-butadiene was observed in the gas phase and (ii) the distribution of butenes obtained from platinum was similar to that obtained by 1,3-butadiene hydrogenation (*15*). However, over rhodium and iridium, no 1,3-butadiene was observed in the gas phase and the distributions of butenes bear little similarity to those obtained by 1,3-butadiene hydrogenation over catalysts from the same stock (*15*). The high *cis*:*trans* ratio in the 2-butene produced by polymerization is a particularly odd feature. It is noteworthy that isobutene was produced over rhodium, and C_3 hydrocarbons were observed using both rhodium and iridium, but not with palladium and platinum. This suggests that cracking also occurred at the sites which catalyzed the formation of C_4 species and that a complex "make-and-break" mechanism operated. We have observed that catalytic cracking accompanies 1,3-butadiene hydrogenation on rhodium and iridium wires at temperatures above 100°; indeed about 90% of the product was methane when the latter metal was used (*17*). Thus this aspect of the mechanism awaits further investigation.

In common with the behavior of palladium and platinum, the selectivity in the C_4 yield was higher than that in the C_2 yield over both rhodium and iridium (see Table 5), indicating that butenes were slightly more easily displaced from the surface by acetylene than was ethylene.

ACKNOWLEDGMENTS

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

REFERENCES

1. SHERIDAN, J., AND REID, W. D., *J. Chem. Soc.*, p. 2962 (1952).

2. SHERIDAN, J., *J. Chem. Soc.*, p. 305 (1945).

3. SHERIDAN, J., *J. Chem. Soc.*, p. 470 (1945).

4. BOND, G. C., DOWDEN, D. A., AND MACKENZIE, N., *Trans. Faraday Soc.* **54**, 1537 (1958).

5. BOND, G. C., AND WELLS, P. B., *J. Catalysis* **4**, 211 (1965).

6. BOND, G. C., AND WELLS, P. B., *J. Catalysis* **5**, 65 (1966).

7. BOND, G. C., NEWHAM, J., AND WELLS, P. B., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **1,** 1177 (Editions Technip, Paris, 1961).

8. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Catalysis* **1,** 74 (1962).

9. Wells, P. B., *Platinum Metals Rev.* **7,** 18 (1963).

10. Wells, P. B., *Chem. and Ind.,* p. 1742 (1964).

11. Bond, G. C., and Wells, P. B., *Advan. Catalysis* **15,** 92 (1964).

12. Phillipson, J. J., Wells, P. B., and Gray, D. W., *Proc. Intern. Congr. on Catalysis, 3rd, Amsterdam, 1964* **2,** 1250 (North-Holland Publ. Co., Amsterdam, 1965).

13. Bond, G. C., Phillipson, J. J., Wells, P. B., and Winterbottom, J. M., *Trans. Faraday Soc.* **60,** 1847 (1964).

14. Schuit, G. C. A., and van Reijen, L. L., *Advan. Catalysis* **10,** 242 (1958).

15. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Chem. Soc.,* p. 3218, (1965).

16. Bond, G. C., and Rank, J. S., *Proc. Intern. Congr. on Catalysis, 3rd, Amsterdam, 1964,* **2,** 1225 (North-Holland Publ. Co., Amsterdam, 1965).

17. Wells, P. B., Trueman, B., and Whitehead, M. L., unpublished work.