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The Hydrogenation of Acetylene

I. The Reaction of Acetylene with Hydrogen Catalyzed by Alumina-Supported Platinum

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The hydrogenation of acetylene has been studied in a static system using a platinum on α-alumina catalyst between 40° and 140°C. Kinetics and product analyses are reported. The percentage of ethylene in the C_2 product, which is initially 70% to 90%, has been measured as a function of initial hydrogen and acetylene pressures, temperature, and conversion. Reactions become more selective for ethylene formation as temperature is raised and hydrogen pressure reduced. Acetylene is selectively removed when mixtures of acetylene and ethylene are hydrogenated. The composition of C_4 hydrocarbons produced by acetylene polymerization was also determined.

A mechanism for the reaction is developed. The ability of this catalyst to produce olefin in preference to paraffin, while at the same time possessing extremely high olefin hydrogenation activity, depends upon the operation of thermodynamic and mechanistic factors.

INTRODUCTION

The platinum-catalyzed reaction between acetylene and hydrogen has been studied twice before (*1*, *2*). Kinetics and yields of products were reported in each case. It has been agreed that ethylene is formed preferentially in the first stage of the reaction, and some mechanistic implications of this have been discussed (*2*).

The objects of the present work were (*i*) to study the kinetic features of the reaction in greater detail than had been reported hitherto, (*ii*) to define the mechanism whereby ethylene is produced preferentially, and (*iii*) to elucidate the factors which govern changes from selective to nonselective behavior.

EXPERIMENTAL

Catalysts. All experimental work described in this paper employed samples of alumina-supported platinum catalyst taken from the same stock. The catalyst consisted of 8–16 mesh α-alumina which supported reduced platinum metal at a concentration of 5 molar %. Preparation of the catalyst stock has been described previously (*2*). Before use each new sample was reduced in about 100 mm hydrogen at 200°C for a period of 1 hr. The hydrogen was then pumped away, fresh hydrogen admitted, and the temperature lowered to that required for experimentation.

Apparatus and materials. The catalyst rested on the bottom of an 80-ml Pyrex reaction vessel connected to a conventional high-vacuum system. Pressures in the vessel were measured by a mercury manometer which could be isolated by a tap, to reduce contamination of the catalyst by mercury vapor (*3*).

Cylinder acetylene (British Oxygen Company) contained acetone and air which were removed by bulb-to-bulb distillation, using liquid air and solid carbon dioxide as refrigerants. No trace of acetone was detected in the product after three distillations.

Ethylene (British Oxygen Company) contained no impurities, besides air, that could be detected by gas chromatography. Before use, it was condensed at liquid air temperature and the air pumped away.

Cylinder hydrogen contained only water

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vapor as an impurity which was frozen out before use.

Procedure and analysis. The reaction vessel and manometer were pumped out separately. Acetylene was added first, then ethylene when appropriate, and lastly hydrogen. Catalysts were found to show maximum reproducibility if the manometer was connected to the reaction vessel only for the time required to take readings; contamination by mercury was thus minimized.

Relative concentrations of ethylene and ethane were estimated by gas-liquid chromatography using a 16-ft column containing a saturated solution of silver nitrate in benzyl cyanide as stationary phase supported on firebrick; hydrogen was used as carrier gas. Polymeric products were analyzed on a 20-ft column containing 30% w/w acetonylacetone on firebrick, nitrogen being used as carrier gas. Both columns were operated at room temperature.

Results

Kinetics

Pressure against time curves. When the initial hydrogen:acetylene ratio was unity the rate of pressure fall during the course of reaction was approximately proportional to the first power of the remaining hydrogen pressure until 90% reaction, as shown in Fig. 1(a). A different form of curve was observed when the initial ratio was two, or greater [Fig. 1(b)]. The reaction was zero order at first (region AB) and this was followed by a slow acceleration (region BC) and then by a rapid acceleration (region CD). A second linear region DE was then observed after which the rate fell away to zero. The "acceleration point," denoted as $-\Delta p_a$, is defined as the pressure obtained by extrapolating the linear portions of the first and second stages of the reaction, as shown in Fig. 1(b). During the zero order period the main product was ethylene, whereas, after the rapid acceleration the main process occurring was the further hydrogenation of ethylene to ethane.

The pressure fall after complete reaction was 3 to 4% greater than that expected from the stoichiometric equation $C_2H_2 + 2H_2 = C_2H_6$ on account of some hydropolymerization of acetylene to C_4 hydrocarbons.

When the initial hydrogen:acetylene ratio exceeded 2, the pressure fell to about 95% of

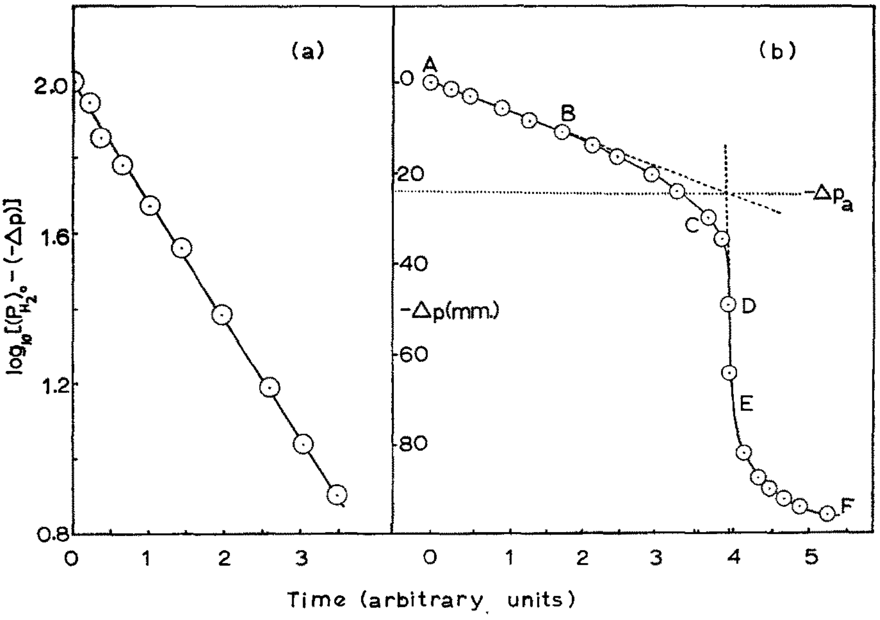


FIG. 1. (a) First order plot for the reaction of 100 mm acetylene with 100 mm hydrogen. Temperature = 110°C. (b) A typical pressure fall, $-\Delta p$ against time curve for a reaction in which $(P_{H_2})_0/(P_{C_2H_2})_0 \geqslant 2$.

the value expected for the uptake of 2 moles at a measurable rate, but the remainder of the reaction took place only very slowly indeed.

Orders of reaction by the initial rate method. Using a fixed acetylene pressure of 100 mm and a wide range of hydrogen pressures, orders in hydrogen of 1.3, 1.6, 1.5, and 1.5 were recorded at 97°, 110°, 112°, and 138°C, respectively. At 109°C the order in acetylene was -0.5 using a hydrogen pressure of 50 mm and -0.8 using a hydrogen pressure of 200 mm. The uncertainty in all determinations of order is ± 0.1 or less.

The dependence of acceleration point upon experimental variables. The acceleration point $(-\Delta p_a)$ decreased linearly with increasing hydrogen pressure at 104°C (Fig. 2). In the temperature range 72° to 112°C the acceleration point showed a fairly linear decrease with increasing temperature as shown in Fig. 3. All points in this figure, except for that at the highest temperature, represent multiple determinations which agreed accurately.

Activation energy. An activation energy of 9.3 ± 0.5 kcal mole^{-1} was obtained from initial rate measurements for reactions of 100 mm acetylene with 200 mm hydrogen between 40° and 96°C.

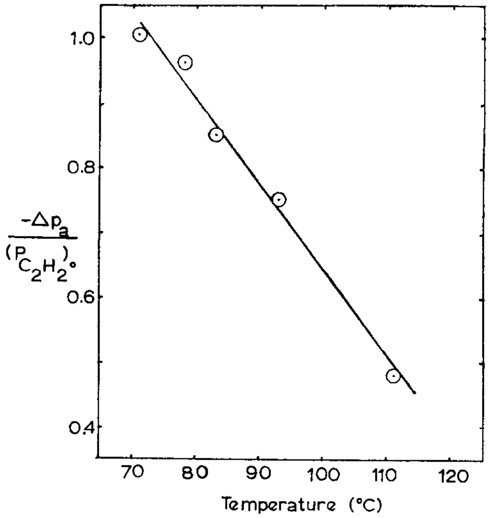


FIG. 3. The dependence of the acceleration point, $-\Delta p_a$, upon temperature; $(P_{H_2})_0/(P_{C_2H_2})_0 = 3.0$.

The Effect of Experimental Variables upon Selectivity

In this paper selectivity will be defined as $P_{C_2H_4}/(P_{C_2H_4} + P_{C_2H_6})$. Both ethylene and ethane were observed as initial products of the reaction under all conditions studied, ethylene being the major product.

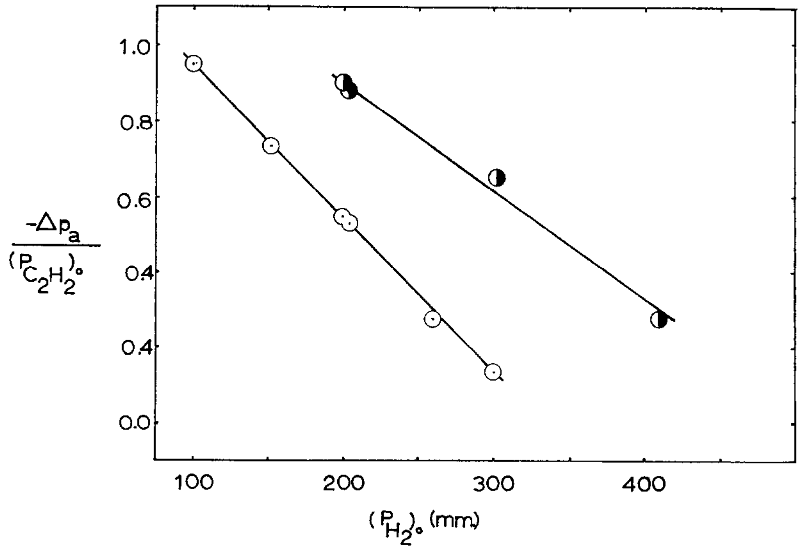


FIG. 2. The dependence of the acceleration point, $-\Delta p_a$, upon initial hydrogen pressure, $(P_{H_2})_0$, at 104°C. ○, $(P_{C_2H_2})_0 = 50$ mm; ◑, $(P_{C_2H_2})_0 = 100$ mm.

Dependence of selectivity upon pressure fall. Three reactions were carried out at each of three values of the pressure fall, and on four occasions the products were analyzed twice. The results given in Table 1 show that the selectivity was reproducible from one experiment to another and was constant until at least 35 mm pressure fall. It had only dropped by about 2% when the reaction reached the acceleration point ($-\Delta p_a =$ 81 mm under the conditions used).

TABLE 1

VARIATION OF SELECTIVITY WITH PRESSURE FALL FOR THE HYDROGENATION OF ACETYLENE OVER A PLATINUM CATALYST AT 107°C[a]

Pressure fall before analysis (mm)	Selectivity	Mean selectivity and mean deviation	Order in which runs were carried out
15.0	0.896, 0.899	0.898 ± 0.002	3
15.0	0.896		8
15.0	0.899, 0.897		5
34.8	0.898	0.896 ± 0.001	9
35.0	0.896, 0.896		2
35.3	0.893, 0.898		6
79.0	0.884	0.879 ± 0.004	7
79.5	0.890		1
80.2	0.874		4

[a] Initial acetylene pressure = 100 mm; initial hydrogen pressure = 250 mm.

Dependence of selectivity upon the initial pressures of hydrogen and acetylene. Measurements were made of selectivity as a function of initial hydrogen pressure at 97°, 110°, and 138°C using one sample of catalyst, and at 41°, 55°, 72°, and 97°C using a second sample. The initial acetylene pressure was 100 mm throughout. Figure 4 shows that selectivity decreased with increasing hydrogen pressure and all of the curves are convex to the origin over the entire range of hydrogen pressure studied. Where extrapolation of these curves to zero hydrogen pressure is possible the limiting value of the selectivity is about 0.950.

No significant variation of selectivity with initial acetylene pressure was observed at 110°C (Table 2).

Dependence of selectivity upon temperature. In the temperature range 41° to 97°C the selectivity increased linearly with increasing temperature. Above 97°C, however, the selectivity increased less rapidly, as might be expected intuitively (see Fig. 4).

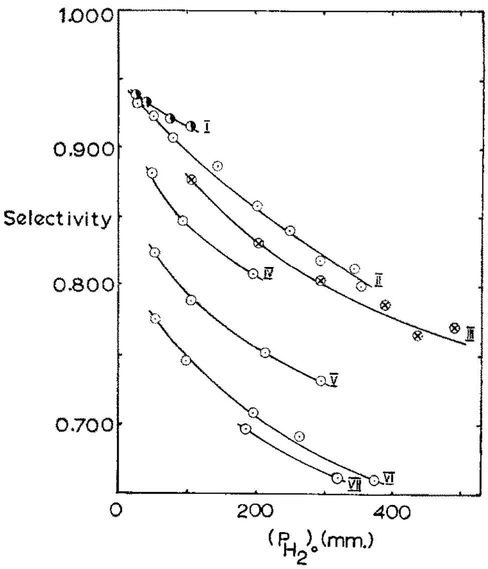


FIG. 4. The variation of selectivity with initial hydrogen pressure, $(P_{H_2})_0$, at various temperatures. $(P_{C_2H_2})_0 = 100$ mm. Curve I, Pt-I at 138°; II, Pt-I at 110°; III, Pt-I at 97°; IV, Pt-II at 97°; V, Pt-II at 72°; VI, Pt-II at 55°; VII, Pt-II at 41°C.

TABLE 2

THE DEPENDENCE OF SELECTIVITY UPON INITIAL ACETYLENE PRESSURE AT 110°C[a]

Acetylene pressure (mm)	100	150	200	275	300
Selectivity	0.815	0.814	0.809	0.818	0.828

[a] Initial hydrogen pressure = 300 mm, products analyzed after 50% removal of acetylene.

The Rate of Removal of Acetylene as a Function of Pressure Fall

The pressure of acetylene remaining in the reaction vessel was measured at five values of the pressure fall, the reaction being carried out at 107°C. As shown in Fig. 5 the rate of acetylene removal increased continuously during the reaction, becoming more marked in the region of the acceleration point.

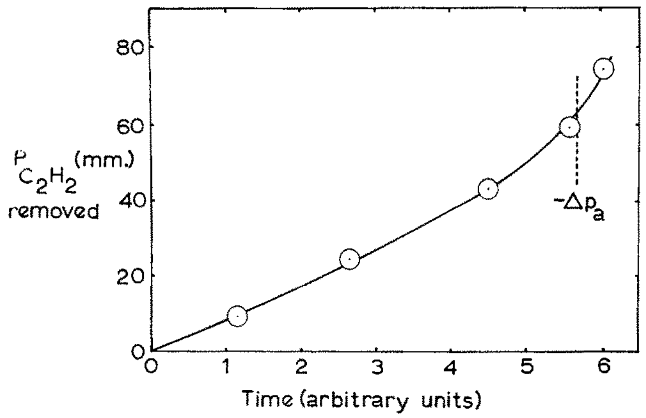


FIG. 5. The removal of acetylene during a reaction; $(P_{C_2H_2})_0 = 100$ mm; $(P_{H_2})_0 = 250$ mm.

The Effect of Initially Added Ethylene upon the Reaction

The effect of initially added ethylene upon the acceleration point and initial rate were studied.

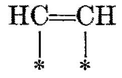
The acceleration point was observed in 13 experiments carried out at 99°C using 50 mm acetylene and 200 mm hydrogen; the mean value of $-\Delta p_a$ was 30 mm (mean deviation, ±2 mm, and maximum deviations, −4 and +3 mm). Four experiments, in which 100 mm ethylene was initially added, gave a mean value for $-\Delta p_a$ of 33 mm (mean deviation = ±2 mm and maximum deviations = −4 and +3 mm). Thus added ethylene slightly delayed the acceleration point.

Acetylene Polymerization

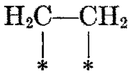
A reaction at 136°C employing 152 mm acetylene and 146 mm hydrogen reacted to completion. Analysis showed that 28% of the acetylene had polymerized to C_4 hydrocarbons and less than 1% to C_6 hydrocarbons. Polymeric products were: 1,3-butadiene, 8%; 1-butene, 47%; *trans*-2-butene, 22%; *cis*-2-butene, 20%; and *n*-butane, 3%.

DISCUSSION

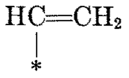
It has been cutomary in the past to represent associatively adsorbed acetylene and ethylene as the di-σ-adsorbed species (I) and (II) respectively, and the half-hydrogenated state as the mono-σ-adsorbed species (III).


$\mathrm{H}\underset{\substack{|\\ *}}{\mathrm{C}}=\underset{\substack{|\\ *}}{\mathrm{C}}\mathrm{H}$

(I)


$\mathrm{H_2}\underset{\substack{|\\ *}}{\mathrm{C}}-\underset{\substack{|\\ *}}{\mathrm{C}}\mathrm{H_2}$

(II)

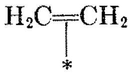

$\mathrm{H}\underset{\substack{|\\ *}}{\mathrm{C}}=\mathrm{CH_2}$

(III)

According to this notation the carbon atoms in (I) exhibit sp^2 hybridization and those in (II) show sp^3 hybridization (*4*). In view of recent developments in our knowledge of the chemistry of the transition elements, and of the Group VIII metals in particular, we propose that the adsorbate-metal bond has essentially the same character as the metal–acetylene and metal–olefin bonds in well-defined organometallic compounds. Systems have been characterized in which (*i*) the four π electrons of the triple bond interact with *d* orbitals of two atoms which themselves are bonded together [e.g. $(C_5H_5Ni)_2HC{\equiv}CH$ (*5*) and $(C_5H_5Ni)_2PhC{\equiv}CPh$ (*6*)] and in which (*ii*) two π electrons of a double bond similarly interact with one metal atom {e.g. $[PtCl_3(C_2H_4)]^-$ (*7*)}. Therefore, in this paper, we shall represent the adsorbed states of acetylene and ethylene as (IV) and (V), respectively. The half-hydrogenated state may still be


$\mathrm{HC}\underset{\substack{|\\ **}}{\equiv}\mathrm{CH}$

(IV)


$\mathrm{H_2C}\underset{\substack{|\\ *}}{=}\mathrm{CH_2}$

(V)


$\mathrm{H}\underset{\substack{|\\ *}}{\mathrm{C}}\underset{\substack{|\\ *}}{=}\mathrm{CH_2}$

(VI)

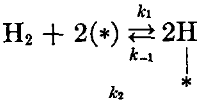
represented as (III) or alternatively as (VI); $CH_3S[Fe(CO)_3]_2HC{=}CH_2$ is an example of a compound in which vinyl acts as a bridging ligand between two metal atoms by the formation of a σ bond to one and a π bond to the other (*8*). Evidence of π bonding of adsorbed hydrocarbon species in catalytic reactions involving larger hydrocarbon molecules has recently been presented (*9–14*).

Two important features follow from this change of notation. First, the state of hybridization of the carbon atoms in adsorbed acetylene and ethylene is probably not far disturbed from *sp* and sp^2, respectively. Secondly, associative adsorption of ethylene requires only one site for adsorption whereas, on the σ-bond notation it required two sites.

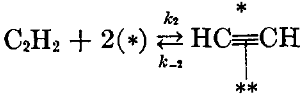
Kinetics

Orders of Reaction by the Initial Rate Method

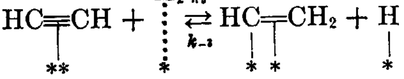
The negative order in acetylene and the positive order in hydrogen show that the former was the more strongly adsorbed reactant and that its surface coverage was high, whereas hydrogen was weakly adsorbed, by comparison, and its surface coverage was correspondingly low. Consider the following equations:



$$H_2 + 2(*) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{*}{2H} \qquad (1)$$



$$C_2H_2 + 2(*) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{**}{HC{\equiv}CH} \qquad (2)$$



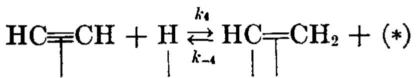
$$\underset{**}{HC{\equiv}CH} + \underset{\vdots\,*}{H_2} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \underset{*\ *}{HC{=}CH_2} + \underset{*}{H} \qquad (3)$$

Equations (1) and (2) describe the adsorption of each reactant at a pair of adjacent vacant sites; such adsorption takes place competitively for a given pair of sites. When a surface is highly covered with adsorbate requiring two adsorption sites, single sites will remain vacant. Hydrogen adsorption may take place noncompetitively at such sites, as shown in Eq. (3), by a quasi-Rideal-Eley mechanism. Alternatively, the site of adsorption may be a *pair* of adjacent metal atoms, if these are not available for acetylene adsorption because of the operation of some geometric factor (i.e., either the adjacent metal atoms form a forbidden lattice spacing or the introduction of a further acetylene molecule would produce intolerable intermolecular repulsions). Thus the requirement of the "single site" in step (3) is that it must be capable of activating a hydrogen molecule. The precise mechanism of the step need not, and indeed cannot at this stage, be more clearly specified. In Part IV of this series (to be published), where the platinum-catalyzed deuteration of acetylene will be described, reactant adsorption is shown to be irreversible. Consequently, Langmuir equations cannot be used to relate the surface coverage of hydrogen, θ_H, to its pressure in the gas phase. For the adsorption process:

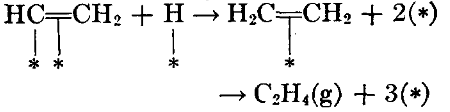
$$\text{rate of hydrogen adsorption} = k_1P_{H_2}[**] + k_3\theta_{C_2H_2}[*]P_{H_2} = KP_{H_2}$$

since $\theta_{C_2H_2} \rightarrow 1$ and the concentrations of single sites and of pairs of sites will be constant for a given acetylene pressure at a given temperature. Consequently, the hydrogen surface coverage is directly proportional to hydrogen pressure.

Ethylene-forming steps are (3) above and (4) and (5) below



$$\underset{**}{HC{\equiv}CH} + \underset{*}{H} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \underset{*\ *}{HC{=}CH_2} + (*) \qquad (4)$$



$$\underset{*\ *}{HC{=}CH_2} + \underset{*}{H} \xrightarrow{k_5} \underset{*}{H_2C{=}CH_2} + 2(*) \rightarrow C_2H_4(g) + 3(*) \qquad (5)$$

Step (5) is not shown as reversible since (*i*) ethylene produced in the gas phase did not readsorb, and (*ii*) adsorbed ethylene so formed is considered either to enter upon the ethane-forming step or to be rapidly displaced from the surface by adsorbing acetylene. Consequently, equating the rates of vinyl formation and removal,

$$k_3[*]P_{H_2}\theta_{C_2H_2} + k_4\theta_{C_2H_2}\theta_H = k_5\theta_{C_2H_3}\theta_H + k_{-4}\theta_{C_2H_3}[*]$$

and the rate of ethylene formation is given by:

$$d(P_{C_2H_4})/dt = k_5\theta_{C_2H_3}\theta_H = \frac{k_5(k_3[*]\theta_{C_2H_2}P_{H_2} + k_4\theta_{C_2H_2}\theta_H)\theta_H}{k_{-4}[*] + k_5\theta_H}$$

Now, if $k_5\theta_H > k_{-4}[*]$, the reaction should be first order in hydrogen pressure, whereas, if $k_{-4}[*] > k_5\theta_H$, the reaction should be second order. Hence the observed order of 1.5 is understandable if $k_{-4}[*] \sim k_5\theta_H$.

The observed negative order in acetylene may be interpreted in one of three ways. It may mean that an increase in acetylene pressure enables the hydrocarbon to compete even more effectively with hydrogen for the surface, which would imply that step (1) is an important mechanism for hydrogen adsorption. Alternatively, acetylene might, at higher pressures, form a more ordered array on the surface, thus reducing the number of vacant single sites and simultaneously reducing the hydrogen adsorption by step (3). Lastly, this may be an effect of physical adsorption, even above 100°C; in this connection it is interesting that the initial addition of ethylene, which has a lower boiling point than acetylene, also reduced the rate of reaction.

Pressure Against Time Curves

The general form of the rate expression is $-d(P_{C_2H_2})/dt = k(P_{H_2})_i^{1.5}(P_{C_2H_2})_i^{-0.7}$, where P_i represents the instantaneous pressure of a given reactant. This expression correctly predicts the observed forms of pressure against time curve: (*i*) the continuously decreasing rate of reaction if the initial hydrogen:acetylene pressure ratio, $(P_{H_2})_0/(P_{C_2H_2})_0$, is unity or less [see Fig. 1(a)], (*ii*) an S-shaped curve if $2.0 > (P_{H_2})_0/(P_{C_2H_2})_0 > 1.0$, and (*iii*) a zero order region followed by an acceleration if $(P_{H_2})_0/(P_{C_2H_2})_0 \geqslant 2.0$ [see Fig. 1(b)]. Furthermore, the zero order region should be shorter, that is, the acceleration should begin earlier, the higher $(P_{H_2})_0/(P_{C_2H_2})_0$ in agreement with observation (see Fig. 2).

A complete account may now be given of the course of a reaction involving a greater than twofold excess of hydrogen [see Fig. 1(b)]. The zero order region AB, and the mildly accelerating region BC, *both* represent the hydrogenation of acetylene, ethylene being formed with a high selectivity. This is confirmed by the increase in the rate of acetylene removal with increasing pressure fall shown in Fig. 5. The restricted ability of ethylene to compete with acetylene in this region AC is demonstrated (*i*) by only 2% fall in selectivity, (see Table 2) and (*ii*) by the inability of initially added ethylene to hasten the onset of nonselective conditions (i.e., to decrease $-\Delta p_a$).

The breakdown of selectivity occurs when ethylene hydrogenation becomes important, and this occurs in the region CD. The very rapid rates usually encountered in this region made it impossible to locate the exact point at which the highly selective conditions broke down, but $(P_{H_2})_i/(P_{C_2H_2})_i \sim 15$ to 25. Since the activity of these catalysts for ethylene hydrogenation was not less than one hundred times their activity for acetylene hydrogenation, the fraction of the surface required by ethylene for its hydrogenation rate to become important must have been very small. Possibly conditions arise in the region CD where acetylene is unable to maintain full surface coverage, and actual competition by ethylene may be unimportant. Thus in the region DE acetylene and ethylene are co-hydrogenating. At the point F, a little acetylene still remains, in the presence of ethane and hydrogen, such a situation being responsible for the extremely slow rates observed over the last 5% of reaction.

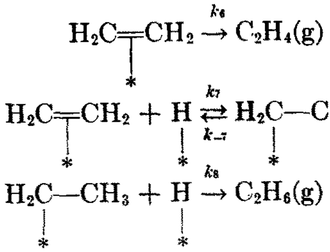
The slight extension of the acceleration point when ethylene was added initially confirms the deduction from selectivity measurements that competitive ethylene hydrogenation was not responsible for the mild acceleration in the region BC [see Fig. 1(b)]; such competition would have caused an earlier acceleration of the rate and a lower value of $-\Delta p_a$. Under the conditions used the acceleration point was extended by 3 mm, this being approximately the pressure of ethane produced by ethylene hydrogenation during the reaction of 30 mm acetylene.

The decrease of $-\Delta p_a$ with increasing temperature may have been caused by the acetylene order becoming more negative. Unfortunately, measurements of acetylene order as a function of temperature were not made.

Selectivity

Several approaches have recently been made to the theoretical treatment of selective reactions, i.e. those systems in which the reactants can, in principle, give two or more products simultaneously (*2, 15–18*). Acetylene hydrogenation is clearly such a system since ethylene, ethane, butadiene, *n*-butenes, and *n*-butane were produced.

Factors governing the relative yields of ethylene and ethane are both thermodynamic and mechanistic in origin. For the purpose of this discussion it will be assumed that ethylene formed by vinyl hydrogenation (step 5) is initially adsorbed and that it subsequently desorbs or is hydrogenated. The latter process has been shown by the present authors, in studies of ethylene deuteration using catalyst samples from the same stock, to proceed via the adsorbed ethyl group which interconverts rapidly with adsorbed ethylene and hydrogen (*19*):



$$\underset{*}{H_2C{=}CH_2} \xrightarrow{k_6} C_2H_4(g) \tag{6}$$

$$\underset{*}{H_2C{=}CH_2} + \underset{*}{H} \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} \underset{*}{H_2C{-}CH_3} \tag{7}$$

$$\underset{*}{H_2C{-}CH_3} + \underset{*}{H} \xrightarrow{k_8} C_2H_6(g) \tag{8}$$

The ratio of the rates of ethylene desorption and ethane formation is thus:

$$\frac{d(P_{C_2H_4})/dt}{d(P_{C_2H_6})/dt} = \frac{k_6 k_{-7}}{k_7 k_8 \theta_H^2} \tag{9}$$

The value of this ratio, from ethylene deuteration studies (*19*), was about 0.5 at 100°C, and this represents the extent to which an *inherent mechanistic factor* promotes ethylene formation. However, in the context of acetylene hydrogenation, two further factors, both *thermodynamic* in origin, operate to increase the rate of ethylene desorption relative to the rate of ethane formation. First, strength of adsorption decreases in the sequence acetylene > ethylene > hydrogen and consequently θ_H is lower during acetylene hydrogenation than during ethylene hydrogenation. Secondly, it may be that acetylene displaces ethylene from the surface; such displacement would be analogous to the known ligand displacement reactions of organometallic chemistry. If this occurred, k_6 would be greater in the presence of acetylene than in its absence.

Variations of Selectivity with Experimental Variables

Selectivity decreased with increasing initial hydrogen pressure. The kinetics showed that the surface coverage of hydrogen atoms increased as $(P_{H_2})_0/(P_{C_2H_2})_0$ was increased, and thus an increase in this ratio is expected to encourage ethane formation at the expense of ethylene formation [see Eq. (9)]. At all temperatures the dependencies of selectivity upon hydrogen pressure shown in Fig. 4 conform to the equation $(0.950 - S) = k(P_{H_2})_0{}^n$, where S is the observed selectivity, $(P_{H_2})_0$ the initial hydrogen pressure, and n and k are constants. The exponent varies with temperature, as shown in Table 3 and only shows the value of 0.5 expected from Eq. (9) at about 100°C.

TABLE 3

THE DEPENDENCE OF THE EXPONENT n UPON TEMPERATURE

$(0.950 - S) = k(p_{H_2})^n$

Temperature (°C)	54	74	97	110	138
$n(\pm 0.04)$	0.25	0.30	0.46	0.85	1.01
Catalyst sample	II	II	I	I	I

The very small decrease of selectivity as reaction proceeds, shown in Table 1, is attributable either to ethylene readsorption or to a decreasing inherent selectivity as the instantaneous value of $P_{H_2}/P_{C_2H_2}$ (and hence θ_H) increases. This inability of ethylene to compete with acetylene initially for vacant surface sites is another manifestation of the thermodynamic factor.

Selectivity increased with increasing temperature. This is related to the observation that the rate of ethylene exchange on platinum increased relative to the rate of deuteration as the temperature was raised from 0° to 200°C (*19*). It is not clear whether these phenomena are predominantly due to (*i*) a decrease in the surface coverage of hydrogen as the temperature is raised or (*ii*) to a genuinely higher activation energy for ethylene desorption relative to hydrogenation.

Acetylene Polymerization

The addition of hydrogen to acetylene is more selective for the production of C_2 than for C_4 hydrocarbons. Hydropolymerization of acetylene on platinum has been reported previously by Sheridan (*1*) who used a pumice-supported catalyst, and who proposed that a free radical form of adsorbed vinyl initiated the polymerization (*20*):

$$\dot{\mathrm{C}}\mathrm{H{-}CH_2\ (ads)} \xrightarrow{+\mathrm{C_2H_2(ads)}} \dot{\mathrm{C}}\mathrm{H{-}C_3H_4\ (ads)} \xrightarrow{+\mathrm{H}} \mathrm{C_4H_6\ (ads)}$$

Evidence for or against this mechanism cannot be gleaned from our single measurement. However, butadiene was certainly an intermediate in the production of the butenes and butane, because the butene distribution is similar to that obtained by the hydrogenation of butadiene itself on platinum catalysts taken from the same stock (*21*) (see Table 4). The selectivity in the polymer yield (0.97) exceeds that obtained in 1,3-butadiene hydrogenation (0.91) (*21*) under the same conditions of temperature and hydrogen pressure. Alkynes are usually more strongly adsorbed than dienes (*22, 23*). Thus, in the polymerization reaction, butene is displaced from the surface by acetylene, which is more effective than is displacement by 1,3-butadiene in the context of diene hydrogenation. This demonstrates again the operation of the thermodynamic factor in selectivity and supports the proposed mechanism whereby di-unsaturated hydrocarbons adsorb by displacement of chemisorbed olefin from the surface.

TABLE 4

COMPARISON OF THE BUTENE DISTRIBUTION AND SELECTIVITY (*S*) OBSERVED IN ACETYLENE POLYMERIZATION (I) AND 1,3-BUTADIENE HYDROGENATION (II)[a]

	1-Butene (%)	*trans*-2-Butene (%)	*cis*-2-Butene (%)	*S*
I	52	25	23	0.97
II	47	32	21	0.91

[a] Temperature: 135°C. Initial hydrogen pressure: 150 mm.

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