122. The Metal-catalysed Reaction between Acetylene and Hydrogen. Part V. Reaction over Palladium, Iron, and Some Other Catalysts.

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A kinetic study, with full analyses of gaseous products, shows that the acetylene–hydrogen reaction over fresh palladium–pumice catalysts resembles that over platinum (Part IV, this vol., p. 305) except that (*a*) ethane formation over palladium is much more strongly suppressed by acetylene, even in the presence of excess of hydrogen, (*b*) the total yield of C_2 products is slightly less than that over platinum under comparable conditions, and (*c*) the presence of oxygen with palladium catalysts causes more rapid oxidation processes than with platinum. Deactivation of palladium catalysts is accompanied by an increase in production of ethane relatively to that of ethylene in the early stages of reaction.

Over iron–pumice catalysts considerable hydrogenation to ethylene and ethane occurs; reaction in general resembles that over nickel (Parts I and II, J., 1944, 373; this vol., p. 133) but is not retarded by oxygen.

The catalytic actions of cobalt, copper, and some mixtures of metals are of the same type as that of nickel, though cuprene formation complicates the reaction over copper.

Acetylene and hydrogen combine over palladium to give ethylene and ethane, *ca.* 10—30% of the unrecovered acetylene being converted into less volatile hydrocarbons (Paal and Hohenegger, *Ber.*, 1915, **48**, 275; Paal, *Chem.-Ztg.*, 1912, **36**, 60; Morris and Reyerson, *J. Physical Chem.*, 1927, **31**, 1332; Yoshikawa, *Bull. Chem. Soc. Japan*, 1932, **7**, 201; *J. Fuel Soc. Japan*, 1933, **12**, 30; Peters and Neumann, *Ges. Abh. Kenntn. Kohle*, 1934, **11**, 423). Specific hydrogenation to ethylene appears more favoured over palladium than platinum (cf. Part IV), and Cremer, Knorr, and Plieninger (*Z. Elektrochem.*, 1941, **47**, 737) regarded ethylene as the only C_2 product up to a point where the rate of hydrogenation passed through a maximum. The kinetics indicated reaction between strongly adsorbed acetylene and weakly adsorbed hydrogen, and acetylene was held to suppress ethane production by reason of its stronger adsorption than ethylene on palladium containing hydrogen (cf. Fischer and Knorr, *ibid.*, 1937, **43**, 608; Dobychin and Frost, *J. Physical Chem. U.S.S.R.*, 1936, **7**, 742). The acetylene pressure was shown to be *ca.* 30 mm. at the point of maximum rate, but since the above course of reaction was not supported by analyses for ethylene and ethane, further study, with such analyses, was desirable and is now reported.

The reaction over iron at 180—400° is stated to be largely decomposition and oil-formation (Sabatier and Senderens, *Compt. rend.*, 1900, **130**, 1628; Fischer, Peters, and Koch, *Brennstoff-Chem.*, 1929, **10**, 383; Pichler, *Ges. Abh. Kenntn. Kohle*, 1934, **11**, 395; Peters and Neumann, *loc. cit.*; Klar, *Z. Elektrochem.*, 1937, **43**, 379; Amemiya, *J. Soc. Chem. Ind. Japan*, 1939, **42**, Suppl. bdg., 329). Considerable hydrogenation was, however, found in the study of the kinetics of reaction over iron described below.

Cobalt and copper appear to resemble nickel in their catalytic action, but are usually less active; over copper, formation of cuprene can become extensive (Sabatier and Senderens, *loc. cit.*; *Compt. rend.*, 1902, **134**, 1185; 1900, **130**, 1559; *Ann. Chim. Phys.*, 1905, **4**, 445; Pichler, *loc. cit.*; Ackermann, *Brennstoff-Chem.*, 1937, **18**, 357; Fischer, Peters, and Koch, *loc. cit.*; Fischer and Peters, *ibid.*, 1931, **12**, 286; Morris and Reyerson, *loc. cit.*; Kwal, *Chim. et Ind.*, 1935, **34**, 773). Extension of the few data for these metals is desirable, however, and some further results with them are therefore presented below, with data for some mixed metal catalysts not already studied.

EXPERIMENTAL.

Gases and experimental methods were as described in Parts I (*loc. cit.*) and III (this vol., p. 301).

All catalysts were carried on the pumice base described in Part I. Palladium catalysts were made from palladous chloride by the procedure given for catalyst Pt-2 in Part IV. Metal : pumice ratios were 1 : 40 (Pd-1) and 1 : 10 (Pd-2); 0·5 g. (or occasionally 1 g.) specimens were introduced. The compositions and conditions of reduction of the other catalysts were as follows:

Catalyst.	Composition (wt. ratio).	Conditions of reduction.
Fe-1	2Fe : 10 pumice	H_2, 300—350°, 10 hrs.
Fe-2	2Fe : 10 pumice	H_2, 250°, 8 hrs., 300°, 6 hrs.
Co	2Co : 10 pumice	H_2 + ethanol vapour, 400—420°, 2·5 hrs.
Cu	2Cu : 10 pumice	H_2, 300—350°, 4 hrs.
Ni–Co-1	2Ni : 2Co : 10 pumice	H_2 + ethanol vapour, 400—450°, 2 hrs.
Ni–Co-2	2Ni : 1Co : 10 pumice	
Ni–Co-3	1Ni : 2Co : 10 pumice	
Ni–Co-4	1Ni : 1Co : 20 pumice	
Ni–Ag	2Ni : 2Ag : 10 pumice	H_2 + ethanol vapour, 410—450°, 2 hrs.
Ni–Co–Ag	1Ni : 1Co : 2Ag : 10 pumice	H_2 + ethanol vapour, 400—420°, 2 hrs.

Iron catalysts were made by treating ferrous sulphate (Fe-1) or ferrous ammonium sulphate (Fe-2) with excess of ammonia, and drying a suspension of the washed precipitate in the presence of pumice. After brief ignition the ferric oxide was reduced. The other catalysts were made from mixed solutions of metal nitrates, by methods similar to those given for nickel catalysts in Part I. With the tabulated catalysts, 2 g. specimens were used for runs at constant volume. In such runs, acetylene was usually admitted first over palladium (except in determination of initial rates at low acetylene concentrations), but hydrogen was generally admitted first over the other catalysts.

Runs (numbered in series over each catalyst specimen) were, as far as possible, in such a sequence as to prevent changes in catalyst activity leading to false conclusions. The ethane contents of the products were taken to equal the contents of saturated hydrocarbons, which always had a mean composition very nearly C_2H_6. With the small weights of metal used, appreciable errors in partial pressures on account of adsorption effects are unlikely, even in the case of the hydrogen pressure over palladium, but the possibility of larger error in this case must be borne in mind.

RESULTS AND DISCUSSION.

A. *Reaction over Palladium.*—(i) *General phenomena and activity of catalysts.* The total pressure–time curves at constant volume resembled those for platinum catalysts (Part IV), though the increase in rate of pressure fall in hydrogen-rich gases was less than with platinum. The catalysts had a negligible action on acetylene alone at the pressures and temperatures which produced rapid reaction in acetylene–hydrogen mixtures, during which some 20—40% of the unrecovered acetylene formed products less volatile than C_2 hydrocarbons.

The fairly rapid deactivation of palladium was accompanied by an increase in the contribution of ethane to the yield of C_2 products (see Table I; in all tables, $\Delta p =$ pressure fall in mm., $t =$ duration in mins., $C_mH_n =$ unsaturated hydrocarbons higher than the C_2 series; runs bracketed together on the left are over the same specimen of catalyst; yields are in percentages of the unrecovered acetylene; unless stated otherwise, tabulated data refer to runs at constant volume).

The fall in ethylene : ethane ratio with deactivation, at stages of reaction up to a point where some 30 mm. of acetylene still remained, was considerable. No change in total yield of C_2 products was found after the activity had fallen to *ca.* 1/20 of its initial value (run 8), but with greater deactivation (runs 13, 15) an increase in total yield of C_2 hydrocarbons appeared to occur. Deactivation is thus partly selective, ethylene formation being arrested more rapidly than ethane production. No simple explanation is apparent; deactivation is probably due to surface contamination by non-volatile products, but to account for the effect we must suppose contamination to affect ethylene and ethane formation unequally; this might be possible if different metal sites are concerned in the hydrogenation of ethylene and acetylene. Contamination might raise the yield of C_2 products by lowering the chance of two acetylene molecules being adsorbed on adjacent sites suitable for their combination.

TABLE I.

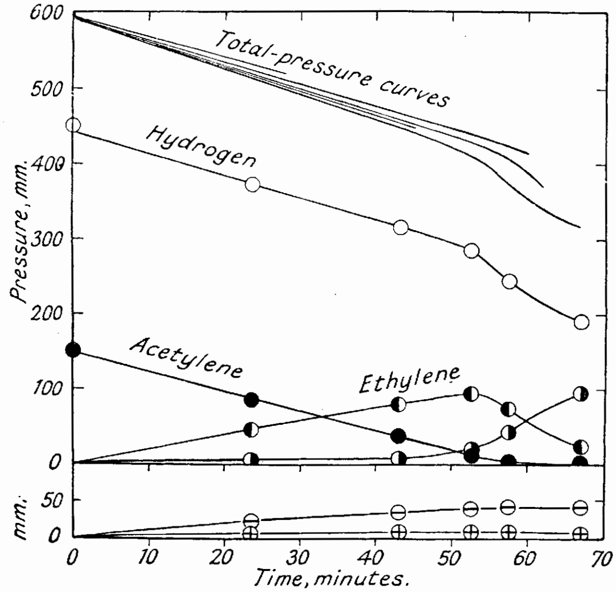
(*Catalyst* Pd-2 ; *acetylene admitted first.*)

No. of run.	Initial press. (mm.). C_2H_2.	H_2.	Temp.	Δp.	*t*.	Press. (mm.) in gaseous product. C_2H_2.	C_mH_n.	C_2H_4.	H_2.	C_2H_6.	Yield (%). C_2H_4.	C_2H_6.	Ratio $\frac{C_2H_4}{C_2H_6}$.
1	198	398	36°	200	34	38	9	119	216	9	74	6	13·2
2	199	401	36	200	35	37	12	115	221	10	71	6	11·5
3	200	409	36	200	38	40	10	114	228	10	71	6	11·4
4	200	395	36	200	40	38	11	114	216	11	70	7	10·4
5	200	404	36	200	84	41	10	109	221	15	69	9	7·3
3	200	404	37	212	26	30	12	126	217	9	74	5	14·0
6	201	400	37	212	191	40	9	105	211	17	66	11	6·2
7	201	400	37	212	298	45	8	98	210	22	63	14	4·4
8	202	396	37	212	615	53	7	84	210	33	56	22	2·5
13	201	399	92	75	56	160	1	10	322	25	25	60	0·4
15	201	398	123	131	23	129	1	19	268	48	26	67	0·4

(ii) *Course of reaction over fresh catalysts at constant volume.* This was determined in the manner described in Parts I and IV, runs of different duration being performed under constant conditions and the analytical results plotted at time co-ordinates equal to the times required for the appropriate pressure fall in the longest run. Fig. 1 shows results with 3 : 1 hydrogen : acetylene mixtures at 24° ; the catalyst activity was increasing slightly. Very similar curves were obtained for a 2 : 1 hydrogen : acetylene ratio at 37°, though in this case an irregular fall in activity occurred. Since smooth curves of similar type were obtained for partial pressures, etc., when activity was both increasing and decreasing, there is no reason to doubt that the course of the longest run in Fig. 1 is that shown. The following table shows yields at various stages.

FIG. 1.

Course of reaction in 3 : 1 $H_2 : C_2H_2$ *mixture over* Pd-1 *at* 24°.



◐ = C_2H_4 ; ◑ = C_2H_6 ; ⊖ = C_2H_2 *removed as products other than* C_2H_4 *and* C_2H_6 ; ⊕ = *unsaturated hydrocarbons higher than* C_2 *in the gas. Initial pressures :* 150—152 *mm. of acetylene* (*admitted first*), 447—452 *mm. of hydrogen. All total-pressure curves are shown.*

Yields from 3 : 1 $H_2 : C_2H_2$ *mixture at* 24° *over a specimen of* Pd-2 (see Fig. 1).

No. of run in series ...	2	5	3	4	6
Duration (mins.) ...	30	45	60	62	67
Yield of C_2H_4 (%) ...	67	69	67	49	15
Yield of C_2H_6 (%) ...	6	6	9	28	63

Ethylene was the chief product, with very little ethane, until Δp was approximately equal to the initial acetylene pressure. In this stage the rate of fall in total pressure, $-dp/dt$, was constant or fell a little. When Δp reached the initial acetylene pressure, or a little later, $-dp/dt$ began to rise, and this acceleration coincided with an increase in ethane formation at the expense of ethylene production. Some 30 mm. of acetylene were present at this stage, with *ca.* 300 mm. of hydrogen and 90 mm. of ethylene. Ethane formation then became dominant, the acetylene pressure falling almost to zero. Ethylene pressure reached a maximum slightly earlier than $-dp/dt$, the maximum value of which was about twice its value in the stage preceding acceleration. Some 22—27% of the unrecovered acetylene, with about the same amount of hydrogen, formed products less volatile than C_2 hydrocarbons at all stages, and the pressure of unsaturated hydrocarbons higher than ethylene was about $\frac{1}{5}$ of the 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.

In a few very fast reactions with large excess of hydrogen, $-dp/dt$ began to rise before Δp equalled the initial acetylene pressure.

The course resembles that over platinum (Part IV), and can only be explained by a stronger adsorption of acetylene than of ethylene, as proposed by Cremer, Knorr, and Plieninger (*loc. cit.*). The total yield of C_2 products is slightly less than over platinum, and ethane formation is much more strongly suppressed by acetylene than with platinum catalysts, even in hydrogen-rich gases. The course found differs in minor respects from that found by Cremer, Knorr, and Plieninger ; *e.g.*, in the present runs the start of appreciable ethane production is generally marked by a beginning of a rise in $-dp/dt$ from a steady or falling value, not by a maximum in $-dp/dt$ (cf. following section).

Over deactivated catalysts, ethylene formation is no longer so selective.

(iii) *Orders of reactions.* The effects of partial pressures on $(-\mathrm{d}p/\mathrm{d}t)_0$, the initial value of $-\mathrm{d}p/\mathrm{d}t$, are shown in the following tables.

Temp. 49°, C_2H_2 pressure 198—203 mm.

No. of run	7	4	9	1	14	3	6	20	5	15	8	2
H_2 press. (mm.)	50	101	198	200	200	201	202	299	300	300	401	401
$(-\mathrm{d}p/\mathrm{d}t)_0$ (mm./min.)	1·7	3·0	5·5	5·0	5·0	6·0	7·0	10·0	12·0	10·0	33	80

Temp. 49°, H_2 pressure 198—203 mm.

No. of run	12	11	14	1	9	6	3	13	10
C_2H_2 press. (mm.)	50	103	200	201	202	202	203	299	398
$(-\mathrm{d}p/\mathrm{d}t)_0$ (mm./min.)	10·0	8·0	5·0	5·0	5·5	7·0	6·0	6·0	4·5

Temp. 49°, H_2 pressure 299—301 mm.

No. of run	18	17	19	16	5	15	20
C_2H_2 press. (mm.)	24	48	74	98	200	200	202
$(-\mathrm{d}p/\mathrm{d}t)_0$ (mm./min.)	21·0	31·0	19·0	12·0	12·0	10·0	10·0

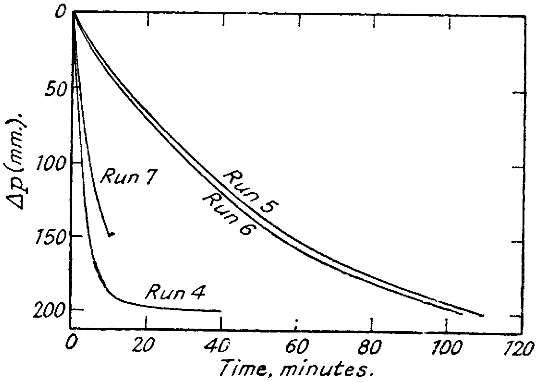
The apparent orders are *ca.* 1·0 with respect to hydrogen and *ca.* − 0·4 to − 0·7 with respect to acetylene; they are in satisfactory harmony with the shapes of the total pressure–time curves before any acceleration, $-\mathrm{d}p/\mathrm{d}t$ being assumed to depend only on the hydrogen and acetylene pressures. Cremer, Knorr, and Plieninger (*loc. cit.*) found a somewhat more negative order with respect to acetylene. High rates in runs 2 and 8 are probably due to non-establishment of diffusion equilibrium in the gas, reaction occurring in a zone of low acetylene pressure at the catalyst. This is supported by an abnormally large ethane production in the early stages of such runs.

The influence of gas pressures on the yield of C_2 products is small, as shown in the following table. An increase from 62% to 80% in the yield of C_2 products is caused by a 20-fold increase in initial hydrogen : acetylene ratio (1 : 4 to 5 : 1; the increase in final ratio is 150-fold). Since ethane formation can probably be neglected in the initial reaction, these data show that the above reaction orders apply approximately to both reactions (I) $C_2H_2 + H_2 = C_2H_4$ and (II) $C_2H_2 + H_2 \longrightarrow$ products other than C_2 hydrocarbons, though their orders differ slightly in the same way as with nickel catalysts (Part I).

Catalyst.	No. of run.	Initial press. (mm.).		Temp.	Δp.	t.	Pressures (mm.) in gaseous product.					Yield (%).	
		C_2H_2.	H_2.				C_2H_2.	C_mH_n.	C_2H_4.	H_2.	C_2H_6.	C_2H_4.	C_2H_6.
Pd-2	21	403	98	49°	101	185	319	6	41	21	10	50	12
	22	400	200	49	200	193	246	12	72	36	29	47	19
	23	201	401	49	202	48	57	10	76	218	34	53	24
	24	101	504	49	100	18	40	2	28	405	19	47	33
Pd-1	2	200	199	43	211	100	19	14	110	34	9	60	5
	4	201	401	43	215	24	20	6	119	216	15	65	8

Interpretation of the kinetics of reaction (I), in terms of strengths of adsorption, is discussed by Cremer, Knorr, and Plieninger (*loc. cit.*), who also considered it probable that reaction (II) possessed similar kinetics. At present there is no reason to suppose that the large amount of hydrogen occluded in palladium gives rise to a mechanism very different in type from that over nickel or platinum for reaction (I) or (II).

FIG. 2.



Initial pressures (in order of admission) : *Run* 4 : 201 *mm.* C_2H_4, 202 *mm.* H_2. *Run* 5 : 200 *mm.* C_2H_4, 201 *mm.* C_2H_2, 199 *mm.* H_2. *Run* 6 : 199 *mm.* C_2H_2, 200 *mm.* H_2. *Run* 7 : 198 *mm.* C_2H_4, 201 *mm.* H_2.

(iv) *Effect of temperature.* This was investigated in eight runs between 0° and 120° over a sample of Pd-2, with initial pressures of 400 mm. of hydrogen and 200 mm. of acetylene. A plot of $\log_{10}(-\mathrm{d}p/\mathrm{d}t)_0$ against $1000/T$ (T = absolute temp.) gave points grouped about a straight line of slope *ca.* − 2·6 with respect to the $1000/T$ axis, though some deactivation occurred, and the ethane/ethylene ratio hence increased with the age of the catalyst. This increase took place with both rising and falling temperature, and there was no evidence of variation of the ratio with temperature apart from the effect of deactivation. The total yield of C_2 products (Δp = 150 mm.) varied only from 72% to 80% between 0° and 120°.

It is therefore concluded that reactions (I) and (II) have very similar heats of activation in the region of 12—15 kg.-cals. (uncorrected for gas desorption).

(v) *Effects of ethylene and oxygen.* Fig. 2 shows a comparison of the acetylene–hydrogen and ethylene–hydrogen reactions over a sample of Pd-2. Ethylene hydrogenation (run 4) was rapid, but with ethylene, acetylene, and hydrogen (run 5), $-\mathrm{d}p/\mathrm{d}t$ was much lower and almost identical with that found with the same pressures of acetylene and hydrogen alone (run 6). Run 7 (ethylene hydrogenation) showed that the catalyst had been only slightly deactivated since run 4. Products from runs 5 and 6 were analysed (Δp = 200 mm.), and, after deduction of the added ethylene in run 5, were almost the same. The yields were : run 5, ethylene 49%, ethane 10%; run 6, ethylene 54%, ethane 8%. There is thus very little increase in ethane production on adding ethylene, which behaves primarily as a diluent, clearly confirming the adsorption relationships already deduced.

When oxygen was added, considerable amounts of it reacted, and the yields of C_2 products could be considerably lowered; for instance, with 200 mm. each of acetylene, hydrogen, and oxygen, $-dp/dt$ was at first the same as with 200 mm. each of acetylene and hydrogen alone, but after *ca.* 5 minutes a very rapid pressure fall of some 200 mm. began. The yield of C_2 products was less than 40% of the unrecovered acetylene (ethylene/ethane ratio = 10). About 100 mm. of oxygen were removed (Δp = 273 mm.); about 10 mm. each of carbon monoxide and dioxide were formed, and almost certainly water vapour. Some free carbon was also present, suggesting reactions such as $2C_2H_2 + O_2 = 4C + 2H_2O$.

B. *Reaction over Iron.*—Some data for iron catalysts are given in Table II. The shapes of the total pressure–time curves resembled those with nickel catalysts (Part I). The catalysts had a negligible action on acetylene alone at temperatures and pressures at which rapid reaction occurred in acetylene–hydrogen mixtures, during which 23—36% of the unrecovered acetylene (with *ca.* $\frac{2}{3}$—$\frac{3}{4}$ of that amount of hydrogen) formed products less volatile than C_2 hydrocarbons. Reaction was not readily detected in acetylene alone until temperatures about 100° higher were reached; *e.g.*, with 300 mm. of acetylene over Fe-1 at 294°, the pressure fell by 47 mm. in 26 mins., the gas, after separation of fog, containing 96% of acetylene at that point. With acetylene–hydrogen mixtures, ethane production was low over Fe-1, but larger over Fe-2 (Table II). The pressures of unsaturated hydrocarbons higher than the C_2 series were $\frac{1}{10}$—$\frac{1}{4}$ of the amounts of acetylene removed as products other than ethylene and ethane. Iron catalysts were fairly readily deactivated (cf. Peters and Neumann, *loc. cit.*).

TABLE II.

Catalyst.	No. of run.	Initial press. (mm.). C_2H_2.	H_2.	Temp.	Δp.	t.	Pressures (mm.) in gaseous product. C_2H_2.	C_mH_n.	C_2H_4.	H_2.	C_2H_6.	Yield (%). C_2H_4.	C_2H_6.
Fe-1	1	203	207	212°	217	10	14	16	118	33	7	62	4
	3	200	207	156	108	10	104	8	56	122	6	58	6
	5	204	399	156	202	10	28	11	120	222	15	68	9
Fe-1	2	320	304	20	265	24, 480	115	12	115	88	34	56	17
Fe-2	20	198	203	135	136	50	107	4	32	82	33	35	36
	21 *	197	202	135	136	58	113	4	220	82	36	23	43
Fe-2	4	201	299	135	161	50	87	5	44	157	35	39	31
	5 †	201	300	135	161	54	98	4	33	144	31	32	30

* 202 Mm. of ethylene added.

† 100 Mm. of oxygen added. A final water vapour pressure of 40 mm. is assumed, when the products also contain 75 mm. oxygen and 2—3 mm. each of carbon monoxide and dioxide.

Study of initial rates (two following tables) showed that $(-dp/dt)_0$ is roughly proportional to the hydrogen pressure and approximately independent of the acetylene pressure. A small increase in yield of C_2 hydrocarbons occurred with increased hydrogen pressure, and it seems that the reactions over iron are kinetically very similar to those over nickel.

Temp. 136°, catalyst Fe-2. Initial acetylene pressure 199—206 mm.

Run no.	14	12	17	11	15	18	4	13	16
H_2 press. (mm.)	50	102	149	200	202	298	300	399	481
$(-dp/dt)_0$ (mm./min.)	0·8	2·5	3·7	7·0	6·0	10·0	13·0	18·0	21·0

As above. Initial hydrogen pressure 298—302 mm.

Run no.	3	7	2	10	6	4	18	9	5	8
C_2H_2 press. (mm.)	51	51	100	101	152	201	202	255	304	344
$(-dp/dt)_0$ (mm./min.)	13	15	16	16	15	13	10	11	10	10

The following table shows the effect of temperature on $(-dp/dt)_0$.

Catalyst Fe-2; initial pressures 446—453 mm. of hydrogen, 146—155 mm. of acetylene.

Run no.	16	14	9	10	13	12	11	15
Temp.	19—20°	90°	105°	118°	138°	160°	178°	200°
$(-dp/dt)_0$ (mm./min.)	0·0024	0·35	0·70	2·25	4·7	14	28	60

The plot of $\log_{10} (-dp/dt)_0$ against $1000/T$ is a good straight line of slope − 3·35 with respect to the $1000/T$ axis. Since a change in temperature from 212° to 20° caused only a slight increase in yield of C_2 products (Table II), it is concluded that reactions (I) and (II) over iron each have activation energies of 15—16 kg.-cals.

The effect of added ethylene was studied as with palladium catalysts. With 200 mm. each of ethylene and hydrogen, $-dp/dt$ was about twice as great as with the same pressures of acetylene and hydrogen (run 20, Table II). With *ca.* 200 mm. each of acetylene, hydrogen, and ethylene (run 21) the rate was almost the same as in run 20, and the increase in ethane yield relatively small, though the catalyst was still as active for ethylene hydrogenation. Acetylene appears to be more strongly adsorbed on iron than ethylene at the same temperature and pressure, though the difference in strengths of adsorption is less marked than with palladium. The body-centred cubic lattice of α-iron cannot be related any more simply to these phenomena than the face-centred lattices of nickel, palladium, and platinum (Part I).

Oxygen in large amount (run 5 over Fe-2 in Table II) had very little retarding effect, though some of it was removed; water was probably the chief oxidation product. The yields of C_2 hydrocarbons were little changed (possibly slightly lowered) by oxygen, the effect of which therefore differs notably from its action with nickel catalysts (Part III). It was also shown that oxygen scarcely lowered $-dp/dt$ in ethylene–hydrogen mixtures over a catalyst previously used in runs with acetylene.

Apart from the influence of oxygen, the phenomena with iron have a general resemblance to those with nickel, though the yield of C_2 products is higher over iron (in disagreement with most earlier work), and ethane production can be larger with certain iron catalysts.

C. *Other Catalysts.*—Some data for these are collected in the following tables. The shapes of all the total pressure–time curves at constant volume resembled those for nickel (Part I).

Runs at constant volume over various catalysts.

		Initial press. (mm.).					Pressures (mm.) in gaseous product.					Yield (%).	
Catalyst.	No. of run.	C_2H_2.	H_2.	Temp.	Δp.	t.	C_2H_2.	C_mH_n.	C_2H_4.	H_2.	C_2H_6.	C_2H_4.	C_2H_6.
Co	3	204	205	197°	142	122	91	6	49	107	6	44 *	5 *
	4	213	418	197	202	95	53	12	85	268	10	53 *	6 *
	12	191	201	250	168	50	46	9	43	115	7	29 *	5 *
Cu	3	206	199	202	197	41	20	8	78	91	8	42	4
	5	202	202	202	196	26	16	7	59	119	6	32	3
	6	197	401	202	197	13	13	7	58	310	8	32	5
Cu	2	197	398	174	201	60	23	12	125	221	10	71	6
Ni–Co-1	1	201	201	91	173	30	69	8	66	72	8	50	6
	3	202	203	91	171	72	66	6	81	66	9	60	6
Ni–Co-3	2	185	499	59	152	40	65	7	62	378	10	52	8
Ni–Ag	2	203	197	126	225	20	40	9	55	49	15	34	9
	4	198	202	124	210	11	45	10	56	62	12	37	8

* These yields should be slightly lower, since fog was formed on withdrawing gas.

Flow experiments (*at ca.* 1 *atm.*) *over mixed metal catalysts.*

		Flow rates (l./hr. of dry gas at N.T.P.).			Vol. % in gaseous product (to nearest unit %).						Yield (%)	
Catalyst.	Temp. (± 5°).	C_2H_2.	H_2.	Gaseous product.	C_2H_2.	C_mH_n.	C_2H_4.	H_2.	C_2H_6.	% C_2H_2 converted.	C_2H_4.	C_2H_6.
Ni–Co-1	164°	1·55	1·51	1·04	3	13	63	8	12	98	43	8
Ni–Co-1	185 *	1·43	1·41	1·06	9	1	40	40	5	93	32	4
	176 *	2·52	2·57	2·20	16	1	38	37	5	86	38	5
Ni–Co-2	166	1·50	1·73	0·78	1	13	26	6	53	100	14	28
Ni–Co-3	233	2·21	2·02	2·27	31	6	33	24	5	68	49	7
Ni–Co-4	182	1·48	1·48	1·49	22	6	36	29	5	78	46	7
Ni–Ag	100	0·97	1·01	1·26	30	6	18	41	3	62	39	6
	134	1·46	1·41	0·80	3	12	54	23	7	98	30	4
Ni–Co–Ag	160	1·51	1·52	1·35	17	8	42	27	5	85	44	5
	241 †	1·47	1·73	1·29	3	10	45	34	6	97	41	5

* 2—3 L./hr. of acetone vapour passed. † 2·4% of nitric oxide in reactants.

The rate and yields of reaction over cobalt at *ca.* 200° resembled those over a nickel catalyst of similar composition at *ca.* 80°. The ratio of the amounts of acetylene removed by reaction (II) to those of hydrogen so removed was about 1·5 in the runs at *ca.* 200°, but at 250° it had risen to 3 and the yield of C_2 products had fallen. The catalyst had only very slow action on 300 mm. of acetylene alone at 200°; at 250° the pressure fell by 54 mm. in 165 mins., and at 303° by 117 mm. in 50 mins., some ethylene, hydrogen, and condensation products being formed. When these data are compared with those for the faster reactions in acetylene–hydrogen mixtures at the same temperatures, there is little doubt that hydrogen promotes reaction (II) over cobalt. Though catalyst deactivation prevented successful study of reaction orders, $-dp/dt$ appeared to increase with the hydrogen pressure and to depend much less on the acetylene pressure. Raising the hydrogen pressure increased the yield of C_2 products slightly, and the data seem in accord with kinetics similar to those with nickel (Part I).

Over little-used copper catalysts at *ca.* 170° and with excess of hydrogen, yields of C_2 products (chiefly ethylene) were 70—80%, and the amount of acetylene removed by reaction (II) was only about twice that of hydrogen so removed. With a 1 : 1 initial gas ratio, however, the yield of C_2 hydrocarbons fell to some 35—45%, and reaction (II) then removed 7—10 times as much acetylene as hydrogen, removal of acetylene in this way increasing with use of the catalyst. These phenomena are no doubt due largely to the autocatalytic production of cuprene, which occurred in acetylene alone (*e.g.*, 200—400 mm.) at the same temperatures. With excess of hydrogen over copper, the chief C_2 product was ethylene, even when the rate of reaction had fallen almost to zero; the catalysts were apparently rendered inactive for the hydrogenation of ethylene to ethane. On account of the complex nature of the reactions, and changes in activity and effect of the catalyst, no good evidence of reaction orders could be obtained.

Nickel–cobalt was at least as active as nickel, but the yields of C_2 products (especially ethylene) were mostly rather greater than with nickel under like conditions. Dilution with acetone vapour or nitrogen had little effect on the reaction over nickel–cobalt, which became less active from the commencement of its use. With Ni–Co-1 at 300°, acetylene alone gave products resembling those formed over nickel at *ca.* 250°, but containing more hydrogen. Nickel–silver showed the early increase in activity characteristic of nickel, which it resembled in action. Nickel–cobalt–silver gave yields similar to those over nickel–cobalt; they were little affected by nitrogen or small amounts of nitric oxide.

D. *General.*—The reactions over nickel, palladium, platinum, iron, and probably cobalt show a close general similarity, which suggests that each has essentially the same types of mechanism (cf. Part II). There remain certain unexplained facts; for example, unless modifications occur at the surface, three different types of lattice are active in the series of metals named, and it is difficult to formulate identical mechanisms on all three lattices, though the important initial steps may occur on them all. Unfortunately, strict comparison of activities (*e.g.*, per unit surface of metal) is not yet possible, but we note that, as here prepared, the face-centred cubic metals, nickel, palladium, and platinum, are considerably more active than iron and cobalt, which suggests the closest similarity of mechanism on the face-centred lattices. This can only be applied to the vertical group, nickel, palladium, and platinum, since copper, with a lattice similar to that of nickel, is much less active than that metal, and gives rise to the peculiarly specific polymerisation of acetylene to cuprene. The relationships between metallic structure and catalytic action in the acetylene–hydrogen reaction are therefore at present explicable only to a very limited extent; the electronic structure of the metal is no doubt important as well as crystal form, a fact which probably explains why the closest similarity of phenomena is found in the vertical group nickel, palladium, and platinum. A better comparison of catalytic actions will probably be possible when more is known of the structures of the hydrocarbons higher than the C_2 series formed over various metals; except in the case of nickel catalysts, present knowledge of these products is very slight.

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