81. *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part IV. Reaction over Platinum.*

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Ethylene is not formed selectively from acetylene and hydrogen over platinum–pumice at 0—163°, though acetylene is more strongly adsorbed than ethylene, and at pressures above a low value (which depends on the pressures of hydrogen and ethylene present) inhibits ethane production to a rate less than, but comparable with, that of ethylene formation. With 1 : 1 and 2 : 1 hydrogen : acetylene mixtures some 6—30% of the acetylene not recovered, and a comparable amount of hydrogen, are removed as products less volatile than C_2 hydrocarbons, though the catalysts are virtually without action on the same partial pressures of acetylene alone at those temperatures. Previous kinetic data are confirmed and amplified, and it is shown that lower temperatures favour ethane production in the early stages. The reactions (I) $C_2H_2 + H_2 = C_2H_4 (\rightarrow C_2H_6)$ and (II) $C_2H_2 + H_2 \longrightarrow$ products other than C_2 hydrocarbons are probably both of approximately first order with respect to hydrogen, and have similar heats of activation [that of (II) being the higher by *ca.* 1—2 kg.-cals.] in the region of 12 kg.-cals. The differences between (I) and (II) are qualitatively the same as for the corresponding reactions over nickel. The stronger adsorption of acetylene than of ethylene is confirmed by the fact that ethylene added to the system acts primarily as a diluent. Oxygen has little effect on the reaction, though some water is formed.

ACETYLENE and hydrogen react over platinum to give ethylene and ethane (von Wilde, *Ber.*, 1874, **7**, 353; Sabatier and Senderens, *Compt. rend.*, 1900, **131**, 40; Paal and Schwarz, *Ber.*, 1915, **48**, 1202; Morris and Reyerson, *J. Physical Chem.*, 1927, **31**, 1332; Lebedev, Gulyaeva, and Vasil'ev, *J. Gen. Chem. U.S.S.R.*, 1935, **5**, 1422). At lower temperatures acetylene is removed almost entirely as these two gases, and reaction is quantitative with a large excess of hydrogen (Conn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 1868); at higher temperatures (*e.g.*, 180°), and with greater proportions of acetylene, some less volatile hydrocarbons are formed.

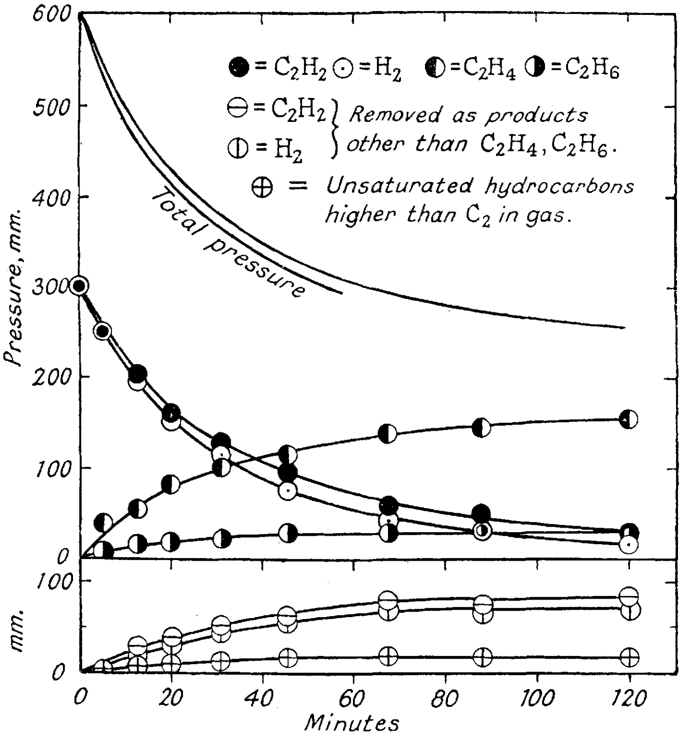
The statement (Farkas, *Trans. Faraday Soc.*, 1939, **35**, 908) that acetylene and hydrogen do not react over platinum unless the hydrogen pressure is the greater is not confirmed by the results of Farkas and Farkas (*J. Amer. Chem. Soc.*, 1939, **61**, 3396), though the kinetics found by these authors indicate reaction between strongly adsorbed acetylene and weakly adsorbed hydrogen. An increase in the rate of fall in pressure (at constant volume) was observed in hydrogen-rich mixtures after a fall in pressure roughly equal to the initial acetylene pressure. Reaction up to this point was regarded as exclusively $C_2H_2 + H_2 = C_2H_4$, ethane formation being completely suppressed, on account of the stronger adsorption of acetylene than ethylene, until all or almost all, the acetylene had been removed, after which a faster hydrogenation of ethylene developed. Acceleration of hydrogenation, regarded as coincident with total acetylene removal, was observed by Lebedev, Gulyaeva, and Vasil'ev (*loc. cit.*); they considered that some ethane was formed at earlier stages, a view supported by results of other workers mentioned. In view of this, and since the course of reaction advocated by Farkas and Farkas was apparently proposed without support from analyses of hydrocarbon products, further kinetic study in conjunction with full gas-analyses has been made.

Experimental.—Experiments were performed at constant volume, the gases (except oxygen, which was taken from a cylinder) and apparatus being those described in Part I (J., 1944, 373). The catalysts were carried on the same pumice base as there described, and had platinum : pumice ratios of 1 : 250 (Pt-1) and 1 : 10 (Pt-2). Pt-1 was made by dissolving platinum in aqua regia, diluting the solution, and evaporating it in the presence of pumice. When, as here, the nitric acid was not removed by repeated partial evaporation, catalysts so made were not highly active, even with a 1 : 10 metal : pumice ratio. After brief ignition in a dish, the platinic chloride was decomposed as required in the reaction bulb by heating it to 300—350° for *ca.* 1 hr. at 10 mm. pressure and then in 400—500 mm. of hydrogen at the same temperature for several hours. The catalyst was cooled in hydrogen or in a vacuum, and not allowed to come into contact with air during use. Pt-2 was made by evaporation of a solution of platinic chloride in the presence of pumice, followed by the same treatment as for Pt-1. The mass of catalyst used for each series of experiments was 2 g. for Pt-2 and 1 g. for Pt-1. Runs were numbered in order of performance over each specimen of catalyst, the order being such that any variations in catalyst activity could not lead to false conclusions about the effects of conditions on the reaction.

Gases were analysed as outlined in Part I (*loc. cit.*) and Part III (preceding paper). The saturated hydrocarbon contents were found by oxidation over copper oxide at 600° to have a mean composition almost exactly C_2H_6, and the ethane contents were taken as the same as the saturated contents.

RESULTS AND DISCUSSION.

FIG. 1.



Initial pressures : 298—301 *mm.* H_2 *(admitted first),* 298—306 *mm.* C_2H_2. *See Table I(a). The limits of variation of total pressure curves are shown.*

(i) *Activity of Catalysts and their Effect on Acetylene Alone.*—Pt-1 retained a fairly constant activity for the acetylene–hydrogen reaction during long series of experiments at 140—165°, but Pt-2, initially much more active, retained a high and steady activity only during the removal of *ca.* 0·1 g. of acetylene per g. of catalyst within the first few hours of its use, after which it became progressively less active. No marked increases in activity were observed and no dependence of the products on the activity of the catalysts was apparent.

Both catalysts were without measurable action on acetylene alone at the temperatures and partial pressures at which acetylene and hydrogen formed some products less volatile than ethylene and ethane. A pressure fall was not observed in the absence of hydrogen until considerably higher temperatures were reached, *e.g.*, with 302 mm. of acetylene over Pt-1 at 353° the pressure fell 15 mm. in 20 mins., the gas, after separation of slight fog, then containing 97·8% of acetylene.

(ii) *The Course of Reaction at Constant Volume.*—This was determined by the method used for nickel catalysts (Part I), runs of different durations being made under the same conditions, and the analytical results plotted at time co-ordinates equal to the times required for the appropriate pressure falls in the longest experiment of each series; this is equivalent to a correction to constant catalyst activity (cf., *e.g.*, Twigg and Rideal, *Proc. Roy. Soc.*, 1939, *A*, **171**, 55; Twigg, *ibid.*, 1941, *A*, **178**, 106). Figs. 1 and 2 show the results for 1 : 1 and 2 : 1 hydrogen : acetylene mixtures over Pt-1 at 163° and 145°, respectively. The yields, in terms of the acetylene not recovered, are given in Table I, (*a*) and (*b*). Despite some variation in catalyst activity, smooth curves are obtained for the partial pressures, etc., and there is no reason to doubt that the course of reaction in the longest experiment is close to that plotted.

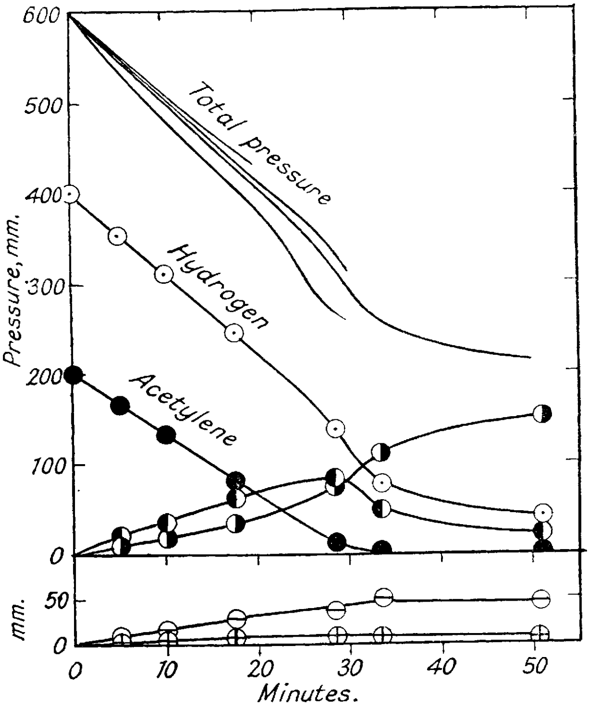
With both gas ratios, hydrogen is more rapidly removed than acetylene, and some ethane is formed almost from the start. Ethylene production is 4—5 times as fast as ethane formation in the 1 : 1 gas mixture, and about twice as fast in the early stages of reaction in the 2 : 1 hydrogen : acetylene mixture. In Fig. 1, as in all reactions with 1 : 1 mixtures, the rate of fall in total pressure ($-dp/dt$) decreases continuously throughout. In Fig. 2 the increase in $-dp/dt$ is first detected when the total pressure fall (Δp) is roughly equal to the initial acetylene pressure, as is seen from Fig. 4 (curve 1). The acceleration coincides roughly with the beginning of an increase in rate of ethane formation and a slowing of ethylene production, the gas at the commencement of the acceleration containing approximately : H_2, 210; C_2H_2, 60; C_2H_4, 72; C_2H_6, 42 mm. The value of $-dp/dt$ then passes through a maximum, roughly coincident with the maximum in ethylene pressure; at this point there are present some 137, 10, 82, and 74 mm., respectively, of the above gases. The remainder of the reaction is mainly $C_2H_4 + H_2 = C_2H_6$, the acetylene pressure falling almost to zero.

The yields of C_2 hydrocarbons were 68—73% for 1 : 1 and 78—85% for 2 : 1 hydrogen : acetylene ratios at all stages of reaction. These values are a little too high because, first, slight fog formation occurred on withdrawing gas, and secondly, acetylene being admitted after hydrogen, a fast initial reaction may have occurred while the acetylene pressure at the catalyst surface was very small (see below), making the recorded initial acetylene pressure too low. In view of the higher products already included in the gas pressures, and of the fact that *ca.* 100 mm. of acetylene were admitted in 1 sec., the true yields cannot be much less than those listed. Not more than a small part of the ethane production in the early stages can be due to the fast initial reaction mentioned, since ethane production continues when diffusion equilibrium is established and also occurs when acetylene is introduced first (see below).

Roughly equal amounts of acetylene and hydrogen are removed as products less volatile than ethylene and ethane; the pressures of unsaturated hydrocarbons higher than the C_2 series are *ca.* $\frac{1}{7}$—$\frac{1}{4}$ of the pressures of acetylene so removed. The less volatile products are therefore largely of relatively low molecular weight, *e.g.*, C_4, C_6, and C_8 compounds. Their formation ceases as soon as all the acetylene is removed, while ethylene hydrogenation continues.

Fig. 3 and Table I (*c*) show the course and yields of reaction in a 2 : 1 hydrogen : acetylene mixture over Pt-2 at 57°. The pressures of unsaturated hydrocarbons higher than ethylene are negligible. The acceleration effect is more marked than in Fig. 2 and the yields of C_2 products are higher, the most accurate figures being 90—94%. The rate of ethane production is about half of that of ethylene formation at almost the earliest stage, and the two rates are almost equal after *ca.* 30 mins. After some 73 mins. (Δp = 235 mm.) an increase in $-\mathrm{d}p/\mathrm{d}t$ is first perceptible (Fig. 4, curve 2), the gas then containing: *ca.* H_2, 170; C_2H_2, 40; C_2H_4, 85; C_2H_6, 59 mm. The value of $-\mathrm{d}p/\mathrm{d}t$ then passes through a very sharp and high peak. At the time of the very large acceleration the acetylene pressure has fallen to some 10—20 mm.; it is clear that the ethylene pressure must pass through a sharp maximum at about this time, and that the very fast reaction is predominantly hydrogenation of ethylene. In harmony with the high ethane production, hydrogen is removed much more rapidly than acetylene from the earliest stages. Deactivation of the catalyst prevented more points being fixed, but the course of reaction must be close to that shown. The amounts of acetylene and hydrogen removed as products other than ethylene and ethane are roughly equal, but the possible errors are a large proportion of the small pressures concerned.

FIG. 2.



Initial pressures: 397—402 *mm.* H_2 (*admitted first*), 200—211 *mm.* C_2H_2. *See Table I*(*b*). *Significance of various types of point as in Fig.* 1 (*the amounts of* H_2 *removed as products other than* C_2H_4 *and* C_2H_6 *are not shown: they are equal within experimental error to the amounts of acetylene removed as such products*). *The limits of variation of total pressure curves are shown.*

TABLE I.

Yields at different stages of reaction.

(*a*) In 1 : 1 H_2 : C_2H_2 mixture over Pt-1 at 163° (see Fig. 1).

No. of expt.	66	62	64	68	69	63	67	65
Duration (mins.)	5	11	20	30	45	60	90	120
Yield of C_2H_4, %	69	55	59	58	56	57	58	58
Yield of C_2H_6, %	14	16	13	13	14	11	12	12

(*b*) In 2 : 1 H_2 : C_2H_2 mixture over Pt-1 [same specimen as in (*a*)] at 145° (see Fig. 2).

No. of expt.	74	72	73	75	70	71
Duration (mins.)	5	10	20	30	30	51
Yield of C_2H_4, %	59	52	50	43	23	11
Yield of C_2H_6, %	26	27	28	38	55	71

(*c*) In 2 : 1 H_2 : C_2H_2 mixture over Pt-2 at 57° (see Fig. 3).

No. of expt.	5	3	4	2
Duration (mins.)	14	27	65	94
Yield of C_2H_4, %	53	60	54	2
Yield of C_2H_6, %	27	30	38	92

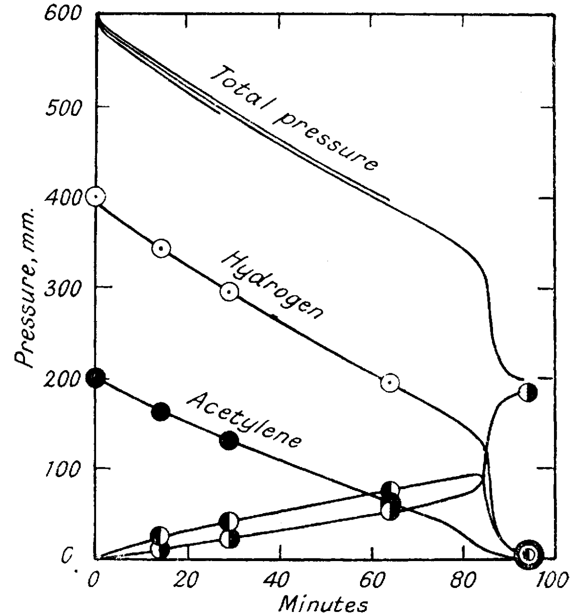
Under the same conditions, over the same catalyst in a less active state, gas was analysed at Δp = 330 mm.

(189 mins.), $-dp/dt$ being about 2·5 times its initial value : H_2, 81; C_2H_2, 6; C_2H_4, 73; C_2H_6, 104 mm. (yields . C_2H_4, 38; C_2H_6, 54%). If deactivation of the catalyst is assumed to leave the relative speeds of the various reactions unchanged, these pressures can be taken as those for Δp = 330 mm. in Fig. 3 (*i.e.*, the region of the maximum in $-dp/dt$).

Further evidence for the course in Fig. 3 was obtained with a new sample of Pt-2 at 65° as follows (acetylene introduced first) : (*a*) With 199 mm. of acetylene and 399 mm. of hydrogen initially, gas was analysed after 67 mins., Δp being 263 mm. and $-dp/dt$ about twice its initial value and rising rapidly; the gas contained : H_2, 145; C_2H_2, 21; C_2H_4, 100; C_2H_6, 64 mm. (yields : C_2H_4, 56; C_2H_6, 36%); $-dp/dt$ in the residual gas was larger than before gas was withdrawn. (*b*) Starting with 42 mm. of acetylene and 100 mm. of hydrogen, an acceleration occurred at Δp = *ca.* 42 mm. (23 mins., Fig. 4, curve 3); whereas (*c*) with 42 mm. of acetylene and 98 mm. of hydrogen, the rate was almost unchanged, and after 10 mins. (Δp = 20 mm.) there were present : H_2, 78; C_2H_2, 27; C_2H_4, 9·4; C_2H_6, 3 mm. (yields : C_2H_4, 63; C_2H_6, 20%); reaction in the residual gas continued and showed acceleration at a later stage.

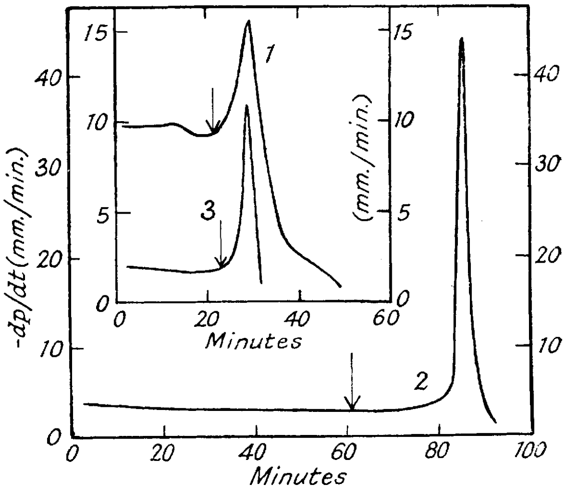
In experiment (*b*) the acetylene pressure must have fallen to 5—10 mm. before $-dp/dt$ began to rise, as compared with *ca.* 40 mm. in Fig. 3. This is probably due largely to the lower hydrogen pressure in the former case [see (iii) below], though the ethylene pressure presumably also influences the time at which acceleration is first detected. Comparison of curves 2 and 3 in Fig. 4 suggests that, at lower total pressures, acceleration is observed at more nearly the point where Δp equals the initial acetylene pressure, but such an effect is probably also caused by an increase in hydrogen : acetylene ratio; with ratios from 3 to 6 (hydrogen pressure = 200—300 mm.) fast rates were observed, increasing before Δp reached the initial acetylene pressure.

FIG. 3.



Initial pressures : 199—200 *mm.* C_2H_2 (*admitted first*), 399—410 *mm.* H_2. *See Table I(c). Significance of various types of point as in Fig.* 1. *The limits of variation of total pressure curves are shown.*

FIG. 4.



Curve 1 = *longest run in Fig.* 2; *curve* 2 = *longest run in Fig.* 3; *vertical arrows indicate the times when* Δp = *initial acetylene pressure.*

The above courses of reaction can be explained only by a stronger adsorption of acetylene than of ethylene, this leading to a retardation of ethane formation until the acetylene pressure has fallen below a low value (which depends on the other pressures prevailing). Conclusions of this type reached by Farkas and Farkas (*loc. cit.*) are thus confirmed. All the experiments in the present paper, however, followed a course differing in some important respects from that postulated by those authors. First, ethane is produced virtually from the beginning in quantities less than, but of magnitude comparable with, those of ethylene, especially in mixtures rich in hydrogen. Thus the hydrogenation of ethylene, though retarded by, *e.g.*, some 50 mm. (or less) of acetylene to a rate only of the order of 1/100 of that expected in the absence of acetylene, is not inhibited so completely that the hydrogenation to ethylene can be described as selective. Secondly, the acceleration can begin and become marked at quite definite acetylene pressures.

The main argument used by Farkas and Farkas for selective ethylene formation appears to be that acceleration occurs suddenly when Δp equals the initial acetylene pressure. The suddenness of the phenomenon is perhaps open to question, but in any case the published total-pressure data of Farkas and Farkas differ little from some of the present results; *e.g.*, the accelerations were scarcely ever any more sudden than in curves 1 and 3 in Fig. 4, where $-dp/dt$ rises when Δp reaches the initial acetylene pressure; yet analyses show the course already described for these reactions. Acceleration at this particular point accordingly seems to be a coincidence due to compensation of two factors, *viz.*, definite ethane production and the presence of a definite acetylene pressure when acceleration begins. In many cases (*e.g.*, Fig. 4, curve 2) acceleration occurs after Δp exceeds the initial acetylene pressure; *i.e.*, the two factors do not balance. It is noted that the lower pressures and higher hydrogen : acetylene ratios of many of the experiments of Farkas and Farkas are conditions which seem to favour the occurrence of acceleration after a pressure fall nearer to the initial acetylene pressure, without giving rise to selective hydrogenation. The work of Farkas and Farkas was performed in the absence of pumice and probably with slightly purer gases than the present experiments, but it would be difficult to account for the early ethane production in the present work in terms of an inactive catalyst base or strong adsorption of even a reactive possible impurity, such as a trace of oxygen. The author therefore considers that at present there is no evidence of a truly selective hydrogenation of acetylene on platinum.

(iii) *Orders of Reaction.*—The effects of partial pressures on the initial rate of fall in total pressure, $(-dp/dt)_0$, over a specimen of Pt-2 (of fairly steady activity) at 73° are shown in Table II (hydrogen was admitted first). The apparent order with respect to hydrogen is *ca.* 1·2. With over 100 mm. of acetylene (in the presence of 300 mm. of hydrogen) the apparent order with respect to acetylene is about $-0{\cdot}7$; it becomes more negative at lower acetylene pressures but the accuracy is less here, the true initial rates probably being lower than those tabulated. A series of 43 runs over a specimen of Pt-1 at 162° gave very similar results; in this case the order with respect to acetylene was zero at pressures of that gas above *ca.* 150—200 mm. in the presence of 200 mm. of hydrogen, but the negative order extended to higher acetylene pressures when more hydrogen was present.

TABLE II.

(*a*) Effect of hydrogen pressure on $(-dp/dt)_0$ over Pt-2 at 73° (C_2H_2 pressure = 199—205 mm.).

No. of expt.	7	4	5	14	2	6	12	15	3
H_2 press. (mm.)	54	100	197	200	201	299	299	398	400
$(-dp/dt)_0$ (mm./min.)	0·8	1·4	3·0	3·5	2·6	5·0	5·5	9·0	6·3

(*b*) Effect of C_2H_2 pressure on $(-dp/dt)_0$ over Pt-2 at 73° (H_2 pressure = 298—301 mm.).

No. of expt.	10	13	9	8	6	12	11
C_2H_2 press. (mm.)	52	75	104	153	201	202	303
$(-dp/dt)_0$ (mm./min.)	*ca.* 40	12	8·6	6·7	5·0	5·5	4·4

These data are in harmony with the more qualitative results of Farkas and Farkas (*loc. cit.*), who have already given their general explanation in terms of strengths of adsorption. The tendency towards zero order with respect to acetylene suggests that the adsorption film becomes saturated with respect to that gas when its pressure exceeds a certain value, which increases with the hydrogen pressure. It is possible that some ethane formation is included in the measured initial rate, especially at the lowest acetylene pressures, and therefore the observed orders cannot be identified with certainty with those of the reaction $C_2H_2 + H_2 = C_2H_4$, but since we expect more hydrogen to favour ethane production and more acetylene to discourage it, we see that the maximum order of the above reaction with respect to hydrogen is *ca.* 1·2, and that its order with respect to acetylene will not be more negative than the apparent orders already given.

The values of $-dp/dt$ during reaction (before any acceleration) are in fair harmony with these orders, ethylene and ethane being supposed to have no influence on $-dp/dt$.

The effect of gas pressures on the yields is not large. For instance, at *ca.* 70° over Pt-2 the yield of C_2 hydrocarbons is about 90% with 200 mm. of acetylene and either 200 mm. or 400 mm. of hydrogen. Reaction leading to products other than C_2 hydrocarbons (reaction II) therefore seems to resemble the simple hydrogenation (reaction I) in its order with respect to hydrogen. A slow increase in yield of C_2 products with hydrogen : acetylene ratio may occur, however, and an increase of this type is indicated by the results of previous workers (see above).

(iv) *Effect of Temperature.*—Table III shows results with 2 : 1 hydrogen : acetylene mixtures over Pt-2 (t_{170} = time in mins. required for Δp to reach 170 mm.). Catalyst activity varied somewhat, but the plot of $\log_{10} t_{170}$ against $1000/T$ (T = absolute temperature) is a reasonably straight line of slope 3·0 with respect to the $1000/T$ axis. With $\log_{10} (-dp/dt)_0$ against $1000/T$ the corresponding slope is *ca.* $-2{\cdot}6$, the points being rather more scattered. During each run, $-dp/dt$ decreased slightly.

The ethylene : ethane ratio is increased by a rise and lowered by a fall in temperature; lower temperatures therefore favour ethane production in the early stages.

To determine the activation energy of $C_2H_2 + H_2 = C_2H_4$ it is necessary to know whether any ethane formation contributes to the measured initial rate, and, if so, how its contribution varies with temperature. If we assume a contribution independent of temperature (the contribution, if any, is probably small in the initial reaction) we have :

$$\frac{d \log_{10} (d[C_2H_4]/dt)_0}{d(1000/T)} = \frac{d \log_{10} (-dp/dt)_0}{d(1000/T)} \approx -2{\cdot}6$$

since the yield of C_2 hydrocarbons varies little with temperature. A variation in initial ethylene/ethane ratio

TABLE III.

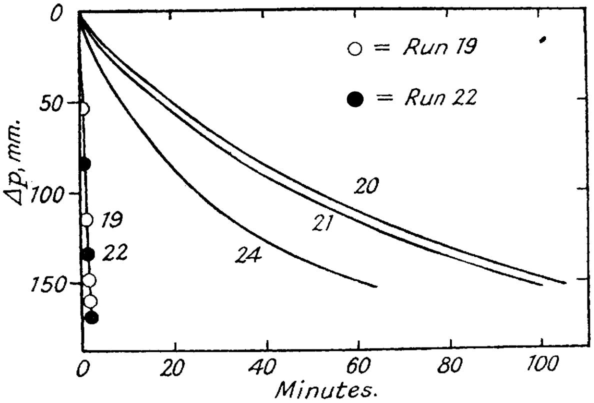
Effect of temperature.

(Acetylene admitted first; $\Delta p = 170$ mm.; the products contained 0—3 mm. of unsaturated hydrocarbons higher than C_2.)

Expt. no.	Temp.	Initial press. (mm.).		$(-dp/dt)_0$, mm./min.	t_{170}.	Press. (mm.) in gaseous product.				Yield (%).		Ratio C_2H_4/C_2H_6.
		C_2H_2.	H_2.			C_2H_2.	C_2H_4.	H_2.	C_2H_6.	C_2H_4.	C_2H_6.	
2	16±1°	201	404	0·05	4130	93	56	240	44	52	41	1·27
3	74	201	404	4·0	38	89	60	240	37	54	33	1·62
4	18±2	200	400	0·27	2520	96	46	235	48	44	46	0·96
5	87	200	404	6·5	27·7	89	59	240	37	53	33	1·60
6	2±2	199	402	0·014	16110	91	48	233	49	45	45	1·0
7	101	199	405	12·0	16	84	62	239	34	54	30	1·8
8	56	199	403	0·8	320	—	—	—	—	—	—	—
9	120	199	390	18·0	9	79	71	232	31	59	26	2·26

sufficient to make the above expression inapplicable is very unlikely. The energy of activation of $C_2H_2 + H_2 = C_2H_4$ is therefore about 12 kg.-cals.; Farkas and Farkas (*loc. cit.*) found 12—17 kg.-cals.

FIG. 5.



Initial pressures (*in order of admission*) *: runs* 19 *and* 22, 196—200 *mm.* C_2H_4, 200 *mm.* H_2*; run* 20, 201 *mm.* C_2H_2, 202 *mm.* H_2*; run* 21, 202 *mm.* C_2H_2, 200 *mm.* C_2H_4, 203 *mm.* H_2*; run* 24, 202 *mm.* C_2H_2, 199 *mm.* O_2, 199 *mm.* H_2.

The total yield of C_2 products appears a little lower at 74—120° (84—87%) than at 0—20° (90—93%); this suggests that reaction (II) has a heat of activation of roughly 1—2 kg.-cals. higher than that of $C_2H_2 + H_2 = C_2H_4$. This is qualitatively in harmony with results of previous workers and with the lower yields of C_2 products over Pt-1 at 145° and 163°.

(v) *Effects of Ethylene and Oxygen.*—Fig. 5 shows the influence of these gases, the Pt-2 catalyst being that used in (iii). Ethylene hydrogenation (run 19) was much more rapid than the acetylene–hydrogen reaction at the same pressures (run 20). With ethylene, acetylene, and hydrogen present (run 21) dp/dt was almost the same as when the ethylene was omitted (run 20), though run 22 (ethylene hydrogenation) showed that the activity of the catalyst had fallen very little. After deduction of the initial ethylene in run 21, the products (Δp = 154 mm.) were almost the same as in run 20 (yields: run 20, ethylene 58, ethane 30%; run 21, ethylene 49, ethane 36%). The ethane yield in run 21 is thus raised only slightly by the added ethylene, which therefore acts principally as a diluent, in harmony with the deduced adsorption relationships.

Addition of oxygen (run 24) increased $-dp/dt$ somewhat, and an abnormally large removal of hydrogen as products other than C_2 hydrocarbons occurred. If 40 mm. of water vapour are assumed to be formed (Δp = 154 mm.), the final pressures are: C_2H_2, 114; C_2H_4, 39; H_2, 38; C_2H_6, 28; O_2, 172; CO and CO_2, each *ca.* 3 mm. (yields: ethylene 45, ethane 32%). The 27 mm. of oxygen removed are accounted for within error as water and oxides of carbon. The simultaneous acetylene–hydrogen reaction appears to be largely unaltered, though the yields of C_2 products are possibly lowered slightly. This is the simplest explanation of the analytical data. It is noteworthy that oxidation (chiefly of hydrogen) can occur without retarding the acetylene–hydrogen reaction; this, and the failure of oxygen to raise the yield of C_2 products, distinguish the effect of that gas over platinum from that observed with nickel catalysts (Part III).

(vi) *General Discussion.*—Except for the above effects of oxygen upon it, the reaction over platinum has a close qualitative resemblance to that over nickel. Thus two types of reaction, (I) and (II), occur at temperatures and acetylene pressures at which acetylene alone undergoes virtually no change over the same catalysts. Reaction (II) leads to hydrocarbons of roughly the same mean molecular weight as the corresponding products over nickel, though the structures formed over platinum remain to be determined. The reaction orders indicate strong adsorption of acetylene and weak adsorption of hydrogen on both metals, and the heats of activation are also similar over both. The differences between the kinetics and heats of activation of reactions (I) and (II) are of the same type over platinum as over nickel. Unknown factors cause a greater yield of C_2 products over platinum, but the general phenomena strongly suggest that similar mechanisms of reaction operate over platinum and nickel (and probably other catalysts; see Part II).

The early production of ethane on platinum shows that some ethylene is present in the adsorption film, despite the stronger adsorption of acetylene. This may be a result of direct competition between acetylene and ethylene for sites which can adsorb either, but it is possible that parts of the surface can adsorb ethylene but not acetylene [*e.g.*, perhaps the (111) crystal face; cf. Herington, *Trans. Faraday Soc.*, 1941, **37**, 361], and that at such sites hydrogenation of ethylene can continue relatively slowly, ethylene being displaced by acetylene from the sites where ethane is formed most rapidly in the absence of acetylene. Alternatively, ethylene when formed may remain long enough on the metal to have a chance of being hydrogenated further before desorption: the increase in ethane formation at higher hydrogen pressures perhaps suggests that this effect is operative.

The catalytic metal influences the selectiveness of ethylene production. For instance, previous workers have claimed that palladium causes more selective ethylene production than platinum (Paal and Schwarz, *loc. cit.*; Paal and Hohenegger, *Ber.*, 1915, **48**, 275; Morris and Reyerson, *loc. cit.*), and total selectiveness over palladium was postulated by Cremer, Knorr, and Plieninger (*Z. Elektrochem.*, 1941, **47**, 737). In the present work (Part V, to be published) the more selective action of palladium than of platinum has been confirmed, and the case of acetylene thus falls into line with many data on catalytic hydrogenation of substituted acetylenes, in which, in general (though the phenomena doubtless depend on the substituents as well as the catalyst), platinum does not promote a truly selective formation of the ethylenic derivative, whereas palladium is more favourable for such selective hydrogenation (*e.g.*, Lebedev and Stern, *J. Gen. Chem. U.S.S.R.*, 1932, **2**, 249; Zal'kind *et al.*, *ibid.*, 1933, **3**, 91, and many other papers; Lebedev, Gulyaeva, and Vasil'ev, *loc. cit.*). In some (but by no means all) such reductions, the rate of hydrogenation increases when the acetylenic substance is almost completely removed. In these cases a stronger adsorption of the triple- than of the double-bonded compound (as with acetylene itself) is indicated, and may well occur even when there is no such increase in rate (cf., *e.g.*, acetylene on nickel, Part I).

At present it is difficult to relate the degrees of selectiveness of hydrogenation of acetylene on various metals to the differences in strengths of adsorption of acetylene and ethylene on those catalysts. For instance, the more selective action of palladium might be related to a weaker adsorption of ethylene by palladium than by, *e.g.*, platinum. Fischer and Knorr's data (*Z. Elektrochem.*, 1937, **43**, 608) indicate that ethylene is not strongly adsorbed on palladium containing hydrogen at room temperature, whereas Farkas and Farkas (*J. Amer. Chem. Soc.*, 1938, **60**, 22) give evidence that, under those conditions, ethylene is strongly adsorbed on platinum. Unfortunately, however, other data (Bruns and Ablezova, *Acta Physicochim. U.R.S.S.*, 1934, **1**, 90) indicate much weaker adsorption of ethylene on platinum, so until more results are available it is premature to ascribe the more selective action of palladium to so simple a cause. We have already seen that other factors than strengths of adsorption (*e.g.*, relative effectiveness of different types of surface sites) may be concerned.

Similarly, though the effect of temperature on the ethylene/ethane ratio over platinum might be related to an increased difference in strengths of adsorption of acetylene and ethylene at higher temperatures, it might also be due to the true activation energy of $C_2H_4 + H_2 = C_2H_6$ being lower than that of $C_2H_2 + H_2 = C_2H_4$ (cf. Farkas and Farkas, *loc. cit.*, 1939).

The author wishes to thank Mr. D. Ll. Hammick for his interest in and advice on the work described in this and the preceding paper, and the Department of Scientific and Industrial Research for a grant.

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