36. *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part II. Further Experiments with Nickel Catalysts.*

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The effect of temperature on the reaction between acetylene and hydrogen over a nickel–pumice catalyst has been systematically studied in the range 0—126°. Lowering the temperature increases the production of ethylene and (more markedly) ethane; the yield of C_2 hydrocarbons, in terms of the acetylene not recovered, is 31% at 126° and 65% at 0—3° for 1 : 1 gas mixtures. The ratio of the acetylene removed as other products to the hydrogen so removed increases as the temperature is raised.

Temperature (0—91°) has little influence on the orders of the reactions occurring.

With some not improbable assumptions, activation energies, uncorrected for desorption of gas, are deduced as follows :

(I) $C_2H_2 + H_2 + Ni \longrightarrow C_2H_4 + Ni$: 10·9 kg.-cals. at 0—126°

(II) $C_2H_2 + xH_2 + Ni \longrightarrow$ products other than C_2 hydrocarbons + Ni : 14·5 kg.-cals. at 0°, falling to 12·7 kg.-cals. at 126°.

The products higher than the C_2 series from 1 : 1 gas mixtures at 200—250° over nickel–pumice cover a wide range of molecular weights. The chief constituents of the fully hydrogenated products boiling below 70° are *n*-hexane, 3-methylpentane, and probably *n*-butane, *i.e.*, those substances the carbon skeletons of which can be formed by linking together C–C units. In addition, *n*-pentane, 2-methylbutane, 2-methylpentane, 3-methylhexane, and probably *n*-heptane are present, as well as octanes and higher hydrocarbons, in the hydrogenated products.

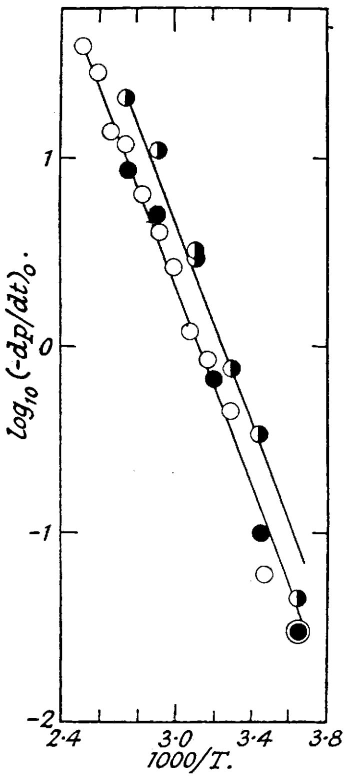
The mechanisms of the reactions are discussed, and it is suggested that reaction (II) is a surface chain reaction, initiated through a half-hydrogenated state in associatively chemisorbed acetylene.

THE effect of temperature on the nickel-catalysed reaction between acetylene and hydrogen has not hitherto been systematically investigated, though there are qualitative indications that an increase in temperature decreases the yields of C_2 hydrocarbons (*e.g.*, Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173). A systematic study of the influence of temperature on the rate and products of the reaction is now reported.

The products other than C_2 hydrocarbons over nickel are known to consist mainly of aliphatic hydrocarbons of various degrees of saturation, covering a wide range of molecular weights (see references in Part I, J., 1944, 373). With nickel–pumice, production of C_6 hydrocarbons has been reported to be slightly favoured (Petrov and Antsus, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4**, 300; *J. Appl. Chem. U.S.S.R.*, 1933, **6**, 1145), but there is little doubt that C_8 derivatives and numerous higher hydrocarbons are formed, and probably also C_4 compounds (cf. Dupont and Lombard, *Bull. Soc. chim.*, 1941, **8**, 851). Oxidation studies (Petrov and Antsus, *loc. cit.*, 1934) give some support for the presence of branched olefins. The available data do not exclude the possibility of minor quantities of derivatives of pentanes, heptanes, etc., being present.

Careful study of individual products has unfortunately only been made in the case of nickel on a highly active base, zinc chloride. With this type of catalyst, Petrov and Antsus (*J. Physical Chem., U.S.S.R.*, 1940, **14**, 1308; *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1940, 274; cf. Russian Patent, 1940, 58,320) report butadiene and especially *iso*butene. Since the work now described was done, evidence has become available (*idem, ibid.*, 1942, p. 125) that the higher fractions over the same type of catalyst contain various mono- and di-olefins with the carbon skeletons of *n*-hexane, 2- and 3-methylpentanes, 2 : 3-dimethylbutane, 3-ethylhexane, and 2-, 3-, and 4-methylheptanes. Traces of benzene were found, and *n*-C_8 hydrocarbons were also considered present. Considerably more *n*-hexane derivatives were formed than any other single type of structure, though both methylpentane skeletons were common. The formation of *n*- and *iso*-butene structures over nickel on a less active base, kaolin, is also mentioned by Antsus and Petrov (*loc. cit.*, 1942), and apparently part of the product examined for C_6 and C_8 compounds was prepared over nickel alone, but scarcely any details are given of the conditions of preparation.

FIG. 1.



Open circles : 197—202 *mm.* H_2, 197—202 *mm.* C_2H_2.
Full circles : 199—201 *mm.* H_2, 400—403 *mm.* C_2H_2.
Half-filled circles : 399—403 *mm.* H_2, 199—202 *mm.* C_2H_2.

More knowledge is required of the yields and structures of individual products over nickel on a base less reactive than zinc chloride, and an account is given below of a study of the products obtained over a nickel–pumice catalyst similar to those used in Part I (*loc. cit.*).

EXPERIMENTAL.

Effect of Temperature on Reaction.—The materials and method were as described in Part I. The nickel–pumice catalyst was a specimen of Ni-2 (nickel : pumice ratio 1 : 5). Temperature control was somewhat less accurate below 20° than at higher temperatures, variations within a range of 2—3° being recorded. Manometer readings were corrected to a constant temperature for each run, and for any changes in barometric pressure. In the fastest reaction (at 126°) time did not permit a preliminary washing of the capillary leads from the reaction bulb before collection of the gas.

The experiments were performed in a sequence unrelated to the variations in conditions, and the satisfactory constancy of the activity of the catalyst (see Part I) is confirmed by the mutually consistent results. The systematic variations in the rate and products of reaction must be an effect of the change in temperature.

Preparation of Hydrocarbon Products higher than the C_2 Series.—The nickel–pumice catalyst was prepared in the same way as Ni-2 (Part I), except that the final reduction was performed in hydrogen at 300° for 12 hours. A 20-cm. layer of this catalyst was placed in the electrically heated Pyrex reaction tube (15 mm. diam.). Acetylene (cylinder gas, passed through 2 wash-bottles of sodium bisulphite solution and through 20% sodium hydroxide) and hydrogen (electrolytic cylinder gas, 99·5% pure with traces of carbon monoxide and dioxide) were passed in at approximately equal rates (total rate 10—20 l./hr.), the combined gases being dried before reaction in a U-tube of anhydrous calcium chloride. Temperature was measured by a thermometer in the catalyst near the point of entry of the gases, and was maintained at 200—250° during reaction. Liquids were condensed from the products in a receiver at room temperature and in a trap at −78°.

The catalyst was heated in hydrogen to 300—350° before each day's working. It remained active and produced similar condensates throughout 3 months' use.

For the distillation analysis of the lower-boiling products, a 120-cm. Podbielniak column was used. Reflux cooling was provided by alcohol at about −50° for distillation below some 20°, and by a stream of air for liquids boiling above this region.

RESULTS AND DISCUSSION.

(i) *Effect of Temperature on the Reaction over a Catalyst of Steady Activity.*—Table I summarises data for the times (in mins.) necessary for the total pressure to fall by 100 mm. (t_{100}) and 200 mm. (t_{200}) for hydrogen : acetylene ratios of 1 : 1, 1 : 2, and 2 : 1. The plots of $\log_{10} t_{100}$ and $\log_{10} t_{200}$ against $1000/T$ (T = absolute temperature) are good straight lines, each of slope 2·85 with respect to the $1000/T$ axis.

The shapes of the total pressure–time curves (plotted to a scale expressed in fractions of t_{200}) showed little variation within each of two groups of experiments : (*a*) runs with 1 : 1 and 1 : 2 hydrogen : acetylene mixtures; (*b*) those with 2 : 1 hydrogen : acetylene ratio. The slight variations in curve shape showed no clear relationship to temperature and were probably due in part to temporary minor variations in catalyst activity. There were no signs that the dependence of the rate on the partial pressures differed anywhere between 0° and 91° from that found at 79° (Part I), and hence t_{100} and t_{200} were approximately the same, at a given temperature, for 1 : 1 and 1 : 2 hydrogen : acetylene mixtures, and reaction in the presence of twice the hydrogen pressure was about twice as fast.

For the calculation of activation energies, use was made of the initial rate of fall in total pressure, $(-\,dp/dt)_0$. Fig. 1 shows the plot of $\log_{10}(-\,dp/dt)_0$ against $1000/T$. Straight lines were obtained, of slope

TABLE I.

No. of expt. in series.		Temp.	$\log_{10}t_{100}$.	$\log_{10}t_{200}$.
35	Initial pressures: 197—202 mm. H_2; 197—202 mm. C_2H_2.	0—3°	3·508	3·907
13		16—18	3·146	3·477
16		31	2·407	2·833
14		42	2·203	2·596
15		52	1·908	2·320
17		62	1·591	2·013
23		71	1·335	1·782
18		81	1·130	1·556
22		94	0·845	1·262
19		103	0·720	1·114
20		114	0·464	0·829
21		126	0·30	0·65
36	Initial pressures: 199—201 mm. H_2; 400—403 mm. C_2H_2.	0—3°	3·502	3·866
32		17—19	2·950	3·341
31		40	2·179	2·584
30		72	1·354	1·774
29		91	0·968	1·346
34	Initial pressures: 399—403 mm. H_2; 199—202 mm. C_2H_2.	0—3	3·322	3·607
33		17—19	2·486	2·817
25		30	2·114	2·436
26		50	1·547	—
27		50	1·500	1·860
24		71	0·929	1·248
28		91	0·52	0·79

—2·64 with respect to the $1000/T$ axis, and once again the effects of gas pressures on the rates were as noted in the preceding paragraph.

The gaseous products were analysed after falls in pressure of 200 mm. The results are plotted against temperature in Figs. 2 and 3. Production of ethylene and, more markedly, of ethane increased as the temperature was lowered. Correction for a possible slight error due to unobserved condensation of less volatile products during withdrawal of gas would increase this effect of temperature on the yields. The total amount of hydrogen removed increased with decreasing temperature, but the total amount of acetylene removed was within 5 mm. of 142 mm. in all the experiments. The approximate yield scale shown in Fig. 2 is calculated on the basis of a removal of 142 mm. of acetylene in each run. The amounts of acetylene and hydrogen removed as products other than C_2 hydrocarbons were about equal at 0°, but the amount of acetylene increased more markedly than that of hydrogen as the temperature was raised.

FIG. 2.

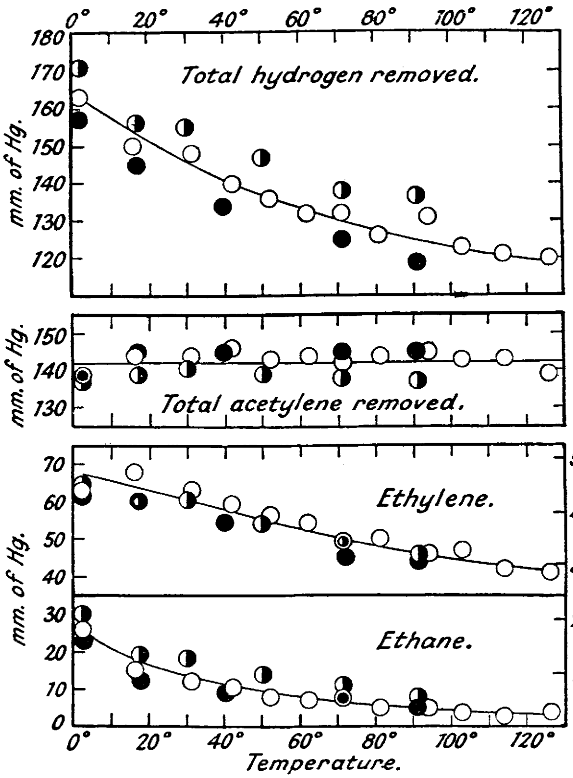
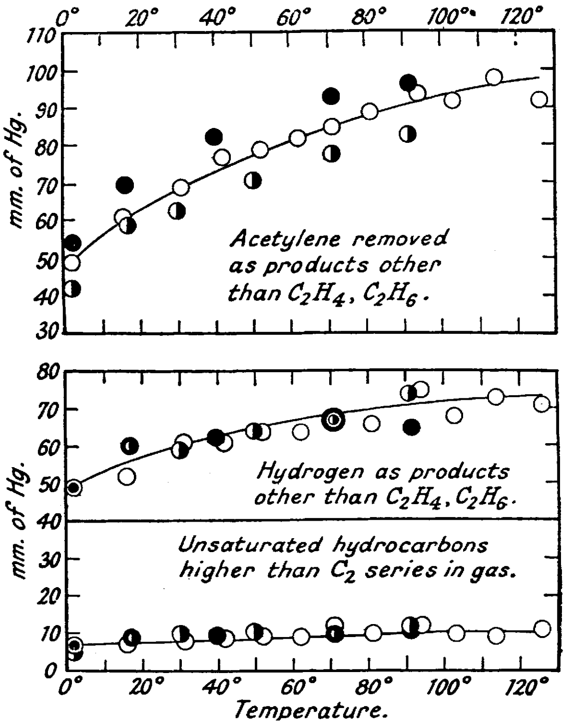


FIG. 3.

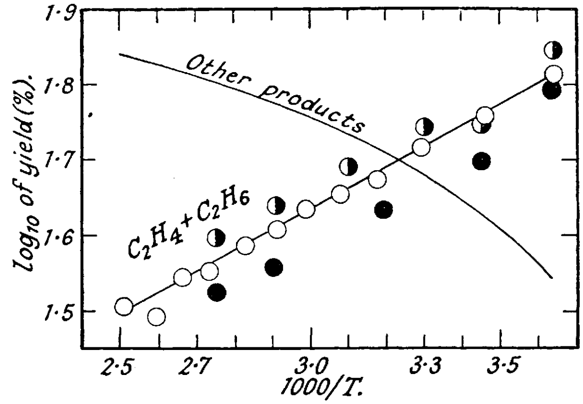


Figs. 2 and 3: *Initial pressures for each type of point are the same as in* Fig. 1.

The effects of gas ratio on the amounts of gases formed and removed at a given temperature were small. The possible errors are larger in quantities which are the differences of pressures (especially the amounts of gases removed as products other than C_2 hydrocarbons, which are obtained by difference from three partial pressures in the product and the initial pressures), but with the present standardised experimental technique variations should be detected more readily than the estimated maximum absolute errors may suggest. Higher hydrogen : acetylene ratios appeared slightly to favour ethane production, hydrogen removal, and acetylene recovery. Removal of acetylene as products other than C_2 hydrocarbons was probably less at the higher hydrogen : acetylene ratios. The effects of the partial pressures on the yields of C_2 hydrocarbons (expressed in terms of the acetylene not recovered) appear on the whole similar at temperatures between 0° and 91° to those found at 83° (Part I) over a very similar catalyst. This is seen from Fig. 4, in which $\log_{10} y$ (y = total yield of C_2 hydrocarbons) is plotted against $1000/T$; reasonable straight lines are obtained for each type of mixture, y increasing, at a given temperature, with hydrogen : acetylene ratio. In a few runs over different specimens of nickel–pumice, values of y slightly higher than in the present series of results were found for temperatures above about 80° (Part I, Table I), but in some such cases the high speed of reaction may have caused increased errors.

The effect of temperature on the yields is qualitatively in harmony with earlier work (*e.g.*, Sabatier and Senderens, *loc. cit.*) and with claims that yields of C_2 hydrocarbons can be increased by closer control of temperature by such means as suspension of the catalyst in a liquid (B.P. 294,787; Fischer and Peters, *Brennstoff-Chem.*, 1931, **12**, 286) or addition of gases such as nitrogen, carbon dioxide, or methane to the reaction mixture (U.S.P. 1,308,777; D.R.-P. 350,429; see also D.R.-P. 262,541; Dupont and Lombard, *loc. cit.*).

FIG. 4.



The experimental points refer to the total yield of ethylene and ethane, those for the yield of other products being omitted. Initial pressures for each type of point are the same as in Fig. 1.

It is clear that the reaction yielding ethylene and ethane has a lower apparent heat of activation than the process by which acetylene and hydrogen are removed as other products. To obtain figures for activation energies it is necessary to make assumptions about the initial reaction, based on the temperature dependence of the products after a pressure fall of 200 mm. Since the total acetylene removed was independent of temperature (Fig. 2) it seems reasonable to assume that the initial rate of removal of acetylene is a constant fraction of $(-\,dp/dt)_0$ at all temperatures. The plot of $\log_{10}$ of the initial rate of removal of acetylene against $1000/T$ will then be parallel to the lines in Fig. 1, and therefore

$$d\{\log_{10}(-\,d[C_2H_2]/dt)_0\}/d(1000/T) = -\,2{\cdot}64$$

between 0° and 126°. It is also assumed that the initial rate of ethane production is zero (which is made probable by the fact that the ethylene yield exceeds the yield of ethane, especially at higher temperatures) and that the initial rate of ethylene formation is given by $(d[C_2H_4]/dt)_0 = (-\,d[C_2H_2]/dt)_0 y$, where y is the total yield of C_2 hydrocarbons after a fall in pressure of 200 mm. This is not improbable, since the effects of gas pressures on the yields are very small. It then follows that

$$\frac{d}{d(1000/T)}\left\{\log_{10}\left(\frac{d[C_2H_4]}{dt}\right)_0\right\} = -\,2{\cdot}64 + \frac{d\log_{10} y}{d(1000/T)}$$

From Fig. 4 the last term is found to be +0·275 in the range 0—126°, and the expression becomes equal to −2·365. This gives 10·9 kg.-cals. as the apparent activation energy of reaction (I) between 0° and 126°.

If r is the initial rate of removal of acetylene as products other than ethylene, then with the above assumptions

$$d\log_{10}r/d(1000/T) = -2{\cdot}64 + d\log_{10}(100 - y)/d(1000/T).$$

The plot of $\log_{10}(100 - y)$ against $1000/T$ corresponding to the linear plot of $\log_{10} y$ in Fig. 4 is shown as the curved line in the same figure; the individual points are omitted for the sake of clarity, but can be calculated from the data plotted; they cluster round the curve in a way very similar to that in which the points shown cluster round the straight line. The slope of the curve with respect to the $1000/T$ axis is given by $-0{\cdot}275y/(100 - y)$ at any point, which gives a value of −0·12 at 126°, becoming more negative as the temperature falls, reaching −0·51 at 0°. Substitution in the last equation gives $d\log_{10}r/d(1000/T)$ values between −2·78 and −3·15. This gives 12·7 kg.-cals. as the apparent activation energy of reaction (II) at 126°; at 0° the value given is 14·5 kg.-cals. Intermediate figures are obtained at temperatures between these limits, *e.g.*, 13·4 kg.-cals. at 36°, where $y = 50$.

The reaction kinetics (Part I) indicate that these activation energies should each be corrected by addition of the heat of desorption of hydrogen.

Extrapolation of the straight line in Fig. 4 would predict values of y increasing as the temperature falls and reaching 100% at about −40°, the slope of the curved line meanwhile becoming more negative and tending to infinity as y approaches 100%; *i.e.*, the heat of activation of reaction (II) should increase, approaching infinity in the region of −40°. This does not seem probable, and the phenomena below 0° require further investigation. Extrapolation of the straight line in Fig. 4 to higher temperatures would predict values of y falling to about 26% in the region of 180°, whereas, in a flow-experiment (one of a series to be reported in detail later) over a very similar catalyst (Ni-1, Part I) at 178°±5°, *y* was found to be about 40% for a 1 : 1 gas mixture at a total pressure of 1 atm. (ethylene yield 35%, ethane yield 5%; 94% of the acetylene removed in a contact time of 6 seconds). Extrapolations of the above types do not therefore seem justified.

Flow experiments of the type referred to above indicated that the total rate of reaction was probably still increasing with temperature in the region of 150—200°.

(ii) *Hydrocarbon Products Higher than the* C_2 *Series.*—The condensate in the receiver at room temperature (condensate 1) was yellow or brown, and was formed at about the same rate as the colourless condensate in the trap at −78° (condensate 2). Uncondensed gas emerged at about a quarter of the total rate of gas entry. No extensive deposition of carbon occurred.

About two-thirds of condensate 1 distilled from 60° to 310° with steadily rising b. p.; roughly one-sixth distilled from 100°/30 mm. to 250°/6 mm., leaving a gummy residue of about one-sixth. The colour deepened with rising b. p.

On distillation of condensate 2 through the Podbielniak column, about half passed over from −10° to 0° without distinct plateaux, and the remainder principally at 60—70°. A sample of gas given off by condensate 2 at room temperature contained about 75% of unsaturated hydrocarbons higher than the C_2-series, and some 25% of saturated hydrocarbon with an average of 4·8 carbon atoms per molecule. A test for butadiene in condensate 2 by the Diels–Alder reaction with maleic anhydride gave only a rubber-like product.

About 100 c.c. of condensate 2 were hydrogenated at 60—70° and 60—80 atm. over Raney nickel for 24 hours, absorption of gas then being complete. A 33% loss accompanied this process; this must be mainly a loss of the most volatile components. The residue was subjected to Podbielniak distillation, and the distillate boiling above 30° divided into cuts of roughly 1 c.c., the refractive indices (and, in certain cases, densities) of which were measured. A fully hydrogenated cut from the higher-boiling condensate (b. p. 176—200°) was added as a driving liquid. Boiling-point plateaux were observed at −4° to 0° (7 c.c.), 30—35° (4 c.c.; $n_D^{20°}$ of last two c.c. 1·3563 and 1·3591), 60—63° (35 c.c.; $n_D^{20°}$ rising from 1·3753 to 1·378 after 3 c.c., then steadily to 1·3830; $d_{15°}^{15°}$ 0·670—0·682), 86—96° (3 c.c.; $n_D^{20°}$ 1·3911—1·3960, $d_{15°}^{15°}$ 0·695—0·697), and 110—120° (4 c.c., $n_D^{20°}$ 1·4031—1·4050, $d_{15°}^{15°}$ 0·720—0·722). The rises in temperature between the plateaux were fairly steep, especially at the lower temperatures. There were no maxima or minima in the curve of $n_D^{20°}$ against volume distilled.

Some 160 c.c. of condensate 1 were hydrogenated over Raney nickel at 80—100 atm. and 200—220° for 72 hours, after which absorption of gas was extremely slow. About 7 l. of hydrogen were taken up. The product, which had a faint green fluorescence, was fractionated into: (*a*) a colourless fraction (through 10″ Dufton column), b. p. 60—200°, 55 c.c.; (*b*) a fraction beginning colourless and becoming pale yellow with rising b. p., b. p. 200—320°, 52 c.c.; (*c*) a brown viscous residue. Fraction (*a*) was distilled through the Podbielniak column, and cuts of about 1 c.c. examined. After a slight plateau (2 c.c.) in the b. p. curve at 62—67° ($n_D^{20°}$ 1·3758—1·3805) and an incline at about 90—112° (3 c.c.; $n_D^{20°}$ 1·3950—1·4033), a fairly well-defined plateau was found at 112—124° (12 c.c.; $n_D^{20°}$ 1·4030—1·4095, $d_{15°}^{15°}$ 0·728—0·735). The b. p. and $n_D^{20°}$ then rose fairly continuously, reaching 176° and 1·4259, respectively, after 40 c.c. had distilled. No maxima or minima were observed in the refractive index, plotted against volume distilled. The residue of fraction (*a*) (b. p. 176—200°) was not examined. Fraction (*b*) was distilled through a 10-cm. glass-packed column heated electrically to 20° below the distilling temperature, cuts of 1—2 c.c. being taken. The first 48 c.c. distilled with almost continuous rise in b. p. from 200° to 320° and in $n_D^{20°}$ from 1·4352 to 1·4701.

The physical properties of the cuts are those of paraffins, though pure fractions were not obtained, presumably on account of the complexity of the mixtures. There is no indication in the refractive indices of any appreciable formation of benzene or *cyclo*hexane, though the refractive indices and densities of the lower fractions are slightly higher than those of paraffins of the same b. p., which suggests that traces of substances of higher refractive index and density are present. The b. p. plateaux and approximately the expected physical properties show that butanes, pentanes, hexanes, heptanes, and octanes are probably present. The refractive indices provide conclusive evidence of the presence of pentanes. The liquid boiling higher than the octane plateau is doubtless a complex mixture of hydrocarbons from about C_9 upwards. The yellow colour and fluorescence of the higher-boiling products after intense hydrogenation show that some aromatic derivatives are probably formed.

Samples of the lower-boiling hydrogenated products were submitted to Dr. H. W. Thompson, to whom the author is indebted for an examination of their infra-red absorption spectra. For the samples of b. p. 33—90° the spectra leave little doubt as to the principal constituents, despite the fact that the b. p. values recorded are sometimes rather lower than expected from the composition. The paraffins found, with the approximate compositions of each cut, are listed in Table II, in which the volume figures refer to the stages at which the cuts were taken from the Podbielniak distillation of condensate 2 after hydrogenation.

Although time did not permit a further fractionation into purer samples, it is clear that the bulk of the hydrogenated C_6 fraction is made up of *n*-hexane and 3-methylpentane. The b. p. plateau in the region of −4° to 0° is fairly good evidence of the presence of *n*-butane (b. p. −0·5°; *iso*butane, b. p. −11·7°), and when it is remembered that much of the lowest-boiling products were lost in completing their hydrogenation, it is seen that the yield of *n*-butane may well have been large. The carbon skeletons of *n*-butane, *n*-hexane, and 3-methylpentane are the simplest which can be formed from C–C units without separating the carbon atoms. It thus appears probable that the products other than C_2 hydrocarbons are all formed principally by a linking

TABLE II.

Position of cut in distillation (c.c.).	B. p.	Composition.
9—10	33—35°	*ca.* 75% *n*-Pentane, *ca.* 25% 2-methylbutane.
11—12	51—58	*n*-Hexane, 2- and 3-methylpentane; probably no 2 : 3- or 2 : 2-dimethylbutane.
12—14	58—61	*n*-Hexane, 2- and 3-methylpentane, roughly 33% each.
18—20	62	*n*-Hexane, 3-methylpentane; $<10\%$ 2-methylpentane.
30—32	62—63	About equal amounts of *n*-hexane and 3-methylpentane.
40—42	63	
45—46	63	*n*-Hexane; not above 20% of 3-methylpentane.
46—47	63—66	*n*-Hexane; some 3-methylpentane, less than in preceding cut.
48—49	86—88	At least 50% 3-methylhexane. Almost certainly *n*-heptane. Possibly traces of 2 : 2-dimethylpentane. Probably no 2 : 4- and 3 : 3-dimethylpentanes.
49—50	88—89	As preceding cut. Slightly less 3-methylhexane.

together of C–C units in this way. Those which cannot be so formed (*e.g.*, 2-methylpentane, pentanes, heptanes) must be produced by isomerisation or cracking at some stage; this stage may be the final one, or it may be followed by addition of one or more C–C units before the final structure is attained. It is unlikely that any extensive isomerisation accompanied the high-pressure hydrogenation of the liquid products.

The results for the C_6 fractions resemble those of Antsus and Petrov (*loc. cit.*, 1942) for nickel–zinc chloride; in the present experiments, however, no 2 : 3-dimethylbutane structures were detected, and the predominance of *n*-hexane structures was not so marked, the yield of 3-methylpentane being almost as large as that of *n*-hexane, with a distinctly smaller amount of 2-methylpentane. Much larger yields of C_4 compounds were found in the present work than under rather similar conditions by Petrov and Antsus (*loc. cit.*, 1934).

The amounts of unsaturated gases higher than ethylene found in products from experiments at lower temperatures (see, *e.g.*, Fig. 3) are about $\frac{1}{7}$ to $\frac{1}{10}$ of the amounts of acetylene removed by reaction (II), the products of which must therefore be largely of relatively low molecular weight at these temperatures also. Reduced polymers of acetylene, chiefly of low molecular weight, are apparently formed over a number of metals, such as iron, cobalt, platinum, and, under certain conditions, copper (*e.g.*, Sabatier and Senderens, *Compt. rend.*, 1900, **130**, 1628, 1559; **131**, 40). Work to be published later has confirmed this, and shown that the reduced polymers formed over palladium also have a relatively low mean molecular weight. The formation of " benzine " from acetylene and hydrogen over mixed metal catalysts is well known (*e.g.*, *inter alia*, Peters and Neumann, *Ges. Abh. Kenntn. Kohle*, 1934, **11**, 423). The main products appear to be aliphatic, and in the few cases where any close study has been made (*e.g.*, Neumann, *ibid.*, p. 434, for iron–nickel catalysts) there is a general similarity to the products over nickel, *e.g.*, large formation of hexenes.

On the basis of the distillation data, the products of reaction (II) over nickel–pumice in the present experiments can be estimated to contain the following approximate percentages by weight : C_4 hydrocarbons 25%, C_5 hydrocarbons 1—2%, C_6 hydrocarbons 25%, C_7 hydrocarbons 1—2%, C_8 hydrocarbons 5%, with some 7% in the range C_9 to (very roughly) C_{14} and about 17% in each of the ranges C_{14} to (very roughly) C_{30} and C_{30} to C_x, where x is unknown but large. If molecular percentages are used the predominance of lower members is even more marked. In more accurate flow experiments under roughly the same conditions the yield of products other than C_2 hydrocarbons was 60—70%; if this applies also to the large-scale experiments, the yields of the cuts listed above will be obtained in terms of the acetylene not recovered by multiplying the appropriate percentages by 0·6—0·7.

(iii) *General Discussion.*—It should be emphasised that, though hydrogenation of acetylene to ethane is quantitative with a large excess of hydrogen on platinum (Conn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 1868), this is exceptional; the normal reaction on all the catalysts so far investigated is accompanied by some formation of hydrocarbons higher than the C_2 series (see, *e.g.*, Sabatier and Senderens, *locc. cit.*; Pichler, *Ges. Abh. Kenntn. Kohle*, 1934, **11**, 395; Ackermann, *Brennstoff-Chem.*, 1937, **18**, 357; Yoshikawa, *Bull. Chem. Soc. Japan* 1932, **7**, 201; Cremer, Knorr, and Plieninger, *Z. Elektrochem.*, 1941, **47**, 737; etc.). In contrast, the hydrogenation of ethylene is always virtually a quantitative reaction on metal catalysts.

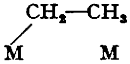
Reference was made in Part I to the ready formation of hydrocarbons higher than the C_2 series from acetylene and hydrogen over nickel under conditions of temperature and acetylene pressure under which the same catalysts caused very little reaction in acetylene alone. This type of phenomenon is probably general among metal catalysts, except those containing appreciable amounts of copper, which has a marked polymerising action on acetylene (see, *e.g.*, Egloff, " The Reactions of Pure Hydrocarbons," 1937). The primary action of hydrogenation catalysts on acetylene alone appears usually to be a decomposition rather than a polymerisation (see, *e.g.*, Egloff, *op. cit.*), yet in the presence of hydrogen hydrocarbons higher than the C_2 series are formed. In the case of nickel there is evidence that a linking together of C–C units without rupture is the primary reaction; this probably applies also to other metals, though more experimental evidence is needed here.

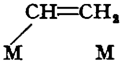
Over nickel the formation of hydrocarbons higher than the C_2 series is a first-order reaction with respect to hydrogen. Determination of orders of reaction is more difficult with other catalysts, but it appears probable that the phenomena on palladium are not unlike those on nickel, and that the resemblance may extend to other catalysts also. Results with catalysts other than nickel will be reported in detail later.

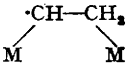
Local overheating of the catalyst by the primary hydrogenation reaction is a totally inadequate explanation of the phenomena outlined above, despite the fact that acetylene is more readily polymerised than ethylene (cf. Damköhler, *Z. physikal. Chem.*, 1943, *A*, **193**, 16). Except in the case of copper, moreover, the overheated metal would be expected to decompose acetylene rather than polymerise it. Acetylene is more strongly adsorbed than ethylene on nickel (see Part I), platinum (Farkas and Farkas, *J. Amer. Chem. Soc.*, 1939, **61**, 3396), palladium (Cremer, Knorr, and Plieninger, *loc. cit.*), iron (work to be published later) and probably other metals, but this is not a satisfactory explanation of the difference in behaviour of these hydrocarbons on hydrogenation, since it has been maintained that ethylene can completely cover a nickel surface (Twigg and Rideal, *Trans. Faraday Soc.*, 1940, **36**, 533; *Proc. Roy. Soc.*, 1939, *A*, **171**, 55). Greater separation of the points of unsaturation for steric reasons may account for the fact that alkylacetylenes do not appear to polymerise as readily as acetylene itself when hydrogenated (see, *e.g.*, Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77).

The greater unsaturation of acetylene as compared with ethylene is a more probable cause of the difference in behaviour of these hydrocarbons on hydrogenation. Herington (*Trans. Faraday Soc.*, 1941, **37**, 361) has pointed out how this difference in degree of unsaturation is especially emphasised if the concept of associative two-point adsorption is correct, since acetylene so adsorbed is still unsaturated, whereas ethylene so adsorbed is not. He cites as evidence for this mode of adsorption the polymerisation of acetylene over cobalt in the presence of hydrogen, compared with the quantitative hydrogenation of ethylene to ethane over that metal. The importance of the presence of hydrogen needs stronger emphasis for the reasons given above.

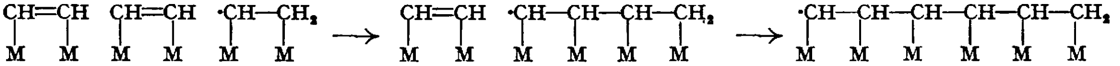
The part played by hydrogen can be explained, without the supposition of such factors as overheating of the catalyst, by a development of the theory of associative adsorption. The formation of a " half-hydrogenated " state has been frequently postulated in the mechanisms of exchange reactions and double-bond migration in olefins according to the theory of associative adsorption (*e.g.*, Twigg and Rideal, *loc. cit.*, 1939; Rideal, *Proc. Camb. Phil. Soc.*, 1939, **35**, 130; *Chem. and Ind.*, 1943, **62**, 335; Twigg, *Proc. Roy. Soc.*, 1941, *A*, **178**, 106) and, by other authorities, also in the hydrogenation itself on metals (*e.g.*, Horiuti and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164; Greenhalgh and Polanyi, *ibid.*, 1939, **35**, 520). For ethylene this state is a bound ethyl radical (I); for acetylene it is possible to write either (II) or (III) (M represents a catalyst atom). Form (III) might be produced by way of form (II), in which case (III) may span a different M–M space from that originally adsorbing the acetylene.


(I.)


(II.)


(III.)

State (III) differs from states (I) and (II) in having a carbon atom with one unpaired electron, and is in this sense a free radical, though still adsorbed on the catalyst. It is then possible to formulate polymerisation by a chain reaction in associatively adsorbed acetylene, resembling the radical-chain mechanisms often postulated in homogeneous polymerisations of olefin derivatives. The process can be written as:

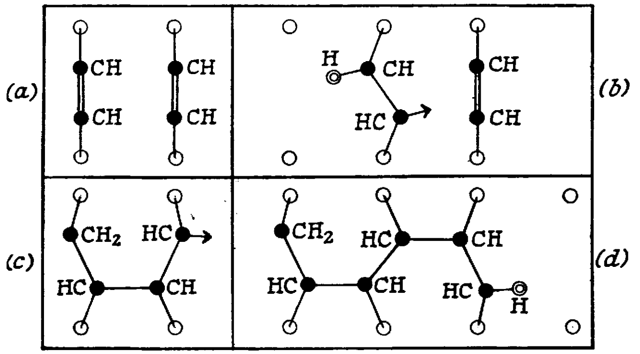

(IV.)

$$\underset{M}{CH}{=}\underset{M}{CH}\ \ \underset{M}{CH}{=}\underset{M}{CH}\ \ \underset{M}{\cdot CH}{-}\underset{M}{CH_2} \longrightarrow \underset{M}{CH}{=}\underset{M}{CH}\ \ \underset{M}{\cdot CH}{-}\underset{M}{CH}{-}\underset{M}{CH}{-}\underset{M}{CH_2} \longrightarrow \underset{M}{\cdot CH}{-}\underset{M}{CH}{-}\underset{M}{CH}{-}\underset{M}{CH}{-}\underset{M}{CH}{-}\underset{M}{CH_2} \quad \text{(IV.)}$$

and so on. In the absence of hydrogen, state (III) cannot be formed, which explains the lack of appreciable polymerisation under those conditions on catalysts other than copper; on that metal, other factors make a mechanism of initiation by hydrogen less necessary. Polymerisation as above could not occur in associatively adsorbed ethylene; since, however, it is not impossible that unsaturated molecules in van der Waals layers above the chemisorbed layer could become involved in the reaction chain, the essential difference between the hydrogenation of ethylene and of acetylene according to these concepts rests at least as much in the possibility of a different type of half-hydrogenated state in acetylene, as in the fact that associatively adsorbed acetylene is still unsaturated, though that fact probably contributes considerably to the causes of the observed phenomena. With adsorptions described as physical (*e.g.*, Hansford and Emmett, *J. Amer. Chem. Soc.*, 1938, **60**, 1185) or dissociative (*e.g.*, Farkas, *Trans. Faraday Soc.*, 1939, **35**, 906), both of which leave acetylene and ethylene unsaturated, the different behaviour of these gases on hydrogenation would have to be explained in terms of such factors as denser packing or more ready polymerisation in acetylene. The polymerisation of ethylene on hydrogenation catalysts can occur, *e.g.*, on nickel at 240—360° (Pscheshetzki and Gladischev, *J. Physical Chem. U.S.S.R.*, 1941, **15**, 333), and has even been reported on very active nickel at room temperature (Morikawa, Trenner, and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1103), but is in general much slower than polymerisation in the acetylene–hydrogen system under comparable conditions. There is no evidence that ethylene polymerisation on metals is promoted by hydrogen.

A study of scale models has been made to determine in what circumstances the type of polymerisation suggested for acetylene in the presence of hydrogen is reasonably possible on steric grounds. Bond lengths used were: C–C 1·54 A., C=C 1·33 A., C–Ni 2·0 A. In nickel the (100) face cannot accommodate forms of the type of (IV), though it may adsorb acetylene. The (111) face might accommodate, with some strain, a C_4 or C_6 polymer, but is probably unsuitable for the associative adsorption of acetylene (Herington, *loc. cit.*). The (110) face, however, would permit a polymer to form from acetylene adsorbed associatively on 3·50 A. spaces without rupture of C–Ni bonds, the increase in strain being insufficient to make the process unlikely. Fig. 5 illustrates the type of mechanism. It is assumed that state (III) is formed from acetylene without rupture of C–Ni bonds, strain being relieved by rotation about the C–C bond (Fig. 5*b*; in this discussion the stereochemistry of a carbon atom with 7 valency electrons is assumed to be the same as that of normal carbon, the unpaired electron replacing one valency). Such rotation may bring the carbon deficient in electrons towards an adjacent acetylene molecule in the manner shown (Fig. 5*b*), and steric conditions are now probably suitable for a change to a *n*-C_4 radical (Fig. 5*c*). At this stage the strain is shown distributed among the valency angles ($\text{C–}\widehat{\text{C}}\text{–C}$ = *ca.* 115°, $\text{C–}\widehat{\text{C}}\text{–Ni}$ = *ca.* 103° across 2·48 A. spaces, *ca.* 115° across 3·50 A. spaces); the necessary distortions from the normal angles are thus probably not large enough to prevent the changes suggested. Interaction of the C_4 radical with another acetylene molecule in the same way is seen to be possible, but in the *n*-C_6 skeleton produced (Fig. 5*d*) the central portion must be under somewhat greater strain than previously ($\text{C–}\widehat{\text{C}}\text{–C}$ increases to about 127°; distortions in $\text{C–}\widehat{\text{C}}\text{–Ni}$ are a little less than before). Since, however, by analogy with gaseous polymerisation of olefins, we expect a considerable release of bond energy (of the order of 17 kg.-cals./mol.) for every acetylene unit added to the radical, such increase in strain may well not make the reaction thermodynamically impossible; if so, the polymer chain could be extended indefinitely as long as acetylene molecules became suitably positioned. In Fig. 5*d* the chain is shown terminated at the C_6 stage by addition of a hydrogen atom, and some redistribution of strain in the terminal C–C units is again assumed.

FIG. 5.



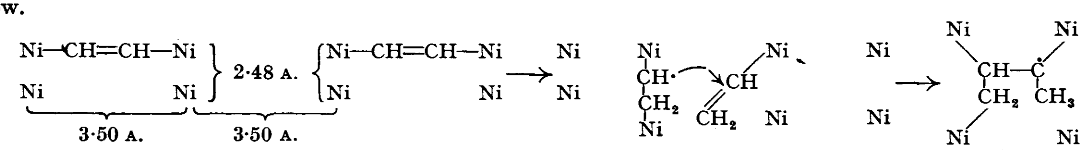
Approximate scale projection on (110) *face of nickel showing an example of a possible mode of polymerisation without rupture of* C–Ni *bonds in associatively adsorbed acetylene. Open circles = nickel atoms, full circles = carbon atoms, double circles = hydrogen atoms; carbon valencies not shown are taken up by other hydrogen atoms, except where arrows are shown, each of which indicates one unpaired electron. The carbon atoms are initially ca.* 1·68 A. *above the plane of nickel nuclei, and in the adsorbed polymers about* 1·58 A. *to* 1·73 A. *above it.*

A possible objection to the above is that one hydrogen nucleus of the terminal $>CH_2$ groups is brought within about 2·6 A. of the nearest non-bonded nickel nucleus; two such terminal hydrogen atoms are shown in Fig. 5 (*b* and *c*). It is perhaps possible that some steric repulsion between these hydrogen and nickel atoms is set up, but insufficient is known of the effective van der Waals radii at the surface for this to be certain. In any case, a repulsion sufficient to make the above processes impossible is unlikely. We note, however, that acetylene adsorbed on a space adjacent to state (III) (as in Fig. 5*b*) would certainly impede rotation about the C–C bond except in such a direction as to bring the carbon deficient in electrons towards the neighbouring acetylene.

Formation of branched carbon skeletons presents greater difficulty. Attack of an unpaired electron on a C–Ni bond, *e.g.*,

$$>\underset{\text{Ni}}{\text{CH}}\quad \cdot\underset{\text{Ni}}{\text{CH}}\text{—}\underset{\text{Ni}}{\text{CH}_2}\longrightarrow\ >\underset{\text{Ni}}{\text{CH}}\text{—}\underset{\text{Ni}}{\text{CH}}\text{—}\underset{\text{Ni}}{\text{CH}_2}$$

or on a C=C link in a desorbed part of a polymer appears in general improbable for steric reasons. A mechanism involving migration of a hydrogen atom, on a (110) face, is sterically more likely, and an example is shown below.



(III.) (II.) (V.)

If states (III) and (II) could be formed as shown, the radical (V) may be produced with migration of hydrogen, and might then add acetylene molecules in the manner shown in Fig. 5, yielding 3-methyl derivatives, *e.g.*, the 3-methylpentane structure. Variations on this process can be formulated.

This yields branched structures without rupture of the original C_2 skeletons. Other branched structures, *e.g.*, of the 2-methylpentane type, can only be formed by way of such a rupture, and this may account for the relatively large amounts of 3-methyl- as compared with 2-methyl-pentane, found in the present experiments. The " cross-polymerisation " mechanism proposed by Antsus and Petrov (*loc. cit.*, 1942), besides leaving out of account the promotion of reaction by hydrogen, does not distinguish so sharply between the methods of production of 2- and 3-methylpentane structures.

It is desirable, however, that the products of reaction (II) at temperatures below 200° should be examined more closely before it is concluded with certainty that there is this distinction between the two methods.

Polymerisation by the suggested mechanisms may be facilitated by desorption (with hydrogenation or otherwise) of parts of the polymer, though by no means all such processes at first sight possible are likely on steric grounds. Many of the products are certainly hydrogenated beyond the stage attained by the polymerisation of adsorbed acetylene induced by state (III). Since migration of double bonds is expected to accompany the reaction, the positions of these in the products are of uncertain value as evidence in deciding the mechanism. It is clear that, with the suggested processes, unsaturation can appear at numerous parts of the polymer.

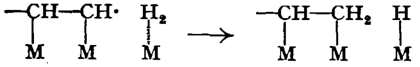
While strain may tend to oppose production of long polymer molecules in the above manner, other factors can also favour short chain length. In particular, if a (110) face is covered with acetylene, at random except for the condition that 3·50 A. spaces be spanned, an arrangement of *n* adjacent molecules abreast (as in Fig. 5*a*) becomes more improbable as *n* increases. The proportion of unoccupied metal atoms in an immobile orientated film of molecules in two-point contact of this type can be shown to be 13·53% by a calculation used in another connexion by Flory (*J. Amer. Chem. Soc.*, 1939, **61**, 1518). The number of groups of *n* adjacent molecules (excluding any contained in groups of more than *n*) will then be the fraction $(0{\cdot}5677)^2(0{\cdot}4323)^{n-1}$ of the number of molecules chemisorbed. For $n = 1, 2, 3, 4$, and 5 the fractions are 32·2%, 13·9%, 6·0%, 2·6%, and 1·1%, respectively. Mobility of the film to reduce the number of unoccupied atoms raises the contribution of larger groups at the expense of the smaller ones, but the decline in number of groups with increase in *n* is still rapid. Experiments with a model of the (110) face (400 atoms), in a manner similar to that used by Roberts (*Proc. Camb. Phil. Soc.*, 1938, **34**, 399), gave results satisfactorily close to those calculated. If the adsorption of acetylene and mechanism of polymerisation are as postulated above, the improbability of large groups of adjacent acetylene molecules may well play a part in causing the predominance of low molecular-weight reduced polymers from acetylene and hydrogen on various metals. Ethylene can presumably be formed on the (110) face also, but probably without intermediate formation of a half-hydrogenated state (see below). Arrangements from which branched polymers may be formed without rupture of C–C units (as discussed above) appear about as probable in the orientated chemisorbed film as arrangements suitable for production of isomeric normal structures; this is not out of keeping with the formation of comparable amounts of *n*-hexane and 3-methylpentane.

In the above treatment it has been assumed that the probability of adsorption of acetylene on a site is independent of the occupation or otherwise of adjacent sites. This is probably unjustified; for example, as was indicated in Part I, molecules adsorbed as in Fig. 5*a* are likely to be subject to mutual steric repulsion on account of the bulk of the carbon atoms; the non-bonded carbon–carbon distance of 2·48 A. may be compared with the interlayer distance in graphite, 3·4 A. Tilting of the molecules may thus occur, and such an effect would further reduce the probability of two or more molecules being adsorbed abreast on adjacent spaces. This probability would also fall if the adsorption film became unsaturated with respect to acetylene, as might happen for example at temperatures above those at which reaction orders could be determined in the present experiments.

The strain set up in polymerisation as in Fig. 5 is increased by extension of the lattice distances, notably by reason of the increase in $\text{C–}\widehat{\text{C}}\text{–C}$ necessitated by the expansion of the shorter spacings. If acetylene is again assumed to span the longer distances, the increase in strain on polymerisation on (110) faces of β(cubic)-cobalt and copper is little larger than in the case of nickel. On the larger face-centred cubic lattices of palladium and platinum more strain is expected in the polymer, *e.g.*, $\text{C–}\widehat{\text{C}}\text{–C}$ would be about 140° in the central part of a structure like Fig. 5*d*. It is tempting to speculate that the lower yields of reduced polymers over palladium and platinum compared with those over nickel are in part caused by this expansion of the lattice, but so simple an explanation is unlikely, since the parallel between increased strain and lower yield of polymers does not extend outside the vertical group nickel–palladium–platinum, or is at most applicable only to face-centred lattices. Thus polymerisation on the (01$\bar{1}$0) face of hexagonal (α-) cobalt (the form stable below 400°) sets up a structure similar to, but more strained than, that on nickel, and on α-iron (body-centred cubic) a polymerisation of the type suggested is quite unlikely on steric grounds, unless, *e.g.*, many C–Fe bonds are broken and re-formed; yet considerable amounts of reduced polymers are formed over both iron and cobalt. Such comparisons show that deductions made from purely steric considerations of a relatively simple mechanism are largely speculative, as can only be expected since many factors, particularly some specific to the metal, must be ignored in the steric model. In addition, the surface lattice may be modified by reaction. It is also possible, as previously mentioned, to formulate mechanisms in which states such as (III) initiate polymerisation in acetylene in a van der Waals layer, where the influence of the lattice is expected to be greatly diminished.

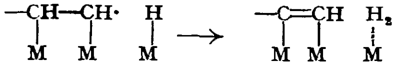
Until many more results are available, the suggested initiation of reaction (II) by the half-hydrogenated state (III) is at least useful in accounting for some general aspects of acetylene hydrogenation-polymerisation.

The reaction chains discussed could be terminated in various ways. These include (*a*) mutual combination of radicals, (*b*) mutual disproportionation of radicals, (*c*) interaction of the unpaired electron with hydrogen, *e.g.*, in a van der Waals layer (compare Rideal, *locc. cit.*),



$$\begin{array}{ccc}\text{—CH—}&\text{CH}\cdot&\text{H}_2\\|&|&\vdots\\\text{M}&\text{M}&\text{M}\end{array}\longrightarrow\begin{array}{ccc}\text{—CH—}&\text{CH}_2&\text{H}\\|&|&|\\\text{M}&\text{M}&\text{M}\end{array}$$

and (*d*) ejection of a hydrogen atom, *e.g.*,



$$\begin{array}{ccc}\text{—CH—}&\text{CH}\cdot&\text{H}\\|&|&|\\\text{M}&\text{M}&\text{M}\end{array}\longrightarrow\begin{array}{ccc}\text{—C=}&\text{CH}&\text{H}_2\\|&|&\vdots\\\text{M}&\text{M}&\text{M}\end{array}$$

Methods (*a*) and (*c*) appear, in general, the most likely on steric grounds. The carbon deficient in electrons might also complete its octet by the removal of a C–metal bond, either as mentioned in discussing branched structures, or within the same radical, as in changes analogous to that from state (III) to state (II). Except in special cases, such as the last-named, these changes are improbable for steric reasons; moreover, since an electrically neutral hydrocarbon with an even number of electrons cannot be desorbed at such a stage, the polymerisation is not truly terminated. Besides the cases (*a*)—(*d*) above, some other possible termination mechanisms are indicated below.

Since the mean chain length is short, propagation and termination must proceed at comparable rates. The simplest kinetic analysis is obtained by assuming that propagation and termination are both much faster than the initiation of chains, and that the chain length is independent of the hydrogen pressure. The observed data could then be accounted for by a rate-determining formation of state (III) from strongly adsorbed acetylene and weakly adsorbed hydrogen, *e.g.*, van der Waals hydrogen in the manner proposed by Rideal. If this initiation step has the energy of activation observed for reaction (II) (12·7—14·5 kg.-cals.), this step does not appear to be involved in ethylene production, since the activation energy in that case is lower. This suggests that ethylene is formed by simultaneous addition, to strongly adsorbed acetylene, of two hydrogen atoms from the same weakly adsorbed hydrogen molecule, which is in harmony with mechanisms at present favoured for hydrogenation in general on metals (*e.g.*, Twigg and Rideal, *Proc. Roy. Soc.*, **1939**, *A*, **171**, 55; Rideal, *Chem. and Ind.*, **1943**, **62**, 335; Farkas and Farkas, *Trans. Faraday Soc.*, **1937**, **33**, 837; Farkas, *loc. cit.*). It is, however, difficult to reconcile the assumption made above, *viz.*, that the chain length is independent of the hydrogen pressure, with the termination mechanisms at first sight most acceptable, *i.e.*, mutual termination, or termination by hydrogen in a manner not unlike the initiation process. With such terminations the chain length is expected to decrease as the hydrogen pressure is raised, and the order of reaction (II) with respect to hydrogen would be less than that of the initial step, *i.e.*, less than unity, since it is unlikely that initiation will be of order higher than the first with respect to hydrogen. If future experiment shows that the chain length is in fact independent of the hydrogen pressure, other modes of termination are indicated, such as spontaneous or monomer termination, though these are unexpected with radical chains. Alternatively, termination might be by some other species, of concentration independent of the hydrogen pressure; such a species might be atomic or molecular hydrogen adsorbed on certain special sites, *e.g.*, uncovered catalyst atoms. If termination involves addition of a hydrogen atom, some factor (*e.g.*, a steric one) presumably prevents appreciable ethylene formation by termination at state (III), otherwise the difference in heats of activation of reactions (I) and (II) is difficult to explain. This difference, other factors being equal, is expected to lead to a greater contribution of ethylene formation to the reaction than is found, a mean chain length of 10 or less being allowed for polymerisation (the observed mean length at 200—250° is about 4). Other factors besides the activation energy, therefore, probably differ slightly for the two types of reaction, favouring reaction (II) somewhat.

A greater complexity than indicated above is quite possible. For instance, although propagation as in Fig. 5 may be relatively fast (as in some analogous vinyl polymerisations of homogeneous type) provided acetylene molecules are suitably placed, it is not impossible that propagation and termination can be slow enough to influence the kinetics profoundly, especially if additional steps occur involving migration of radicals on the catalyst, *e.g.*, as in the suggested mechanism of formation of branched structures; a complex series of successive reactions then takes place. An attempt at general kinetic analysis is almost certainly premature, the difficulties being magnified by the heterogeneous nature of the reaction and the fact that the chains are predominantly short, with several possible modes of termination. Explanation of the observed order with respect to hydrogen again presents some difficulty. Other complicating factors have already been indicated; to these should be added the possibility of deposition of polymers on the catalyst, especially in so far as it may affect the observed heats of activation. Propagation of chains in the gas phase and decomposition of acetylene might also occur, but there is no evidence that the extent of either process is sufficient to demand modification of the main arguments of the discussion.

The slight difference in orders of reactions (I) and (II) (Part I) is presumably to be explained in terms of a greater proportion of hydrogen in the adsorption layers at higher hydrogen : acetylene ratios, in such a way as to favour ethylene production somewhat, at the expense of polymerisation, but an attempt to interpret this and other smaller details of the results more precisely is speculative in view of the more general uncertainties.

Closer elucidation must await knowledge of the structures of the products at *ca.* 100° or less (especially contributions of branched structures), and study of the effects of temperature and gas pressures on the chain length and distribution of structures in the products of reaction (II).

The author has pleasure in thanking Mr. D. Ll. Hammick for much help and advice, and the Department of Scientific and Industrial Research for a grant.

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[*Received, September* 29*th*, 1944.]