553. *The Catalytic Hydrogenation of Unsaturated Hydrocarbons. Part I. The Kinetics of the Hydrogenation of Acetylene over a Nickel–Pumice Catalyst.*

By G. C. Bond.

The kinetics of acetylene hydrogenation over a nickel–pumice catalyst have been studied in a static system under a wide variety of conditions between 80° and 110° c. The kinetic form of pressure–time curves depends on (i) the initial hydrogen : acetylene ratio, (ii) the order of addition of the reactants if added separately, and (iii) the pretreatment of the catalyst, if the reactants are added together. When acetylene is added first, the pressure–time curves are of the first order in hydrogen if the initial hydrogen : acetylene ratio is less than about two, in agreement with the observed initial rate expression. If this ratio is greater than about two, the pressure–time curves are of zero order and the initial rate of pressure fall is given by:

$$-\mathrm{d}P/\mathrm{d}t = k_{\mathrm{A}}P_{\mathrm{H}_2} + k_{\mathrm{B}}(P_{\mathrm{H}_2} - P^{\circ}{}_{\mathrm{H}_2})$$

where $P^{\circ}{}_{\mathrm{H}_2} \gtrsim 2P_{0,\mathrm{H}_2}$; the temperature-dependence of the rate constants k_{A} and k_{B} gives activation energies of respectively 10·3 and 23·8 kcal./mole. The addition of various pressures of hydrogen during an experiment under these conditions leads to faster rates which conform with the above rate expression. If hydrogen is admitted to the reaction vessel before the acetylene, the pressure–time curves generally show two distinct zero-order regions, and the initial rates are proportional to hydrogen pressure over a wide range.

A comparison is made with previous work on similar systems, and possible mechanisms are advanced; physically adsorbed hydrogen molecules may be concerned in the process whose specific rate constant is k_{B}.

METAL-CATALYSED hydrogenation of acetylene has been the subject of numerous experimental studies, many of which have been described in a recent review.[1] Most of the metals in Group VIII of the periodic classification are efficient for this reaction: but, in addition to the expected products, namely, ethylene and ethane, polymers are formed.[2] The extent of polymerisation varies greatly with the nature of the Group VIII metal, being more marked with iron, cobalt, or nickel than with metals in the palladium and the platinum triad. This variation has been attributed to an effect of the metallic radii.[3] The extent of polymerisation is moreover much less with methylacetylene than with acetylene itself, probably owing to the steric hindrance by the methyl group.[4] The formation of polymers greater than dimers is almost unknown for higher acetylenes.[5]

Other features of interest often met in this system are, first, highly selective production of the corresponding olefin under favourable conditions and, secondly, stereospecific

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[1] Bond, in "Catalysis," Vol. III, edited by Emmett, Reinhold Publ. Corp., New York, 1955.
[2] Sheridan, *J.*, 1945, 133.
[3] Sheridan and Reid, *J.*, 1952, 2962.
[4] Bond, *Trans. Faraday Soc.*, 1952, **48**, 651.
[5] Campbell and Campbell, *Chem. Rev.*, 1942, **31**, 77.

production of a *cis*-olefin when a disubstituted acetylene is hydrogenated. Some results to be presented in Part II will bear on this point.

A further feature of this system, which has received less attention, is the abnormal kinetics. The method of initial rates almost invariably leads to a rate expression of the form:

$$-\mathrm{d}p/\mathrm{d}t = kP_{\mathrm{H_2}}P^{\circ}_{\mathrm{C_2H_2}}$$

although negative orders in acetylene have sometimes been reported. The integrated form of this expression, however, describes the pressure fall as a function of time throughout an experiment in a static system only if the initial hydrogen : acetylene ratio is less than about 2.[6] When this ratio is 2 or more [7] the rate of pressure fall is constant until most of the acetylene has been removed. These statements apply equally to the hydrogenation of acetylene on most of the metals of Group VIII (the exceptions being ruthenium and osmium, which are almost inactive [3]), and to methylacetylene. It is unlikely therefore that the occurrence of the zero-order reaction is connected in any way with polymerisation. No explanation of this effect has yet been proposed.

The present paper describes a detailed study of the kinetics of hydrogenation of acetylene over a nickel–pumice catalyst. This type of catalyst has been used before [2,4,6] and has the merit that it is not poisoned by acetylene as are most unsupported nickel catalysts. All the present work (some 300 runs in all) has been carried out with only two catalyst samples. Particular attention has been paid to studying the conditions under which the zero-order reaction is set up, and to the properties of the reactive layer when this kinetic form obtains.

EXPERIMENTAL

Apparatus.—The apparatus consisted of a standard high-vacuum system with arrangements for purification, storage, and transfer of gases; reactions were carried out in a 100 ml. cylindrical Pyrex vessel. In early experiments, the catalyst granules lay at the bottom of the vessel, but later they were supported on a saucer-shaped spiral of thin glass rod held in the centre of the vessel. Periodic cleaning of the vessel was necessitated by the gradual formation of an involatile liquid polymer.

Temperature Control and Measurement.—The reaction vessel was surrounded by an electrically heated furnace, maintained within ±0·1°. Temperatures were measured with a calibrated chromel–alumel thermocouple.

Reactants and Catalyst.—Hydrogen (British Oxygen Co.) was passed through a bed of platinised asbestos at 200° in an electric furnace, then through a trap immersed in liquid nitrogen.

Acetylene (British Oxygen Co.) was subjected to repeated bulb-to-bulb distillation, with rejection of generous head and tail fractions. In some early experiments, acetylene was prepared by the action of water on calcium carbide, and this behaved identically with the commerical product.

A batch of pumice-supported nickel catalyst containing 9·5% of nickel was prepared by the standard procedure; [4] all the work described in this and the following paper was carried out on two 1 g. samples drawn from it. The first sample (A) was initially reduced with hydrogen *in situ* at 250° for $\frac{1}{2}$ hr., then several times under similar conditions after accidental or intentional exposure to air. 240 runs were performed over this sample during 15 months, after which time it was about five-fold less active than initially; however, some irreversible changes had also occurred, since it did not then exhibit certain kinetic features characteristic of its earlier history. Sample B was reduced with hydrogen *in situ* at 300° for $\frac{1}{2}$ hr.

Analysis.—While most of the work described in this paper relies solely on the interpretation of the observed pressure–time curves, a few product samples were subjected to mass-spectrometric analysis. The instrument has been fully described elsewhere: [8] accelerating voltages of 50 and 12·7 ev were employed. The mass spectrum of each component was measured separately at the appropriate voltage, and the analyses were performed by standard methods.

[6] Sheridan, *J.*, 1944, 373.
[7] de Pauw and Jungers, *Bull. Soc. chim. belges*, 1948, **57**, 618.
[8] Dainton and McElcheran, *Trans. Faraday Soc.*, 1955, **51**, 657.

RESULTS

Effect of Variables on the Form of Pressure–Time Curves.—A large number of experiments between 80° and 110° showed that, in addition to the expected effect of reactant ratio, there was a marked dependence of the form of the pressure–time curves on both the order of addition of the reactants to the reaction vessel and the pretreatment of the catalyst. It is convenient to classify the observed types of pressure–time curves as follows:

Type I: zero-order reaction, the rate being constant up to a pressure fall about equal to the initial acetylene pressure.

Type IIA: a " broken " curve, consisting of two linear portions of different rates.

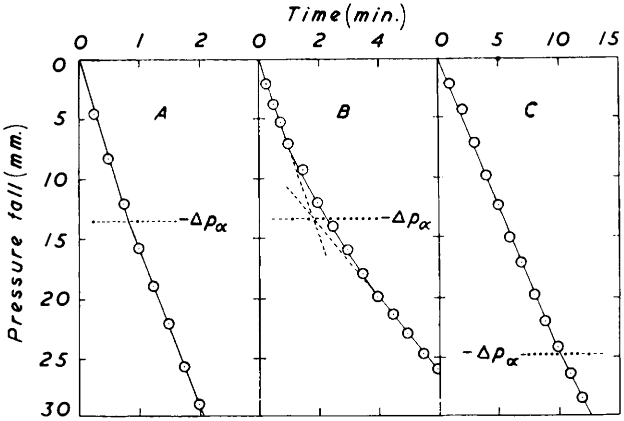
Type IIB: a " broken " curve, consisting of a curved portion (order greater than zero) followed by a linear (zero-order) portion.

Type IIC: as type IIA, but with the break occurring after a greater percentage reaction.

Type III: first-order reaction in hydrogen.

In agreement with previous findings,[4, 6] type I curves were only encountered with initial $H_2 : C_2H_2$ ratios greater than about 2, and type III curves with ratios less than about 2. The precise ratio at which the transition from type III to type I occurs will be discussed below. The various type II curves were also only met with when initial $H_2 : C_2H_2$ ratios greater than about 2 were used; few experiments were carried out with lower ratios under conditions where type II curves result. Typical examples of the type II curves are shown in Fig. 1; in these curves, the first and the second portion will be referred to respectively as the α- and the β-phase, and the rates as R_α and R_β, the former being the *initial* rate in curves of type IIB. The points of transition between the phases, $-\Delta p_\alpha$, are obtained as shown in Fig. 1. The conditions in the reactive layer which result in a type I curve will be called a type I state; similarly for other types.

FIG. 1. *Examples of pressure–time curves. A, a curve of type* IIA; *B, a curve of type* IIB; *C, a curve of type* IIC. *The initial acetylene pressures were about* 30 *mm. in each case.*



When the reactants were admitted to the reaction vessel consecutively, an interval of about 2 min. elapsed between the admissions: such a procedure is equivalent to a 2 min. pretreatment of the catalyst with the first-added reactant before starting the reaction. Type I curves almost invariably resulted when acetylene was admitted first, regardless of the type of curve in the previous experiment, provided only that the initial $H_2 : C_2H_2$ ratio was greater than about two. The only exception was with a freshly reduced catalyst, where the first run showed a type IIA curve; in the second run, a type I curve was obtained by admitting the acetylene 5 min. before the hydrogen, and normal behaviour was then found in succeeding experiments.

Prior addition of hydrogen generally gave curves of type IIB when the initial $H_2 : C_2H_2$ ratio was greater than about two, again regardless of the form of the curve in the previous run. However, pretreatment with hydrogen for 2 min. was insufficient to change the surface state to that of type IIB if the previous run had involved excess of acetylene, and a type I curve resulted instead. It was. however, sufficient to nullify the effect of pretreatment with acetylene for 15 min.

The types of curve observed when premixed reactants ($H_2 : C_2H_2$ ratio slightly greater than two) were used depended very markedly on the pretreatment to which the catalyst had been subjected. In the reaction of a premixture over a freshly reduced new sample of catalyst, the first two runs gave type IIB curves while the third and subsequent runs gave type IIA curves. This change of behaviour was apparently peculiar to the new sample, as after later reductions following accidental oxidations of the catalyst type IIA curves were immediately obtained with the premixture. When a premixture was used for a series of experiments, the curves were all of type IIA if there had been a hydrogen pretreatment before the first run, or if excess of hydrogen had remained from the previous experiment. However, where there had been an acetylene pretreatment lasting 15 min. or longer (followed by pumping), curves of type I resulted and continued to be given if the interval between runs was not too great. Acetylene pretreatments of up to 3 hr. had no adverse effect on the rate of the following reaction. A run with the premixture following acetylene pretreatment for 10 min gave a curve of type IIC: the period of acetylene pretreatment necessary to convert the surface state from IIA or IIB into I is therefore 10—15 min. at about 100°, and the type IIC curve is regarded as being intermediate between types IIA or IIB and I.

A run in which premixing followed acetylene pretreatment for 17·5 hr. and hydrogen pretreatment for 5 min. gave a type IIA curve, but a further run where the times were respectively 2½ hr. and 1 min. gave a type IIC curve. Hydrogen pretreatment for 1—5 min. is therefore necessary to nullify the effect of a lengthy acetylene pretreatment, and the type IIC curve again denotes a surface state intermediate between that of types I and IIA.

A run with premixture over a catalyst pretreated with either reactant is therefore of the same in type as, or similar to, that obtained when that reactant is admitted first to the reaction vessel.

In series of experiments with (i) various pressures of a standard premixture or (ii) premixtures of various compositions, $-\Delta p_\alpha$ for type IIA curves was 0·34—0·49 times the initial acetylene pressure, depending on temperature and hydrogen pressure. The addition of a further quantity of acetylene during the α-phase of a reaction where prior hydrogen addition was employed increased $-\Delta p_\alpha$ to the value to be expected if the amount added had been present from the beginning.

In the first fourteen runs performed under a variety of initial conditions over the second catalyst sample between 80° and 100°, the rate increased after a pressure fall about equal to the initial acetylene pressure. The relative activity of the catalyst for this second stage declined with time; if the maximum observed fast rate be designated R_γ, the ratio $R_\gamma : R_\beta$ in the case of type II curves and $R_\gamma : R$ in the case of type I curves (R being the zero-order rate) fell from an initial value of about five to about two after ten runs. From a series of experiments performed in close sequence it appeared that R_γ was proportional to the hydrogen pressure at the onset of the acceleration. Similar behaviour has been observed with palladium and platinum catalysts,[4, 9, 10] and over nickel at lower temperatures,[7] but not in other work with nickel catalysts of the type used here.[4, 6] The increased rate is attributable to the faster reduction of the ethylene formed in the first stage of the reaction as compared with that of acetylene, but its occurrence under these conditions is somewhat surprising.

In numerous cases where a type IIA or IIB curve was obtained in a run immediately following or preceding one which gave a type I curve, it was generally found that R_β rather than R_α corresponded to the zero-order rate in the latter case.

Kinetic Behaviour under Type I *and Type* III *Conditions.*—(a) *Orders in hydrogen obtained by the initial-rate method.* Series of experiments were performed to determine the order of the reaction in hydrogen by the initial-rate method, acetylene being admitted first to the reaction vessel, so that curves of types I and III resulted when the initial $H_2 : C_2H_2$ ratios were respectively greater or less than about two. Reaction orders were obtained by using (*a*) differing initial acetylene pressures at the same temperature and (*b*) a constant initial acetylene pressure at varying temperatures, the initial $H_2 : C_2H_2$ ratios lying between about one and eight. A typical set of results is shown in Fig. 2, and all other series gave results of a similar type. The rate–pressure plot is characterised by an inflexion at the point where the initial hydrogen pressure is about twice that of the acetylene pressure, this corresponding approximately to the point at which the pressure–time curves change their form. The rate is directly proportional

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[9] Sheridan, *J.*, 1945, 305.
[10] Sheridan, *J.*, 1945, 470.

to hydrogen pressure below the break, and at higher hydrogen pressures it may be assumed that the observed rate is the sum of two separate rates, one of which is directly proportional to hydrogen pressure (a continuation of the first-order process observed at lower pressures), the other being proportional to ($P_{H_2} - P^\circ_{H_2}$) where P_{H_2} is the initial hydrogen pressure and $P^\circ_{H_2}$ the hydrogen pressure at the point where the inflexion occurs, *i.e.*, the threshold pressure for the second reaction. The latter quantity is obtained by interpolation. Thus for type III curves

$$\text{Rate} = k_A P_{H_2}$$

and for type I curves

$$\text{Rate} = k_A P_{H_2} + k_B(P_{H_2} - P^\circ_{H_2})$$

Table 1 summarises the dependence of the ratio k_B/k_A and of $P^\circ_{H_2}$ on the experimental variables: in this Table, $P_{C_2H_2}$ is the mean initial acetylene pressure, individual values being within 1 mm. of the stated value. At 86°, $P^\circ_{H_2}/P_{C_2H_2}$ is independent of initial acetylene pressure, while k_B/k_A shows a slight but barely significant tendency to increase with increasing acetylene pressure. The quotient $P^\circ_{H_2}/P_{C_2H_2}$ decreases slightly with increasing temperature, while k_B/k_A increases very rapidly. The only previous rate measurements made with excess of hydrogen are those by de Pauw and Jungers;[7] using nickel powder at very much lower temperatures, they observed a dependence of rate on hydrogen pressure similar to that described here.

FIG. 2. *The dependence of initial rate of pressure fall on initial hydrogen pressure at 93·5°; acetylene pressure, 30·5 ± 1·0 mm.*

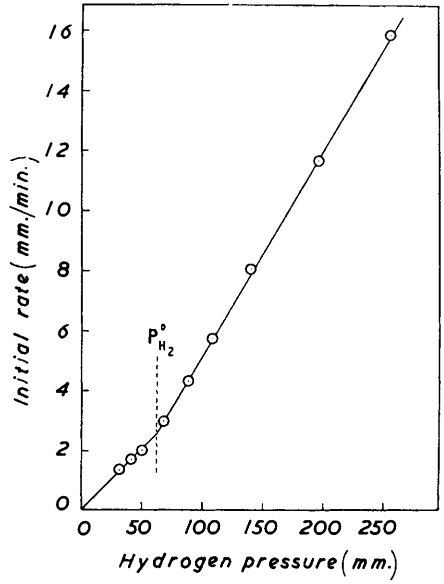
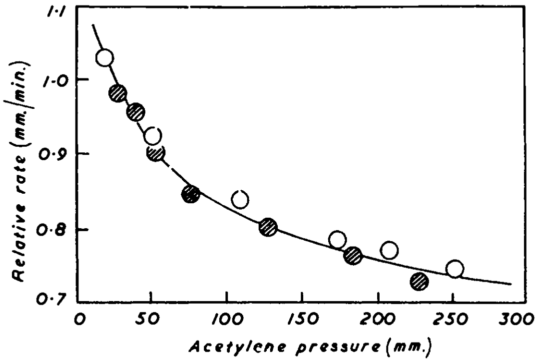


FIG. 3. *The dependence of rate on acetylene pressure.*



○, *Values by the direct method at* 85·7°. ●, *Values by the addition method at* 98·2°. *See text for further description.*

TABLE 1. *The dependence of k_B/k_A and of $P^\circ_{H_2}$ on initial acetylene pressure and temperature.*

Temp.	$P_{C_2H_2}$ (mm.)	$P^\circ_{H_2}$ (mm.)	k_B/k_A *	$P^\circ_{H_2}/P_{C_2H_2}$ †	Temp.	$P_{C_2H_2}$ (mm.)	$P^\circ_{H_2}$ (mm.)	k_B/k_A *	$P^\circ_{H_2}/P_{C_2H_2}$ †
86·0°	14·7	32±1	0·35	2·18	93·5°	30·8	67±2	0·62	2·16
86·0	31·7	70±2	0·41	2·21	110·0	31·2	64±2	0·32	2·05
86·0	60·5	130±4	0·43	2·15					

* ±0·04. † ±0·07.

(b) *Order in hydrogen obtained by the addition method.* The implication of the zero-order reaction is that the rate depends solely on the initial partial pressures of reactants and not on their changing concentrations during the experiment, despite the dependence of rate on hydrogen pressure just described. It might therefore be reasonably expected that the addition of further quantities of either acetylene or hydrogen during a run would have little effect on the rate. Experiments were carried out to test this, and on the contrary it was found that (i) addition of hydrogen led to an increased zero-order rate, and (ii) addition of acetylene led to a decreased rate. These experiments were performed with a premixture whose $H_2 : C_2H_2$ ratio was slightly greater than two, the catalyst having been pretreated with acetylene to establish type I conditions.

A series of experiments was performed at 98·6° with a fixed pressure of a standard premixture to which various hydrogen pressures were added after a fixed pressure fall. By reason of the polymerisation, the rate of total pressure fall is greater than the rate of hydrogen pressure fall by a factor which for the present experimental conditions has been found [11] to be about 1·30. The pressure of the original hydrogen which had not reacted at the time of the addition was calculated with the aid of this factor, and added to the hydrogen pressure which was subsequently admitted. A possible error of $\pm 0{\cdot}1$ on the figure of 1·30 affects this calculation only slightly. The ratio of the rates before and after the addition, R_2/R_1, was then plotted against the total hydrogen pressure after the addition; the points lay closely about a straight line which made an intercept of 28 mm. on the pressure axis. From Table 1 it is apparent that the rate measurements made with initial $H_2 : C_2H_2$ ratios greater than two, when plotted against hydrogen pressure and extrapolated, likewise make intercepts on the pressure axis: the values are however temperature-dependent and the expected value at 98·6° is 29 mm. The results obtained by the addition method therefore correspond to those found by the initial rate method when initial $H_2 : C_2H_2$ ratios are varied, in that they measure $(k_B + k_A)$. One assumption must however be made before k_B/k_A can be determined for these results. By interpolation into the results in Table 1, the value of $P^\circ_{H_2}$ at 98·6° and 33·2 mm. of acetylene (the mean value in the addition experiments) is 70·5 mm.; this defines the value of k_A and hence also of k_B/k_A which has a value of 0·805. This agrees well with the value of 0·78 which the initial-rate method would be expected to give at this temperature.

(c) *Temperature-dependence of the rate constants.* The difference between the activation energies E_B and E_A for the two processes whose rate constants are respectively k_B and k_A was determined by plotting log (k_B/k_A) against reciprocal absolute temperature; the four points lay on a straight line from the slope of which $(E_B - E_A)$ was found to be $13{\cdot}5 \pm 0{\cdot}1$ kcal./mole. The activation energy E_A was measured between 68° and 152° for an initial $H_2 : C_2H_2$ ratio of 1·45, the acetylene being added first. A value of $10{\cdot}3 \pm 0{\cdot}3$ kcal./mole was obtained; this is somewhat lower than the values reported by Sheridan.[2] It therefore follows that E_B has a value of $23{\cdot}8 \pm 0{\cdot}4$ kcal./mole, which is remarkably high for a hydrogenation.

More recent work by Mr. R. S. Mann has however shown that $(E_B - E_A)$ is not a fixed quantity, but varies from one catalyst sample to another in a manner which is at present irreproducible. This aspect of the work will be reported later.

(d) *Orders in acetylene obtained by the initial-rate method.* The order in acetylene was determined by the initial-rate method at 85·7° and a mean initial hydrogen pressure of 51·3 mm.; initial acetylene pressures were between 15 and 254 mm. In the majority of the experiments, the pressure–time curves were of type III, but a plot of initial rate (regardless of the kinetic form of the curve) *versus* acetylene pressure showed no discontinuity of rate in passing from curves of type III to type I. The results are shown in Fig. 3, where the rates are expressed as fractions of the value for an acetylene pressure of 25 mm.: this is to facilitate comparison with results to be described in the next paragraph. The points lie closely about a curve corresponding to an order in acetylene of $-0{\cdot}14$.

A second series of experiments was carried out at 92·0° with a mean initial hydrogen pressure of 102·2 mm. and initial acetylene pressures between 15 and 101 mm. In this case the rates (regardless of the kinetic form of the curve) were within error independent of acetylene pressure.

(e) *Orders in acetylene obtained by the addition method.* It has been noted above that addition of acetylene during an experiment giving a type I curve results in a decrease in rate, and several series of experiments (cf. Table 2) were performed to determine the order in acetylene by this method. In the first two and the last two series, the acetylene was added before the hydrogen, while in series III a premixture was used after an acetylene pretreatment. Acetylene pressures within the ranges shown in column 5 were added after the pressure falls given in column 6.

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[11] Bond, Ph.D. thesis, Birmingham, 1951.

In series I, the pressure–time curves both before and after the addition of acetylene were of type III, and the rates were measured from the first-order rate constants after conversion of the observed pressure fall into fall in hydrogen pressure by means of the analytical data.[11] The ratio of the rate constants before and after the addition was plotted against total acetylene pressure after the addition, and the points lay about a curve corresponding to an order in acetylene of −0·19.

TABLE 2. *Summary of the conditions employed and the results obtained in determining orders in acetylene by the addition method.*

Series	Temp.	Initial $H_2 : C_2H_2$	Mean initial p_{H_2} (mm.)	C_2H_2 added (mm.)	$-\Delta p_\alpha$ (mm.)	Order in C_2H_2
I	92·0°	0·99 ± 0·05	50·0	15—157	10·9 ± 0·5	−0·19
II	88·5	1·94 ± 0·11	67·0	12—17	Variable	−0·2
III	98·2	1·98	66·5	29—205	11·3 ± 0·4	−0·14
IV	92·0	2·95 ± 0·10	104·0	19—64	11·8 ± 0·4	0
V	88·0	5·27 ± 0·13	190·0	15—63	11·7 ± 0·7	+0·25

Acetylene added first, except in series III where a premixture was used.

In the second series, the pressure–time curves were presumably initially of type III, but the changes in rate before the additions were insufficient to warrant the determination of rate constants. Initial rates, designated R_1, were therefore measured directly. After the additions, values of k_2 were determined as before and values of R_2 calculated therefrom for a hydrogen pressure of 67 mm.: the change in the hydrogen pressure is thereby allowed for, and the rates R_1 and R_2 are then directly comparable. In the first two experiments, the acetylene was added after pressure falls of respectively 6 and 12 mm. in amounts to give a total acetylene pressure of 43 ± 1 mm. Values of R_2/R_1 were respectively 0·92 and 0·89, *i.e.*, essentially independent of pressure fall. In further experiments, the pressure fall was varied from 6 to 17 mm. and the pressure of added acetylene fixed at 12·5 mm. Values of k_2 were constant within 2%, indicating as expected that the first-order R_2 is proportional to the hydrogen pressure at the time the acetylene is added. When R_2 was corrected to a hydrogen pressure of 67 mm., the ratio R_2/R_1 fell with increasing total acetylene pressure, corresponding to an order in acetylene of about −0·2. The pressure range covered was, however, not large enough to give this value great precision.

In the third series, values of R_1 and R_2 were obtained as described in the last paragraph. The plot of R_2/R_1 *versus* total acetylene pressure is shown in Fig. 3, together with the results obtained by the initial-rate method: the close concordance is strong confirmation of the validity of the addition method of determining reaction orders. Similar experiments at 87·4°, but covering a smaller range of added acetylene pressures, confirmed that the temperature-dependence of the order in acetylene is not great.

In series IV, without allowance for the decrease in hydrogen pressure, the ratio of the rates, R_2/R_1, was unity within 2%, *i.e.*, the order in acetylene was zero. Allowance for the decreased hydrogen pressure at the time of additon changed R_2/R_1 to give a very slightly positive order in acetylene.

In series V, the zero-order rates following the additions were 1·21—1·27 times faster than the initial rates, showing no regular trend with changing total acetylene pressure. Taking the ratio of the rates as unity for an acetylene pressure of 27 mm. gives results corresponding very roughly to an order in acetylene of +0·25.

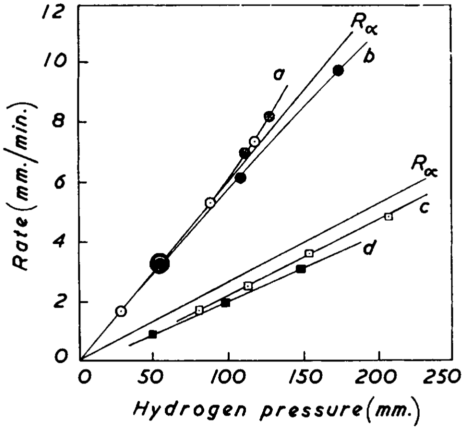
The effect of adding premixed reactants during a type I reaction was studied at 93·5°. Initial $H_2 : C_2H_2$ ratios of 2·12 were used, the acetylene being added first, and variable pressures of a standard premixture ($H_2 : C_2H_2$, 2·10) were added after a pressure fall of 12 mm. Both reactants affected the rate, and it was assumed that the two effects were independent. The action of the added hydrogen was derived from the results described in an earlier section; the ratio $R_2 : R_x$, where R_x is the rate expected simply due to the changed hydrogen pressure, was plotted against total acetylene pressure, and an order in acetylene of about −0·4 was deduced. Since this is much lower than the values found by the other methods, it is likely that the assumption concerning the independence of the effects of the added reactants is not justified.

(f) *Reactant ratio for transition from type I to type III curves.* The initial reactant ratio at which pressure–time curves change from type III to type I has been found to depend on whether the reactants are added singly or in admixture. A premixture having a $H_2 : C_2H_2$

ratio of 1·97 gave a type I curve at 98°, but with prior addition of acetylene a type III curve was obtained with a $H_2 : C_2H_2$ ratio of 2·11 at 93·5° and a type I curve with a ratio of 2·16 at 105°. These results therefore confirm the supposition that the inflexions in the rate–hydrogen pressure plots described above correspond to the point at which the kinetic form of the pressure–time curves change; the transition ratios expected from the hydrogen order plots are respectively 2·16 and 2·08 at 93·5° and 105°.

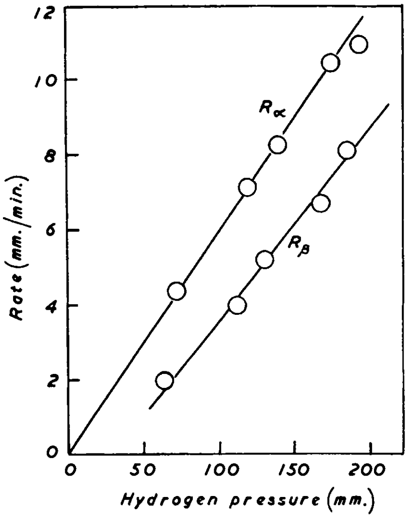
Kinetic Behaviour under Type II Conditions.—(a) *Kinetics under type* IIA *conditions.* As has been described in an earlier section, pressure–time curves showing two distinct zero-order rates were obtained when premixed reactants reacted over a hydrogen-pretreated surface, the inflexion occurring after a pressure-fall equal to obout one-half the initial acetylene pressure. Series of experiments were carried out at temperatures close to 85° and 100°, to determine the dependence of the two rates on partial-pressure variations at these temperatures. The experiments were of two types: the first employed variable pressures of a standard premixture, so that the partial pressures of both reactants were varied simultaneously, while the second employed pressures of premixtures of various compositions chosen to make the initial pressure of acetylene constant in all cases.

FIG. 4. *The dependence of rates on hydrogen pressure under type* IIA *conditions (premixed reactants).*



a, R_β relative to R_α at 101·5°; *open circles,* ○, *series* IV; ●, *series* VI. *b, R_β relative to R_α at* 101·3°, *series* VII. *c, R_β relative to R_α at* 85·3°, *series* VIII. *d, R_β relative to R_α at* 85·6, *series* V. *(Individual values of R_α are omitted for clarity.)*

FIG. 5. *The dependence of R_α and R_β on hydrogen pressure under type* IIB *conditions (prior admission of hydrogen) at* 92·0° *(series* II, *Table* 4).



The conditions used in these experiments are detailed in Table 3; where the premixed reactant composition is stated to be fixed, the initial $H_2 : C_2H_2$ ratios were 2·02 ± 0·02. The results are shown graphically in Fig. 4, where values of R_α are plotted against initial hydrogen pressures, and the corresponding values of R_β against the hydrogen pressure at $-\Delta p_\alpha$, the point at which the rate curves intersect (see Fig. 1). This second hydrogen pressure was obtained by assuming, as before, that the rate of hydrogen removal is 0·77 times that of the

TABLE 3. *Summary of conditions employed in studying kinetics by use of premixed reactants.*

Series	Premixed reactants Compn.	Pressure	Temp.	P_{H_2} range (mm.)	$P_{C_2H_2}$ range (mm.)
IV	Fixed	Variable	101·5°	36—142	18—71
VI	,,	,,	101·3	67—158	33—77
VIII	,,	,,	85·3	96—248	47—121
VII	Variable	Fixed $P_{C_2H_2}$	101·3	67—188	32·9 ± 0·5
V	,,	,,	85·6	81—184	26·0 ± 1·0

rate of total pressure fall: an error of ±10% on this factor would not affect the results significantly.

The rates R_α are always proportional to initial hydrogen pressure. Series IV and VI (performed respectively over catalyst samples A and B) are in good agreement: in Fig. 4, the rate constant k_α for the latter series has been normalised to fit the value in the former series, and the values of R_β from both series then lie on one curve (curve *a*). The same procedure was then applied to series VII, but the R_β values lie below those for R_α (curve *b*). Similar treatment has been given to the results obtained at 85°, but here both the sets of R_β values (curve *c*, series VIII, and curve *d*, series V) lie below the R_α line.

The results at the higher temperature indicate that for hydrogen pressures less than about 100 mm. R_β is within error proportional to the hydrogen pressure at $-\Delta p_\alpha$: this is more nearly true for series IV and VI than for series VII. Above this pressure, deviations in opposite directions become marked, and increase more rapidly with increasing hydrogen pressure in the case of series IV and VI. The situation at the lower temperature is clearly substantially different.

Values of $-\Delta p_\alpha/P_{C_2H_2}$ (where $P_{C_2H_2}$ is the initial acetylene pressure) vary somewhat with temperature and initial hydrogen pressure: at about 85° values increased smoothly from 0·34 to 0·42 as the hydrogen pressure rose from 60 to 160 mm., while at about 100° they increased from 0·43 to 0·49 in the same hydrogen-pressure range.

(b) *Kinetics under type* IIB *conditions.* Series of experiments at 81·5°, 92·0°, and 104·6° employed a fixed initial pressure of acetylene (~30 mm.) and a variable pressure of hydrogen, the latter being admitted to the reaction vessel before the acetylene. Pressure–time curves were of type IIB. The results of a typical series of experiments are shown in Fig. 5, where R_α (obtained as described earlier) is plotted against the initial hydrogen pressure, and R_β against the hydrogen pressure at $-\Delta p_\alpha$, the point at which the extrapolated rate curves intersect (see Fig. 1). This second hydrogen pressure was estimated in the usual manner. Since $-\Delta p_\alpha$ is approximately constant in all these experiments, an error in the factor of 0·77 will lead to a constant error in the calculated hydrogen pressure; this will affect only the lateral position of the R_β–hydrogen pressure line (and only slightly), and not the slope. The series at the other temperatures gave results of the same form. Table 4 gives details of these experiments. The equations relating the quantities in the Table are $R_\alpha = p_\alpha P_{H_2}$ and $R_\beta = k_\beta(P_{H_2} - P'_{H_2})$, but the second equation is not valid at hydrogen pressures less than about 70 mm. The ratio $k_\alpha : k_\beta$ is seen to be only very slightly temperature-dependent. In these experiments, values of $-\Delta p_\alpha/P_{C_2H_2}$ (which cannot be determined with great accuracy) are rather smaller than in experiments with premixed reactants. Individual values range between 0·33 and 0·40, but are too scattered to reveal any dependence on initial hydrogen pressure: mean values at the three temperatures show no regular dependence on temperature.

TABLE 4. *Kinetic results obtained with prior addition of hydrogen.*

Series	Temp.	P_{H_2} (mm.)	$P_{C_2H_2}$ (mm.)	k_α (min.$^{-1}$)	Mean $-\Delta P_\alpha$	k_β (min.$^{-1}$)	P'_{H_2} (mm.)	$k_\alpha : k_\beta$
I	81·5°	75—226	32·0 ± 1·0	0·0531	12·5	0·0435	25	1·220
II	92·0	73—197	32·3 ± 1·3	0·0587	11·0	0·0498	27	1·180
III	104·6	74—153	32·5 ± 1·5	0·0991	12·0	0·0860	28	1·151

Selectivity.—The products of a few runs were subjected to mass-spectrometry, to determine the ethylene : ethane ratio. The results are in Table 5; the analyses were performed after pressure falls equal to the initial acetylene pressure. The degree of selectivity is here expressed as ethylene yield divided by the sum of the ethylene and the ethane yield. Sheridan's results [2] obtained at the same temperature are included in the Table.

TABLE 5. *Dependence of the degree of selectivity on hydrogen pressure, at* 99·0° ± 0·5°.

Run	$P_{C_2H_2}$ (mm.)	P_{H_2} (mm.)	Selectivity	Reference	Run	$P_{C_2H_2}$ (mm.)	P_{H_2} (mm.)	Selectivity	Reference
A-231	38·2	52·0	0·866	This work	B-46	35·0	124·8 *	0·902	This work
A-232	35·0	124·5	0·854	,,	—	200	200 *	0·890	Ref. 2
B-45	37·9	131·0	0·864	,,	—	200	400 *	0·846	,,

* Hydrogen added first to the reaction vessel.

The selectivities found when the normal order of addition is followed agree well with Sheridan's values, although he employed the reverse order of addition. They are independent of hydrogen pressure. There is evidence that in this work prior addition of hydrogen to the reaction vessel results in a somewhat higher selectivity (run B-46); the age of the catalyst sample is apparently irrelevant (compare runs A-232 and B-46).

Reactions between Adsorbed and Gaseous Reactants.—Experiments were conducted to determine the products of the reactions between (i) gaseous hydrogen and adsorbed acetylene, and (ii) gaseous acetylene and adsorbed hydrogen. These experiments were expected to yield information concerning the species adsorbed on the surface under the various conditions giving rise to the various forms of pressure–time curves.

The procedure was as follows: Catalyst sample A was treated with acetylene for 20 hr. at 88·6° and pumped at this temperature for 3 hr., after which time the pressure in the reaction vessel was below 10^{-6} mm.; 155 mm. of hydrogen were added immediately the pumping was stopped, and portions of the gas removed for analysis by mass-spectrometry after 1 and 12 min. (run A-76). 18 hr. later the remainder of the hydrogen was evacuated at 88·6°, the pumping being continued for 2½ hr., after which time a hard vacuum was obtained. 127 mm. of acetylene were then admitted, and samples removed for analysis after 1 and 12 min. (run A-77). The cycle of operations used in run A-76 was then repeated, the acetylene added in run A-77 effecting the pretreatment: 89 mm. of hydrogen were used in this experiment (run A-78).

The samples from runs 76 and 78 contained chiefly hydrogen, with small amounts of hydrocarbons and larger amounts of nitrogen (resulting from the original air content of the hydrogen): the analyses were therefore only semiquantitative. In neither case did the 1-min. samples contain any acetylene, only ethylene being detected: the 12-min. samples both contained acetylene (about twice as much in run 76 as in run 78), and ethylene in the same concentration as in the samples taken after 1 min. The ethylene concentration lay between the two 12-min. acetylene concentrations. No ethane was detected in any sample. These results suggest that, on addition of hydrogen, part of the adsorbed acetylene is rapidly hydrogenated to ethylene and part is slowly displaced. The fact that the 12-min. sample from run 76 contained more acetylene than that from run 78, and that a higher hydrogen pressure was used in the former case, might mean that the rate of displacement increases with increasing hydrogen pressure. It is therefore possible that the displacement was not complete even after 12 min. The failure of the ethylene and acetylene to be further reduced is probably explained by saying that their chances of adsorption in an overwhelmingly predominant hydrogen atmosphere were negligible.

The sample from run 77 was chiefly acetylene, but ethylene was detected and its concentration did not change with time: no ethane was found. Work to be described in Part II provides evidence that the reaction is not simply the one-stage addition of two adsorbed hydrogen atoms to an acetylene molecule.

DISCUSSION

It must now be recognised that an unsuspected number of variables affect the kinetics (and therefore the mechanisms) of hydrogenation reactions over supported metal catalysts. Those made apparent by the present work are: (1) the ratio of the partial pressures of the reactants, (2) the order of their addition to the reaction vessel, and (3) the pretreatment of the catalyst. Comparison of this work with an earlier study on nominally the same system indicates a fourth, namely, (4) the method of preparing the catalyst. Thus Sheridan [2, 6] consistently obtained type I curves although adding hydrogen to his reaction vessel before the acetylene; he reduced his catalysts in hydrogen containing ethanol vapour at about 400°. This order of addition when used here always gave type IIB curves. More recent work, to be reported later, suggests that the above list is by no means exhaustive. Any detailed interpretation of the kinetics in a given system should therefore be limited to that system, and may not have wider validity. With this reservation, the results presented above will be discussed.

The Shapes of Pressure–Time Curves.—The results make it clear that the nature and concentrations of the species in the reactive layer vary with experimental conditions, and that changes in their concentrations as the composition of the ambient gas mixture is altered are not always instantaneous. It may be assumed as a starting point that pretreatment of the surface by acetylene results in the formation of a complete chemisorbed layer of this species. Subsequent addition of hydrogen results in a type I or type III curve (depending on the initial hydrogen : acetylene ratio), and it is therefore thought that in a type I or type III surface state the reactive layer is initially poor in hydrogen, and that this state of affairs is maintained throughout the reaction. The principal species in the reactive layer may be adsorbed acetylene and adsorbed vinyl radicals.

On the other hand, it is believed that pressure–time curves of types IIA and IIB result when the reactive layer is initially richer in hydrogen. This additional hydrogen may exist in the form of atoms or more probably combined with acetylene as vinyl radicals. The time required to convert a type I surface state into a type IIA or IIB state depends in some measure on the length of the acetylene pretreatment, and on the procedure in the test run. The situation is roughly the same whether the hydrogen treatment is followed by addition of acetylene (prior hydrogen addition, curve type IIB) or by evacuation of the hydrogen before the addition of premixed reactants (curve type IIA). In the former case, hydrogen pretreatment for 2 min. is sufficient if the foregoing acetylene pretreatment has been short, while in the latter case a hydrogen treatment of 1—5 min. nullifies the effect of lengthy acetylene pretreatment. The times required for the hydrogen concentration in the reactive layer to build up to those values which give rise to curves of type IIA and IIB are therefore appreciable.

As a general principle it is proposed that the kinetic form of the pressure–time curve depends on the nature and especially on the concentrations of the species in the reactive layer at the moment the massive reaction begins; and that if the initial surface state is near its equilibrium state, a steady rate results; and that if it is not the rate alters (from R_α to R_β) as the surface adjusts itself towards the equilibrium state.

Consideration may now be briefly given to the reconversion of a type IIA orIIB surface state into a type I state. Acetylene pretreatment for 2 min. is sufficient to effect this change if the hydrogen is then added to the acetylene to start the massive reaction, whereas a longer acetylene pretreatment (10—15 min.) is required if the acetylene is pumped off and premixed reactants added to effect the massive reaction. The following qualitative explanation can be advanced. The 10—15 min. period is required to form an adsorbed acetylene layer which is stable to pumping: if evacuation is started after a shorter time, some weakly adsorbed acetylene is removed, leaving some surface vacancies which can interact with the hydrogen in the premixture, yielding a surface state giving a type IIC pressure–time curve. If however the acetylene is not pumped off, but hydrogen is added to start the reaction, the hydrogen is presented with a coherent layer of adsorbed acetylene and a type I curve results. This explanation implies either surface heterogeneity (for which there is other evidence) or a relatively slow migration of acetylene from a weakly bound state to a more strongly bound state.[12]

Further evidence supporting these concepts comes from studying the reaction between one gaseous and one adsorbed reactant. If one assumes again that prolonged exposure of the surface to acetylene leads to a complete layer of chemisorbed acetylene, the reaction of gaseous hydrogen with adsorbed acetylene converts a type I surface state into a type IIA or IIB state. The appearance first of ethylene and then of acetylene shows that there must be appreciable but not complete coverage of the surface by chemisorbed hydrogen (or vinyl radicals) in the type II state. The fact that in this process the adsorbed acetylene suffers either desorption or hydrogenation is evidence for an energetically heterogeneous surface.

Further, that the reaction of gaseous acetylene with adsorbed hydrogen leads to the *rapid* formation of ethylene shows that the adsorbed hydrogen layer is quickly replaced by an adsorbed acetylene layer, and this lends weight to the suggestion that the concentration of adsorbed hydrogen in the type I state is low.

Kinetics under Type I *and Type* III *Conditions.*—A change in the form of pressure–time curves as the ratio of the partial pressures of the reactants is changed has been found previously,[4,6] although its significance has not been discussed. The most difficult observation to interpret (and the one which probably contains the key to the problem) is the zero-order kinetics found when the initial hydrogen : acetylene ratio is greater than about two. Disagreement between kinetic expressions derived from initial-rate measurements and those derived by analysing the course of the reaction is by no means uncommon in heterogeneous catalysis; a number of such cases have been discussed theoretically by Thon and Taylor,[13] who suggested the importance of surface chain reactions. They proposed that in the initial stages of a reaction a chain-carrying intermediate determines the rate; if this maintains its concentration through the reaction, the later kinetics will be of zero order, but if its concentration declines during the reaction, the later kinetics will be complex and in disagreement with the initial-rate expression. In the limit, if the chain reaction is not sustained, the integrated form of the initial-rate expression will describe the change in rate throughout the reaction.

This concept is however not without its difficulties, especially when applied to the interpretation of a zero-order rate. First, a stationary concentration of intermediates must be maintained throughout the reaction, and it is difficult to see why the intermediate-forming process should cease after the early stages of the reaction. All conceivable combinations of initiation, propagation, and termination processes lead to a concentration of intermediates which may be instantaneously constant but which nevertheless must respond to changes in the pressures of the reactants and thus change through the reaction. Secondly, the product-forming step involves at least one reactant whose pressure will decline through the reaction, and a zero-order rate can only result if the stationary concentration of intermediate is inversely proportional to the pressure of that reactant which reacts with it to form the product. Application of this concept to the present system has not proved fruitful.

The situation in the case of type III pressure–time curves is relatively straightforward: the integrated form of the initial-rate expression (neglecting the slightly negative order in acetylene) describes the change of rate during any reaction. For type I pressure–time curves, the situation is more complex, for they have three characteristics which require interpretation. (1) The rate is constant and thus apparently not responsive to *slow* changes in the gas composition. (2) *Abrupt* changes in the partial pressure of either reactant do affect the rate in a manner which reflects the initial-rate dependence on gas pressures. (3) The initial-rate expression is complex and suggests that the transition in the form of the pressure–time curves from type III to type I is caused by the opening of a second reaction path.

In constructing a tractable reaction mechanism, certain simplifications must be introduced and these must be justified at the outset. It is proposed to set up a reaction scheme leading only to the production of ethylene. Neglect of processes leading to ethane in the early stages of the reaction (*i.e.*, before the acetylene pressure has fallen to near zero) is justified by the observation (Table 5) that the selectivity does not change very significantly within the range of experimental conditions to which this discussion relates. Thus the rate of pressure fall due to the further hydrogenation of ethylene will account for an approximately constant fraction of the total rate. The neglect of steps leading to polymers may be more serious, but there are good grounds for believing that the kinetics of such processes are similar to, if not identical with, those producing ethylene and ethane.[2,6] For the present purpose it therefore suffices to assume that the observed rate of pressure fall is proportional to the rate of ethylene formation.

[12] Dowden, in " Chemisorption," edited by Garner, Butterworths, London, 1957.

[13] Thon and Taylor, *J. Amer. Chem. Soc.*, 1953, **75**, 2747.

The initial adsorption processes (bold type indicates adsorbed species),

$$\mathrm{H_2} \underset{k'_{\mathrm{H}}}{\overset{k_{\mathrm{H}}}{\rightleftharpoons}} 2\mathbf{H} \text{ and } \mathrm{C_2H_2} \underset{k'_{\mathrm{C}}}{\overset{k_{\mathrm{C}}}{\rightleftharpoons}} \mathbf{C_2H_2}$$

are assumed to be followed by

$$\mathbf{H} + \mathbf{C_2H_2} \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} \mathbf{C_2H_3} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

the relative magnitudes of k_1 and k'_1 being such that the equilibrium lies far to the right and the concentration of adsorbed hydrogen atoms sufficiently low to render unnecessary the consideration of other possible processes involving them. Ethylene is taken to be formed in the process

$$2\mathbf{C_2H_3} \xrightarrow{k_2} \mathrm{C_2H_4} + \mathbf{C_2H_2} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

If competitive adsorption of the two reactants is assumed, then:

$$[\mathbf{H}] = \frac{b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}}{1 + b_{\mathrm{C}} P_{\mathrm{C_2H_2}} + b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}}$$

and

$$[\mathbf{C_2H_2}] = \frac{b_{\mathrm{C}} P_{\mathrm{C_2H_2}}}{1 + b_{\mathrm{C}} P_{\mathrm{C_2H_2}} + b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}}$$

where $b_{\mathrm{H}} = k_{\mathrm{H}}/k'_{\mathrm{H}}$ and $b_{\mathrm{C}} = k_{\mathrm{C}}/k'_{\mathrm{C}}$. The hydrogen atoms are then rapidly converted into vinyl radicals whose stationary concentration is given by:

$$[\mathbf{C_2H_3}] = \frac{k_1}{k'_1} [\mathbf{C_2H_2}] \frac{b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}}{1 + b_{\mathrm{C}} P_{\mathrm{C_2H_2}} + b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}}$$

on the permissible assumption that $k'_1 \gg k_2$. If $[\mathbf{C_2H_2}]$ is set equal to unity (*i.e.*, a low concentration of vinyl radicals is assumed), the rate of production of ethylene, step 2 being taken as the only relevant process, is given by:

$$\begin{aligned} \mathrm{d}p_{\mathrm{C_2H_4}}/\mathrm{d}t &= k_2[\mathbf{C_2H_3}]^2 \\ &= k_2\left(\frac{k_1}{k'_1}\right)^2 \cdot \frac{b_{\mathrm{H}} P_{\mathrm{H_2}}}{(1 + b_{\mathrm{C}} P_{\mathrm{C_2H_2}} + b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}})^2} \quad . \; . \; . \quad (A) \end{aligned}$$

If as is likely $b_{\mathrm{H}} \gg b_{\mathrm{C}}$, this expression gives a rate which is proportional to hydrogen pressure and to a small negative power of acetylene pressure (depending on the magnitude of b_{C}), in agreement with observation under type III conditions.

An alternative and essentially equivalent treatment is to suppose that the hydrogen is introduced into the reactive layer by the mechanism:

$$2\mathbf{C_2H_2} + \overset{\mathrm{H_2}}{\vdots} \underset{k'_3}{\overset{k_3}{\rightleftharpoons}} 2\mathbf{C_2H_3} \quad . \; . \; . \; . \; . \; . \quad (3)$$

whence

$$\left(\frac{k_3}{k'_3}\right)^{\frac{1}{2}} \equiv \frac{k_1}{k'_1} \cdot \frac{b_{\mathrm{H}}^{\frac{1}{2}}}{1 + b_{\mathrm{C}} P_{\mathrm{C_2H_2}} + b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}}$$

If the terms $b_{\mathrm{C}} P_{\mathrm{C_2H_2}}$ and $b_{\mathrm{H}}^{\frac{1}{2}} P_{\mathrm{H_2}}^{\frac{1}{2}}$ are each much less than unity,

then

$$\left(\frac{k_3}{k'_3}\right)^{\frac{1}{2}} \equiv \frac{k_1}{k'_1}\left(\frac{k_{\mathrm{H}}}{k'_{\mathrm{H}}}\right)^{\frac{1}{2}}$$

The stationary concentration of vinyl radicals is then given by:

$$[\mathbf{C_2H_3}] = \left(\frac{k_3}{k'_3}\right)^{\frac{1}{2}} \cdot P_{\mathrm{H_2}}^{\frac{1}{2}} \cdot [\mathbf{C_2H_2}]$$

and equating $[\mathbf{C_2H_2}]$ to unity as before gives

$$\frac{\mathrm{d}p_{\mathrm{C_2H_4}}}{\mathrm{d}t} = \frac{k_2 k_3}{k'_3} \cdot P_{\mathrm{H_2}}$$

This treatment thus also gives a rate which is of the first order in hydrogen, but owing to the assumption concerning the size of the term $b_{C}P_{C_2H_2}$ it does not allow a negative order in acetylene.

With reference to the kinetics under type I conditions, the overall rate is a function of hydrogen pressure, while for a given hydrogen pressure the relative contributions of the two mechanisms depend on the acetylene pressure. Now the orders of reaction show that acetylene is much more strongly adsorbed than hydrogen, so that it is unlikely that the concentration of chemisorbed acetylene is the relevant variable: the onset of the second mechanism may, however, be determined by the reactant concentrations in a physically adsorbed layer above the reactant layer. Owing to the substantially higher " boiling " point of acetylene, this reactant will be much more strongly physically adsorbed than hydrogen, and it is therefore proposed that the second mechanism comes into operation when the hydrogen : acetylene ratio in the gas phase exceeds a certain critical value which is sufficient to secure the initial entry of the hydrogen into the second layer. The concentration of molecular hydrogen in this layer, designated $[H_2^*]$, is then given by:

$$[H_2^*] = k[P_{H_2} - P^{\circ}_{H_2}] \doteqdot k[P_{H_2} - 2P_{C_2H_2}] \qquad . \quad . \quad . \quad . \quad (B)$$

The required rate expression is most readily obtained if it is supposed that this hydrogen can add directly to an acetylene molecule, *viz.*:

$$\mathbf{C_2H_2} + \overset{H_2}{\vdots}\xrightarrow{k_4} C_2H_4 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the alternative method for the derivation of the type I kinetics is used, the total initial rate becomes, on equation of $[\mathbf{C_2H_2}]$ to unity as before:

$$\mathrm{d}p_{C_2H_4}/\mathrm{d}t = \frac{k_2k_3}{k_2 + k'_3} \cdot P_{H_2} + k_4[H_2^*]$$

which when combined with equation B quantitatively describes the dependence of rate on hydrogen pressure over a wide range of conditions.

We cannot explain the apparent dependence of the order in acetylene on hydrogen pressure; Table 2 reveals that zero orders (or greater) in acetylene are recorded under conditions where the initial hydrogen : acetylene ratio is generally greater than about two (except in Series IV), and that negative orders relate to conditions where the initial reactant ratio is less than about two. Now negative orders in acetylene under type III conditions have already been qualitatively interpreted (equation *A*), and it is suggested that step 4 has in fact an order in acetylene which is positive to just the same extent as the order for step 2 is negative. The effects therefore tend to cancel when steps 2 and 4 make approximately equal contributions to the total rate, and the overall order in acetylene may even become slightly positive when step 4 predominates over step 2. No more quantitative treatment is justified at present.

It is now necessary to enquire into the cause of the zero-order course rate. From equation *B*, the quantity $[H_2^*]$ increases proportionately as P_{H_2} decreases, and these effects tend to cancel; and for the specific case where $k_4 = k_2k_3/(k_2 + k'_3)$, the cancellation is complete and a zero-order course rate should result. The fact that constant rates are observed even where this equality does not hold even approximately indicates that additional factors are operating. For example, when $k_4 = k_2k_3/(k_2 + k'_3)$ an increase in rate would be predicted, and its non-occurrence may be due to a decrease in the rate of step 4 through the decreasing acetylene pressure. Similarly, when the reverse holds, the expected decrease in rate may be partly off-set by the negative order in acetylene of steps 1 and 2.

The effects observed when either reactant is added during a type I experiment are now readily explicable. The addition of hydrogen increases both P_{H_2} and, disproportionately, [H_2*], and hence from equation *B* the overall rate. This equation relates equally to initial hydrogen pressures and to hydrogen pressures throughout a run, whether additional hydrogen has been introduced or not. It is thus inevitable that consistency should be obtained between reaction orders determined by the initial-rate and " addition " methods. The same arguments apply *mutatis mutandis* to variation of acetylene pressure.

Kinetics under Type II *Conditions.*—No comprehensive interpretation of all the various features associated with the kinetic measurements under type II conditions is possible at present. The experiments covered a much smaller range than that employed in studying type I and type III conditions, and further work is called for. For premixed reactants (type IIA state, Table 3 and Fig. 4), the initial rate R_α has been shown to be proportional to hydrogen pressure and essentially independent of acetylene pressure, the peculiar hydrogen-pressure dependence characteristic of type I and type III states not being exhibited. It follows that the surface is still effectively saturated with acetylene and that the direct-addition mechanism (step 4) does not occur in these circumstances. The same is true of experiments involving prior addition of hydrogen, save that here no experiments were performed to determine the order in acetylene.

An even more puzzling feature of the type II state is that there is no return to the " equilibrium state " (*i.e.*, that supposed to exist when acetylene is added before the hydrogen) during the course of the experiment. The hydrogen-pressure dependence of the β-rates is in neither case the same as the dependence of the zero-order rate under type I conditions. The absence of the direct-addition mechanism in the β-phases also is therefore inferred: for example, the temperature dependence of k_β (Table 4) corresponds to an E_β of 7—8 kcal./mole as against about 23 kcal./mole for the zero-order rates. The apparent equivalence of R_β and the zero-order rate must therefore be fortuitous.

Although it is felt that an explanation can most profitably be sought in terms of a varying initial hydrogen content of the reactive layer, a number of as yet unappreciated factors are at work, and an interpretation of the results in terms of detailed mechanisms must await the conclusion of further work.

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