# **100.** *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part I. Nickel Catalysts.*

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The rate of fall in total pressure in hydrogen–acetylene mixtures over nickel–pumice catalysts increases, under constant conditions, during the early stages of use of the catalysts. The yields of ethylene, ethane, and higher hydrocarbons, expressed in terms of the acetylene not recovered, are the same on fresh and old catalysts. The course of reaction in 1 : 1 and 2 : 1 hydrogen : acetylene mixtures on catalysts of constant activity is plotted. Ethylene is produced at about 5 times the rate of ethane formation until most of the acetylene is removed. The products other than $C_2$ hydrocarbons have an empirical gross composition of about $C_4H_7$, and are formed in yields of 55—60% of the acetylene not recovered at all stages of reaction, with both gas ratios. The initial reaction on catalysts of constant activity is of first order with respect to hydrogen and of approximately zero order with respect to acetylene. The hydrogenation to ethylene and the formation of reduced polymers of acetylene both have kinetics of approximately this type, but differing slightly such that an increase from 1 : 8 to 8 : 1 in initial hydrogen : acetylene ratio causes an increase from about 40% to 67% in the yield of $C_2$ hydrocarbons, expressed in terms of the acetylene not recovered. Ethylene added to the system acts principally as an inert diluent, and is apparently less strongly adsorbed than acetylene on nickel. The same catalysts have negligible action on acetylene alone under conditions of rapid reaction in acetylene–hydrogen mixtures. The results are discussed with special reference to previous work on the chemisorption of ethylene and acetylene.

It has long been known that the reduction of acetylene by hydrogen in the presence of metal catalysts is not normally a quantitative hydrogenation to ethylene and ethane, but is accompanied by the formation of reduced polymers of acetylene under almost all conditions. It is remarkable that the latter process usually takes place at temperatures well below those at which the metals have any appreciable effect on acetylene alone. Previous work has been principally of a qualitative nature, and a systematic study of the kinetics of the reaction on various catalysts appeared desirable, with special attention to the analysis of the products. Such a study has accordingly been made with a number of metals under varied conditions of temperature and partial pressures of reactants. In the present communication an account is given of the kinetics of the reaction in the presence of nickel.

Sabatier and Senderens (*Compt. rend.*, 1899, **128**, 1173) found that acetylene and hydrogen reacted over nickel to give ethylene, ethane, and higher hydrocarbons. Later workers have reported widely varying yields of these products (Ross, Culbertson, and Parsons, *Ind. Eng. Chem.*, 1921, **13**, 775; Yoshikawa, *Bull. Chem. Soc. Japan*, 1932, **7**, 201; Pichler, *Ges. Abh. Kennt. Kohle*, 1934, **11**, 395; Ackermann, *Brennstoff-Chem.*, 1937, **18**, 357; Fischer and Peters, *ibid.*, 1931, **12**, 286; Petrov and Antsus, *J. Appl. Chem. U.S.S.R.*, 1933, **6**, 1145; Dupont, *Bull. Soc. chim.*, 1936, **3**, 1030; Dupont and Lombard, *ibid.*, 1941, **8**, 851; see also U.S.P. 1,392,852, 1921; B.P. 336,999, 1929). The differences among the results of these investigators are to be traced partly to differences in the conditions of reaction and partly to difficulties in controlling the flow methods almost always employed. There has been no previous investigation of the kinetics of the reaction, and very little systematic study of influences of conditions on the products. The reduced polymers of acetylene formed are principally aliphatic, and cover a wide range of molecular weights from the $C_4$ series upwards, but the literature provides little detailed knowledge of their structure (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, **4**, 445; *Compt. rend.*, 1902, **134**, 1185; Charitschkow, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 880; Oda, *J. Chem. Ind. Japan*, 1921, **24**, 1161; Binnie, *Chem. and Ind.*, 1931, **50**, 297; Petrov and Antsus, *loc. cit.*; *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4**, 300; *Refiner Natural Gasoline Manfr.*, 1934, **13**, 79; Russian Patent 49,724, 1936; *J. Physical Chem. U.S.S.R.*, 1940, **14**, 1308; *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1940, 274).

The present research aimed at more detailed and systematic investigation, especially of the kinetics of the reaction, for which purpose use has been made of the greater control afforded by a static reaction system. The complexity of the reaction has demanded frequent full analysis of the gaseous products. An investigation of some of the reduced polymers of acetylene formed has also been carried out, and will be reported later.

## EXPERIMENTAL.

*Acetylene.*—Cylinder gas was passed in succession through the following solutions: chromic acid, 10% mercuric chloride in dilute hydrochloric acid, sodium hydrosulphite, sodium bisulphite (two wash bottles), 20% sodium hydroxide. It was dried by passage through a U-tube containing anhydrous calcium chloride. Periodic analyses by the methods described below showed a minimum acetylene content of 99·5%, with about 0·2% of other unsaturated hydrocarbons. Small amounts of hydrogen and nitrogen were probably present. No attempt was made to remove the very last traces of oxygen; if it was present, its amount was less than 0·1%.

*Hydrogen.*—Electrolytic cylinder gas was used. The minimum hydrogen content was 99·5%, with about 0·1% each of carbon monoxide and dioxide. No oxygen was detected by pyrogallol absorption.

*Ethylene.*—Cylinder gas, about 99% pure and containing traces of air, was used without further treatment.

*Catalysts.*—Pumice granules, 2—5 mm. in diameter, were used as carrier substance. They were cleaned by boiling with concentrated hydrochloric acid, and had no measurable action on acetylene alone or mixed with hydrogen, at 358°. The catalysts used in the present experiments, designated as Ni-1 and Ni-2, had nickel : pumice ratios of 1 : 10 and 1 : 5 by weight respectively. They were prepared by evaporation of solutions of nickel nitrate containing pumice, ignition in an open dish till decomposition was nearly complete, followed by reduction in hydrogen containing ethanol vapour at 400—425° for 2 hours.

*Apparatus.*—Experiments were performed in a static system at constant volume. The Pyrex reaction bulb (300 c.c.) with capillary leads (capacity about 2 c.c.) formed part of an all-glass system, consisting in addition of gas-storage vessels, a McLeod gauge, and a mercury-vapour pump and oil pump in series. The bulb was surrounded by steel turnings and metal screens inside a heavily lagged furnace. Temperature (20—170°) was controlled by a sealed mercury-in-glass thermometer regulator. Even in experiments lasting several hours temperatures did not vary by more than 0·5° from the stated value. Gases were admitted in succession to the bulb, pressure being measured on a mercury capillary manometer. In most experiments hydrogen was admitted first. Gas was withdrawn from the bulb at selected times into a mercury-filled gas burette. Error due to a dead space in the capillary leads was reduced by withdrawing and rejecting about 2 c.c. of gas some 30 secs. before the collection.

The weight of catalyst placed in the bulb was 2 g.; it was normally heated to 300—350° in 400—500 mm. of hydrogen for several hours before experiments were performed over it, and was not allowed to come into contact with air during the period of its use.

*Analysis of Gaseous Products.*—A Bone and Wheeler apparatus was used. An alkaline solution of mercuric cyanide (Treadwell and Tauber, *Helv. Chim. Acta*, 1919, **2**, 601) proved a satisfactory absorbent for acetylene. Two minutes' shaking with 10 c.c. of this solution sufficed to absorb the acetylene in samples (up to 40 c.c.) containing over 99% of this gas. Ethylene absorption in this reagent was negligible, despite high ethylene contents in many cases. The separate estimation of ethylene and higher unsaturated hydrocarbons was more difficult. Tests showed that all the higher unsaturated hydrocarbons could be absorbed in 10 c.c. of 85% sulphuric acid in 5—10 minutes, but it is probable that traces of ethylene were also taken up, especially when much of this gas was present. In practice, a 7-minute exposure to 85% acid was used (after the acetylene absorption), followed by absorption of the ethylene. The error in ethylene and higher unsaturated contents was probably not more than 1% of the total gas. Other gases were estimated by standard methods.

*Results.*—The analytical figures were usually converted into partial pressures (expressed to the nearest mm.) for comparison with the initial pressures. There were no indications that the adsorption of gases by the catalysts caused appreciable errors in the pressure data. An error of ±2 mm. seems a reasonable one in most cases, though the uncertainty may be greater in the case of fast reactions. The 1—2% of the final pressures not accounted for in the listed products must be due in part to traces of nitrogen picked up during the gas analysis. No correction has been applied for the possible condensation of less volatile products during the withdrawal of gas for analysis. Condensation was not apparent in the present experiments, and there is no indication that any important correction for it is necessary.

The value of $n$ in $C_nH_{2n+2}$ for the saturated hydrocarbons in the products, after removal of hydrogen, was always very close to 2·0. Since methane production is not likely to be appreciable, it is improbable that compounds higher than ethane were present in large amount. The stated ethane contents are the saturated hydrocarbon contents; the real ethane figures will be slightly less if traces of higher hydrocarbons or methane were present.

Admission of hydrogen first to the evacuated bulb was followed by a fall in pressure of 5—15 mm. in about 10 minutes, except when the catalyst had not previously been used. This was probably due to hydrogenation of non-volatile unsaturated hydrocarbons on the catalyst, and had normally proceeded almost to completion before the pressure was read and taken as the initial pressure of hydrogen.

## DISCUSSION.

(i) *Shape of Pressure–Time Curves.*—A nearly linear pressure–time curve was usually obtained for the first stages of reaction in hydrogen–acetylene mixtures, though in some examples the rate of fall in total pressure increased slightly in the early phase of reaction. This early acceleration was a little more marked at higher temperatures, but was not more pronounced in mixtures rich in hydrogen. In all cases the fall in pressure gradually became slower towards the end of the reaction, with no increase in rate at a late stage such as occurs in hydrogen–acetylene mixtures over platinum (Farkas and Farkas, *J. Amer. Chem. Soc.*, 1939, **61**, 3396) and palladium (Cremer, Knorr, and Plieninger, *Z. Elektrochem.*, 1941, **47**, 737).

(ii) *Ageing of Catalysts.*—The activity of the catalysts, as measured by the rate of fall in total pressure in similar hydrogen–acetylene mixtures at the same temperature, always increased markedly in the early stages of use of the catalysts. For example, with some 300 mm. each of acetylene and hydrogen at 95—96° on a new sample of Ni-2, the initial rates of fall in total pressure were about 5, 14, and 30 mm./min. in that sequence for the first three experiments. The rates at equal falls in pressure were in roughly the same ratio throughout the reactions. The increase in activity occurred even after very long pre-reduction of the nickel (40 hours at 340—370° in 470 mm. of hydrogen). After several experiments in which the reaction ran most of its course, the increase in activity of the catalysts ceased, and their activity towards hydrogen–acetylene mixtures then remained fairly steady for considerable periods. The effects of variations in conditions on the reaction were studied, unless otherwise stated, on catalysts in this state of steady activity.

Since the slight acceleration in the early stages of some experiments persisted after the activity of the catalyst had ceased to increase, the acceleration appears to have a cause other than that leading to the general increase in activity, which is presumably due to some modification of the catalyst surface.

(iii) *Yields of Various Products.*—Table I summarises data for some experiments on new catalysts and on the same catalysts in a used state. Each group of experiments refers to a separate specimen of catalyst, the runs in each group being numbered in the sequence of their performance. Unsaturated hydrocarbons higher than the $C_2$ series accounted for 6—14 mm. of the final pressures. With 209—400 mm. of hydrogen and 199—317 mm. of acetylene at 83—146° the yields, expressed as percentages of the acetylene not recovered, were :

ethylene, 30—39% ; ethane, 4—9% ; other products, 52—66%. These yields refer to stages of reaction up to the point when the acetylene pressure had fallen to 5 mm. The products other than ethylene and ethane accounted for the removal of rather more acetylene than hydrogen, having an empirical overall composition in the region of $C_4H_7$. Little change in the yields of ethylene, ethane, and other products, or in the composition of the last, accompanied the increase in activity of the catalysts during the first few experiments over them, and this increase is therefore not specifically in favour of a particular type of reaction in the system. In this table $\Delta p$ refers to the fall in pressure (in mm.), and $t$ to the duration of the experiment (in mins.).

TABLE I.

| Catalyst. | No. of expt. in series over each specimen. | Initial pressure (mm.). |  | Temp. | $\Delta p$. | $t$. | Press., mm., in gaseous product. |  |  |  | Yield (%). |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | $H_2$. | $C_2H_2$. |  |  |  | $C_2H_2$. | $C_2H_4$. | $H_2$. | $C_2H_6$. | $C_2H_4$. | $C_2H_6$. |
| Ni-1 | 1 | 221 | 274 | 101° | 295 | 51 | 56 | 69 | 47 | 12 | 32 | 6 |
|  | 2 | 209 | 208 | 146 | 296 | 11 | 5 | 66 | 17 | 18 | 33 | 9 |
|  | 4 | 224 | 273 | 101 | 297 | 20 | 59 | 76 | 36 | 14 | 35 | 7 |
|  | 5 | 217 | 275 | 104 | 292 | 17 | 60 | 75 | 36 | 12 | 35 | 6 |
|  | 6 | 221 | 272 | 101 | 293 | 19 | 61 | 72 | 37 | 13 | 34 | 6 |
| Ni-2 | 1 | 301 | 306 | 95 | 412 | 75 | 5 | 105 | 52 | 17 | 35 | 6 |
|  | 2 | 300 | 317 | 96 | 348 | 23 | 64 | 96 | 82 | 13 | 38 | 5 |
|  | 5 | 295 | 307 | 96 | 344 | 11 | 66 | 73 | 87 | 10 | 30 | 4 |
|  | 11 | 307 | 304 | 79 | 342 | 40 | 61 | 86 | 86 | 13 | 36 | 5 |
|  | 19 | 303 | 298 | 88 | 338 | 30 | 59 | 82 | 88 | 15 | 34 | 6 |
| Ni-1 | 1 | 400 | 199 | 83 | 200 | 21 | 56 | 56 | 252 | 13 | 39 | 9 |
|  | 17 | 400 | 200 | 83 | 200 | 9 | 62 | 51 | 257 | 11 | 37 | 8 |

TABLE II.

| Catalyst. | No. of expt. | Temp. | $C_2H_2$ (mm.). | $\Delta p$. | $t$. | Product, volume %. |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | $C_2H_2$. | $C_mH_n$. | $C_2H_4$. | $H_2$. | $C_2H_6$. |
| Ni-1 | 1 | 207° | 478 | 71 | 27 | 84·0 | 1·4 | 12·4 | 0·3 | — |
|  | 2 | 244 | 484 | 107 | 21 | 90·1 | 0·7 | 5·4 | 1·3 | — |
|  | 3 | 280 | 483 | 124 | 26 | 87·0 | 1·0 | 4·2 | 4·7 | 2 |
|  | 4 | 283 | 492 | 131 | 26 | 86·3 | 0·8 | 4·5 | 5·1 | 2 |
|  | 5 | 255 | 486 | 85 | 31 | 90·4 | 0·8 | 3·8 | 2·1 | 1 |

(iv) *Comparison of the Acetylene–Hydrogen Reaction with the Reaction in Acetylene alone over the Same Catalysts.*—In the experiments represented in Table I large amounts of acetylene and hydrogen were converted into products less volatile than $C_2$ hydrocarbons. Under the same conditions of temperature and acetylene pressure over the same specimens of catalyst acetylene alone underwent only very slow change. For instance, with 217 mm. of acetylene at 160° over a specimen of Ni-1 the fall in pressure was 6 mm. in 20 minutes, whereas in the preceding experiment (208 mm. of acetylene, 209 mm. of hydrogen) 119 mm. of acetylene were removed as products less volatile than $C_2$ hydrocarbons in 11 minutes at 146°. Subsequent experiments showed that no deactivation of the catalyst had occurred when the experiment with acetylene alone was performed. Acetylene alone did not react at readily measurable rates over these catalysts until the temperature exceeded about 200°. Table II gives some data obtained under these conditions; the initial pressure of acetylene is given, and $C_mH_n$ represents higher unsaturated hydrocarbons. The activity of the catalyst appeared to be varying somewhat, but the products are consistent with the known catalysis of the decomposition of acetylene into carbon and hydrogen by nickel, followed by reaction of hydrogen with acetylene (see, *e.g.*, Egloff, "Reactions of Pure Hydrocarbons," 1937, p. 429). Some of the acetylene must have been removed as products less volatile than $C_2$ hydrocarbons, but it cannot be said whether this removal is partly by direct polymerisation or only accompanies hydrogenation after decomposition of acetylene has produced hydrogen in the system.

(v) *Course of Reaction in Hydrogen–Acetylene Mixtures at Constant Volume over Catalysts of Steady Activity.*—This was determined by performing runs of different durations over the same specimen of catalyst, under constant conditions of temperature and partial pressures of gas. The pressure–time curves were reproducible within fairly narrow limits, but greater consistency of the results was obtained by plotting the data obtained from the gas analysis at time co-ordinates corresponding to the same fall in total pressure in the longest experiment. These times differed from the actual duration of the experiments to an extent determined by the deviations of the total pressure curves from that of the longest experiment. Figs. 1 and 2 show the results for 1 : 1 and 2 : 1 hydrogen : acetylene mixtures at 79° and 72° respectively. The sequence of performance was not related to the duration of the runs, as can be seen from Tables III and IV, which also show the yields of ethylene and

TABLE III.

Yields at different stages in reaction in 1 : 1 $H_2 : C_2H_2$ mixture (Catalyst Ni-2, runs 7—18 on the same specimen; see Fig. 1).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt. no. | 17 | 9 | 8 | 10 | 11 | 12 | 7 | 15 | 14 | 16 | 13 | 18 |
| Duration (mins.) | 5 | 10 | 18 | 30 | 40 | 50 | 60 | 74 | 90 | 104 | 120 | 180 |
| Yield of $C_2H_4$, % | 36 | 37 | 34 | 36 | 36 | 36 | 33 | 35 | 35 | 35 | 35 | 33 |
| Yield of $C_2H_6$, % | — | — | 5 | 6 | 5 | 7 | 6 | 7 | 8 | 8 | 7 | 11 |

TABLE IV.

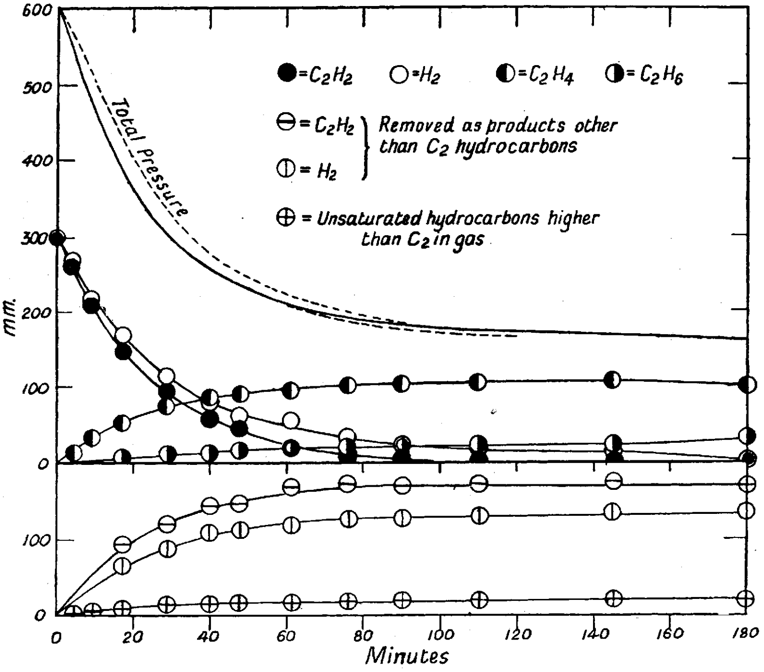
Yields at different stages in reaction in 2 : 1 $H_2$ : $C_2H_2$ mixture (Catalyst Ni-2; runs 8, 9, 11, and 12 on same specimen; see Fig. 2).

| Experiment no. | 11 | 8 | 12 | 9 |
|---|---|---|---|---|
| Duration (mins.) | 10 | 25 | 40 | 55 |
| Yield of $C_2H_4$, % | 36 | 37 | 34 | 25 |
| Yield of $C_2H_6$, % | 7 | 7 | 11 | 19 |

ethane at each stage, expressed as percentages of the acetylene not recovered. The narrow range within which the total pressure curves were reproducible, and the smooth curves for partial pressures, etc., leave little doubt that reactions represented by the longest total pressure curves follow the courses shown.

FIG. 1.

*Course of reaction in* 1 : 1 $H_2$ : $C_2H_2$ *mixture at* 79° *over catalyst* Ni-2.



*Initial* $H_2$ *pressure* = 299—307 *mm. Initial* $C_2H_2$ *pressure* = 297—306 *mm.*

*The continuous total-pressure curve is that for the experiment of* 180 *minutes' duration. The dotted lines show the extremes of deviation of the other total-pressure curves from the continuous line.*

In the early stages acetylene was removed a little more rapidly than hydrogen, and ethylene formation was about five times as fast as ethane production. The total yield of ethylene and ethane was 40—45% of the unrecovered acetylene at all stages of reaction and for both gas ratios. The products other than ethylene and ethane had an empirical overall composition of about $C_4H_7$ at all stages. The pressure of unsaturated hydrocarbons higher than the $C_2$ series rose in proportion to the amounts of acetylene and hydrogen removed as products other than $C_2$ hydrocarbons. Ethane production increased, notably in the case of the 2 : 1 gas ratio, when almost all the acetylene had been removed and some hydrogen remained. The ethylene pressure passed through a maximum on account of this effect. The rate of ethylene hydrogenation in the 2 : 1 mixture when the acetylene had been removed was slow compared with the original acetylene–hydrogen reaction.

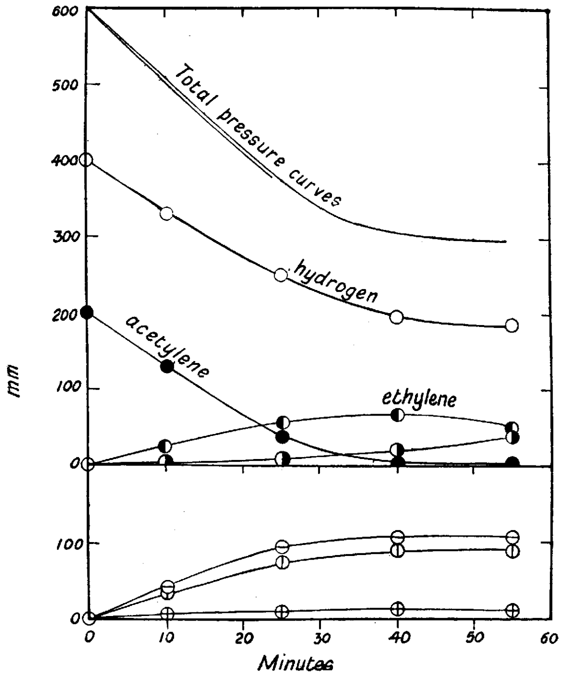
(vi) *Kinetics of Reaction in Hydrogen–Acetylene Mixtures.*—Fig. 3 shows the effect of variations in partial pressures of acetylene and hydrogen on the initial rate of fall in total pressure over a catalyst of constant activity. The pressure–time curves were almost linear initially, and $(dp/dt)_0$ was taken as the mean rate for the first 15—40 mm. of fall. A fast initial fall of some 2 mm. at high acetylene pressures (admitted after hydrogen) was presumably due to adsorption of acetylene, and the initial rates recorded were the rates in the period of linear fall in pressure which followed. The experiments were performed in a sequence in no way related to the changes in partial pressures, and the rates were reproducible within reasonable limits.

The initial rate was directly proportional to the hydrogen pressure. It appears to be independent, within the limits of error, of the acetylene pressure, though possibly it increased slightly as the acetylene pressure was lowered.

By analysis after falls in pressure of 15—50 mm. figures were obtained for the mean rates of formation of ethylene and of removal of hydrogen and acetylene in the early reaction. Ethane production was very slight. The linear course of fall in total pressure with time suggests that these mean rates may be taken as the initial rates of the processes concerned. The rate of ethylene production was always about a quarter of the initial rate of fall in total pressure. The rates of removal of acetylene and hydrogen were equal within the error of measurement, and were about two-thirds of the initial rate of fall in total pressure in all cases. The ratio of ethylene formation to acetylene (and hydrogen) removal was thus approximately 3 : 8, which is about the ratio made probable by the data in Figs. 1 and 2. No change in this ratio within the limits of conditions represented by Fig. 3 could be demonstrated. The relationships between the total and the partial initial rates in a given experiment were the same when the catalyst was still increasing in activity, which is in harmony with the fact that the yields are not dependent on the activity of the nickel.

FIG. 2.

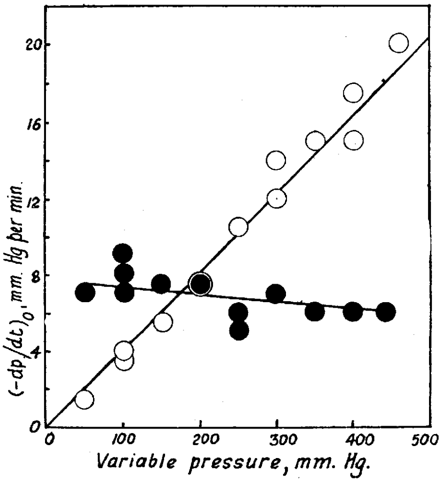
*Course of reaction in* 2 : 1 $H_2$ : $C_2H_2$ *mixture at* 72° *over catalyst* Ni-2.



*Initial* $H_2$ *pressure* = 399—401 *mm. Initial* $C_2H_2$ *pressure* = 199—203 *mm.*
*Significance of various types of point as in Fig.* 1.
*The two total-pressure curves shown are the extremes within which all the curves fall.*

FIG. 3.

*Effect of partial pressures on initial rate.*



*Expts.* 19—43 *on one specimen of* Ni-2.
*Temperature* = 79°.
*Open circles* = 200 ± 5 *mm.* $C_2H_2$; $H_2$ *pressure varied.*
*Full circles* = 200 ± 5 *mm.* $H_2$; $C_2H_2$ *pressure varied.*

If the initial rate of ethane formation is assumed to be zero, the initial reaction can be divided into (I) $C_2H_2 + H_2 \longrightarrow C_2H_4$ and (II) $C_2H_2 + H_2 \longrightarrow$ products other than $C_2$ hydrocarbons. The results indicate that both these reactions have the same kinetics on catalysts of constant activity, being of first order with respect to hydrogen and approximately zero order with respect to acetylene.

The initial rates became less reproducible at acetylene pressures below about 50 mm., whichever gas was admitted first, but there was no sign of any great increase in rate on lowering the acetylene pressure as far as 9 mm. in the presence of 400 mm. of hydrogen at 63—83°.

Additional evidence for the kinetics described above was found in the times necessary for a pressure-fall equal to the initial hydrogen pressure, in the presence of excess of acetylene. These may be regarded as times of approximately equal fractional change, if any influence of gas pressures on the nature of the reaction is ignored. Eight experiments at 83° with 400 ± 5 mm. of acetylene and hydrogen pressures varying from 26 to 288 mm. required 32—54 minutes for pressure falls equal to the initial hydrogen pressures. The times appeared rather longer at lower hydrogen pressures, but were essentially independent of the amount of hydrogen. This is in harmony with the suggested kinetics.

The kinetic equation

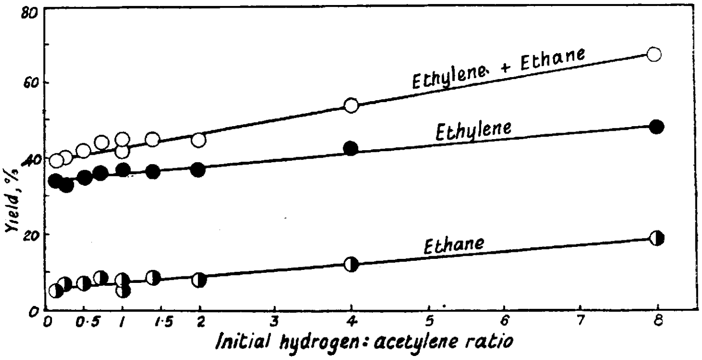
$$\text{rate of fall in total pressure} = k\,[\text{hydrogen pressure}]$$

is in rough agreement with the form of the total pressure–time curves for the complete reaction up to the time when most of the acetylene is removed (Figs. 1 and 2), though it does not account for the increase in rate in the early stages of some experiments (*e.g.*, Fig. 1) or the long period of constant rate of fall in pressure such as occurred in the experiments represented in Fig. 2. Deposition of non-volatile products on the catalyst may have some influence on the form of the pressure curves, especially in the later stages.

(vii) *The Effect of Gas Pressures on the Products from Hydrogen–Acetylene Mixtures.*—Preliminary experiments showed that the total yield of $C_2$ hydrocarbons was increased to about 60% of the acetylene not recovered with initial hydrogen : acetylene ratios of about 10. Fig. 4 shows the results of a systematic study on a catalyst of constant activity at 83°, the yields of ethylene and ethane (as percentages of the acetylene not recovered) being plotted against the initial hydrogen : acetylene ratio. For ratios below unity, the acetylene pressure was 399—401 mm. and for those above unity the hydrogen pressure was 398—400 mm. The results for 1 : 1 mixtures refer to 100 mm. and 200 mm. of each gas. Analyses were performed after a pressure fall equal to the smaller of the initial pressures. The errors were larger at the extreme ratios, but all the results agree fairly well with a linear increase in yields of both ethylene and ethane with initial hydrogen : acetylene ratio. An increase in yield of $C_2$ hydrocarbons from about 40% to 67% was caused by a 64-fold (1 : 8 to 8 : 1) increase in initial ratio. The final ratios varied from 0·05 : 1 to 16·5 : 1, a 330-fold increase. The effect of gas ratio on the $C_2$ hydrocarbon yield is therefore very slight. The rates of reaction varied by a factor of about 8, being mainly determined by the hydrogen pressure. The ratio of the ethane yield to the ethylene yield at the time of analysis rose with hydrogen : acetylene ratio, from about 1 : 7 at $H_2 : C_2H_2$ = 1 : 8 to 1 : 2·5 at $H_2 : C_2H_2$ = 8 : 1, though by no means all the acetylene had been removed even at high initial $H_2 : C_2H_2$ ratios (lowest acetylene pressure at analysis = 21 mm.).

FIG. 4.

*Effect of initial* $H_2 : C_2H_2$ *ratio on yields.*



*Experiments* 6, 8, 9, 11, 14—18, 21 *on one specimen of Ni*-1.
*Temperature* 83°.

The increase in yield of $C_2$ hydrocarbons on lowering the acetylene pressure at constant hydrogen pressure seems beyond doubt. The increase on raising the hydrogen pressure at constant acetylene pressure is perhaps scarcely outside experimental error.

These results confirm the view that the initial reactions (I) and (II) (see p. 377) have essentially the same kinetics. Reaction (I) is apparently of slightly lower order with respect to acetylene than (II), and possibly of slightly higher order with respect to hydrogen.

The ratio of the amount of hydrogen removed as products other than $C_2$ hydrocarbons to that of acetylene so removed appeared to increase with the initial hydrogen : acetylene ratio, though the error in these figures became large at ratios considerably removed from unity. Less unsaturation in the higher hydrocarbons produced, as the $H_2 : C_2H_2$ ratio is increased, is not unexpected.

The influence of gas ratio on the yields is that anticipated from the few indications of such an effect in previous work (Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173; Ackermann, *loc. cit.*). The quantitative production of ethane from 2 : 1 hydrogen : acetylene mixtures over Raney nickel reported by Dupont (*loc. cit.*) appears to have been deduced from the fall in pressure, and no analysis of the gases is quoted. The 100% yield of ethane from 5 : 1 hydrogen : acetylene mixtures at 18 atm., reported by Petrov and Antsus (*J. Appl. Chem. U.S.S.R.*, 1933, **6**, 1145), is possibly a result of the high pressure, though on the whole unexpected. The claim (D.R.-P. 262,541) that increased yields of $C_2$ hydrocarbons can be obtained by adding one gas gradually to the other is only justified, in the case of nickel catalysts, for the addition of acetylene to hydrogen.

(viii) *Experiments with Added Ethylene.*—Over a catalyst of steady activity, the addition of 53—380 mm. of ethylene to hydrogen–acetylene mixtures caused no detectable differences in rate of fall in total pressure from the rates obtained with the same pressures of hydrogen and acetylene alone. This result is not unexpected, since during the formation of ethylene in the acetylene–hydrogen system the rate of fall in total pressure is apparently still determined mainly by the hydrogen pressure alone.

Catalysts which had been used for the hydrogen–acetylene reaction were much less active than new catalysts towards the hydrogenation of ethylene, though the induction period due to traces of oxygen (Rideal, J., 1922, **121**, 309) was not observed when catalysts previously used in the acetylene–hydrogen reaction were used to hydrogenate ethylene. A series of experiments showed that, on the used catalysts, ethylene–hydrogen and acetylene–hydrogen mixtures of similar composition gave pressure–time curves of roughly equal slope at the same temperature, though the reproducibility was not good.

Table V shows the results of two experiments under the same conditions, except for the presence of added ethylene in one case. The significance of the headings is the same as for Tables I and II. The pressure–time curves were almost identical in shape. After deduction of the extra ethylene from the product of the second run, the figures become nearly the same for the two experiments. The acetylene–hydrogen reaction took place independently of the presence of a large ethylene pressure, although, in the absence of acetylene, the rate of ethylene hydrogenation would have been similar to that of the acetylene–hydrogen reaction.

TABLE V.

Effect of added ethylene on the products at 83° on a catalyst (Ni-1) of steady activity.

| No. of expt. | Initial pressures (mm.). | | | | | Products (mm.). | | | | | Yield, %. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$. | $C_2H_2$. | $C_2H_4$. | $\Delta p$. | $t$. | $C_2H_2$. | $C_mH_n$. | $C_2H_4$. | $H_2$. | $C_2H_6$. | $C_2H_4$. | $C_2H_6$. |
| 21 | 198 | 200 | — | 200 | 44 | 62 | 8 | 50 | 67 | 7 | 36 | 5 |
| 22 | 200 | 199 | 201 | 200 | 45 | 64 | 9 | 244 | 67 | 8 | 32 | 6 |

The results are evidence that acetylene is more strongly adsorbed on the catalyst than ethylene under similar conditions of pressure and temperature. Such an adsorption relationship is in harmony with the small production of ethane in the early stages of the hydrogen–acetylene reaction over nickel. Phenomena of this type have already been reported for platinum (Farkas and Farkas, *loc. cit.*) and palladium (Fischer and Knorr, *Z. Elektrochem.*, 1937, **43**, 608; Cremer, Knorr, and Plieninger, *loc. cit.*). Ethane formation over nickel, however, does occur to some extent even in the presence of large acetylene pressures.

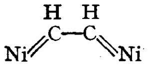
(ix) *General Discussion.*—In the presence of hydrogen, hydrocarbons higher than the $C_2$ series form from acetylene over nickel at rates of the order of 100 times the rate of reaction in acetylene alone under the same conditions. The difference in speeds is so large that local overheating of the catalyst by hydrogenation reactions in the presence of hydrogen can scarcely explain it. Moreover, the effect of nickel on acetylene alone is at least to a large extent a decomposition to carbon and hydrogen. There is no evidence that such decomposition is extensive in the hydrogen–acetylene reaction under the conditions of the present experiments; but the possibility of local overheating of the catalyst playing some part in the reaction should not be entirely overlooked—*e.g.*, it is a possible cause of the early acceleration of reaction in some experiments.

Another possible cause of this acceleration may be traces of oxygen in the gas. Addition of about 1—2 mm. of oxygen had little effect on the rate, though higher pressures of oxygen caused increasing retardation of reaction; but no induction period or accentuated acceleration effect was observed. The results of these experiments will be reported in detail later.

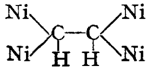
The kinetic results show that strongly adsorbed acetylene and weakly adsorbed hydrogen (or hydrogen derived directly from the gas phase) are involved in the steps which determine the rates of both the reactions (I) and (II) (see p. 377). There is little evidence of a rise in rate due to an increase in metal surface available for hydrogen as the acetylene pressure is lowered in the range studied. A negative order with respect to acetylene of this type has been reported for platinum (Farkas and Farkas, *loc. cit.*) and palladium (Cremer, Knorr, and Plieninger, *loc. cit.*). The results with nickel suggest a very strong adsorption of acetylene down to the lowest pressures investigated. Detailed discussion of the mechanism of the nickel-catalysed reaction is postponed till further experimental evidence is available.

The strong adsorption of ethylene on nickel (*e.g.*, Twigg and Rideal, *Proc. Roy. Soc.*, 1939, **171**, *A*, 55, etc.) has frequently been interpreted as a chemisorption (*e.g.*, Rideal, *Proc. Camb. Phil. Soc.*, 1939, **35**, 130; *Chem. and Ind.*, **1943**, 335, etc.), and the adsorption of acetylene on nickel is thus equally probably a chemisorption phenomenon. Distances in the metal lattice have already received discussion from previous workers with regard to the theory of associative adsorption of ethylene and acetylene (Twigg and Rideal, *Trans. Faraday Soc.*, 1940, **36**, 533; Herington, *ibid.*, 1941, **37**, 361), and it is therefore reasonable to examine what light such spatial considerations may throw on the relative strengths of adsorption of acetylene and ethylene on nickel, palladium, and platinum. Single carbon–metal bonds to these catalysts should have the following lengths, obtained by summing the single-bond radii (Pauling, " The Nature of the Chemical Bond," 1940): C–Ni, 2·0 A.; C–Pd, C–Pt each 2·1 A. The uncertainty about the valency of the metal atom could only introduce a second-order variation from these lengths. The length 1·82 A. previously used for C–Ni and C–Co in this type of calculation is the length of bonds which probably possess some double-bond character and resonance shortening (Pauling, *op. cit.*) in carbonyl-type compounds. Using the distances first mentioned, the normal lengths for C–C and C≡C, and the concept of adsorption as depicted by Twigg and Rideal and by Herington, we find the most favourable lattice distances to be, in the case of ethylene, 2·87 A. for nickel and 2·94 A. for palladium and platinum, and in the case of acetylene, 3·33 A. and 3·43 A. respectively. The available distances in the face-centred cubic lattices are 2·48 A. and 3·50 A. for nickel, *ca.* 2·75 A. and 3·88 A. for palladium, *ca.* 2·75—2·85 A. and 3·88—4·04 A. for palladium hydride, and *ca.* 2·75 A. and 3·91 A. for platinum. The adsorption of ethylene on the shorter distances, which Twigg and Rideal describe in detail for nickel, should therefore also be favoured as the mode of ethylene adsorption on the other metals. When so adsorbed, the molecule would be subject to strain, greatest in the case of nickel, which could not be relieved by a twisting of the molecule, as suggested by Twigg and Rideal, since it is readily shown that the metal–C–C angle has a maximum value when the metal–C–C–metal quadrilateral is planar. Acetylene adsorption, on this theory, would presumably favour the longer distances, as maintained by Herington with special reference to nickel and to cobalt in the face-centred cubic form. Strain would be in the opposite sense to that in the case of ethylene adsorption, and would be least with nickel catalysts. From considerations of strain alone, it seems possible that acetylene adsorption may be favoured on nickel, but in the larger lattices ethylene adsorption is likely to be more favoured. The greater abundance of shorter distances in the lattice should, if other factors were equal, favour ethylene adsorption (Herington, *loc. cit.*).

Previous workers have, of course, recognised that factors other than purely spatial ones must play a large part in determining the phenomena, and it would seem that in general it must be such other factors which give rise to the stronger adsorption of acetylene than of ethylene on the metals concerned. In particular, the energy necessary to desorb the hydrocarbon may be more important than the number of sites available for adsorption, since acetylene more firmly held than ethylene might displace the latter from the surface without necessarily covering all the metal atoms. On the associative theory such displacement appears possible on the (110) and (100) faces of the nickel–palladium–platinum group, but could hardly occur on the (111) faces, which have none of the longer lattice distances. In seeking to account for a firmer adsorption of acetylene, it may be pointed out that the heats of formation of carbon–carbon bonds are such that, in general, the addition of a substance to an acetylenic compound to give an ethylenic derivative should be accompanied by evolution of about 18 kg.-cals. more than accompanies the addition of the same substance to the ethylenic compound to give a saturated derivative. If the associative theory is correct, this energy difference may well be an important factor in accounting for the stronger adsorption of acetylenic compounds than of the corresponding ethylene derivatives, which appears rather a general phenomenon on various metals (see, *e.g.*, Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77). The difference in heats of adsorption may be increased if the unsaturated linkage concerned forms part of a conjugated resonance system, or if the greater unsaturation in the acetylene derivatives affects the adsorption in other ways, such as by permitting states of the type (I) or (II). A four-point contact of the latter type, though not probable, might be sterically possible on a (110) face.



(I.)



(II.)

It should be pointed out that the complete covering of the (110) face by associatively adsorbed acetylene (Herington, *loc. cit.*) may involve some interference between non-bonded carbon atoms, if the van der Waals radius for these is taken as about 1·5 A., which is the figure given by the approximate rule of adding 0·8 A. to the single-bond radius of the element (Pauling, *op. cit.*). In a film of adsorbed acetylene, however, there would be less interference between hydrogen atoms than in the case of ethylene, where, for total covering of the most readily covered face (110) it is necessary to take a rather low value for the van der Waals radius of hydrogen, even with the larger lattices; for instance, Twigg and Rideal (*Trans. Faraday Soc.*, 1940, **36**, 533) take 0·78 A., whereas Pauling (*op. cit.*) favours 1·2 A. as the best average figure.

It is possible that modification of the surface of the catalyst by reaction may affect adsorption relationships of the types considered.

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