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The Hydrogenation of Ethylacetylene

II. Reaction of Ethylacetylene with Hydrogen Catalyzed by Nickel, Cobalt, and Iron

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The hydrogenation of ethylacetylene has been studied in a constant-volume static system over supported and unsupported nickel, cobalt, and iron catalysts between 25° and 230°C. Kinetics and products analyzed are reported. The percentage of 1-butene has been measured as a function of initial hydrogen and ethylacethylene pressures, temperature, and conversions. The selectivity was generally found to be independent of ethylacetylene pressures, though it depended upon and decreased with initial hydrogen pressure. The apparent activation energies for supported nickel, cobalt, and iron and unsupported nickel and cobalt were 10.0, 7.5, 7.18, 12.1, and 9.2 kcal/mole, respectively.

INTRODUCTION

A systematic study of methylacetylene hydrogenation over transition metals of the eighth group, and nickel-copper alloys revealed some very interesting results (*1–3*). We investigated the hydrogenation of ethylacetylene (*4*) over nickel-pumice catalyst for purposes of comparison and to find the effect of the ethyl group in the acetylene series. The results of this investigation have been communicated in Part I of this series (□). A general similarity between the hydrogenation of methylacetylene and ethylacetylene has been observed. In this paper we report the reaction of ethylacetylene with hydrogen catalyzed by supported and unsupported nickel, cobalt, and iron catalysts, investigated to obtain information on (i) the kinetics of the reaction and (ii) yields of α-butylene, butane, and *cis*- and *trans*-2-butene.

EXPERIMENTAL

The apparatus, preparation of the catalyst, experimental procedure and analytical technique have been described earlier (*1, 2*). The initial rates ($-dp/dt$) were obtained from manometric measurements, that is the change in pressure as a function of time. The course of the reaction was followed by measuring the change in pressure, and analyzing the reaction products as a function of conversion. The activity of the catalysts remained constant during the series of runs. The experiments were performed in random order to nullify any effects due to slight changes in the catalytic activity. The reaction products were analyzed by a Fisher gas partitioner employing two columns, a 7 ft long column packed with 30% hexamethyl phosphoramide on 60–80 mesh Columnpack and a 13-ft column packed with 30–60 mesh activated 13X molecular sieve. The temperature of the Fisher gas partitioner was maintained at 60°C. Polymers were determined by difference.

RESULTS

Supported and unsupported nickel and cobalt and supported iron catalysts were found to be quite active and did not get poisoned when ethylacetylene or hydrogen was admitted first into the reactor. The activity remained fairly constant for several days. Unsupported iron was found to be much less active as a catalyst as compared to other catalysts. It also lost its activity rapidly. The specific reaction rate (k) for unsupported iron was 1.78×10^{-2} min^{-1} g^{-1} at 130°C as compared to nickel powder,

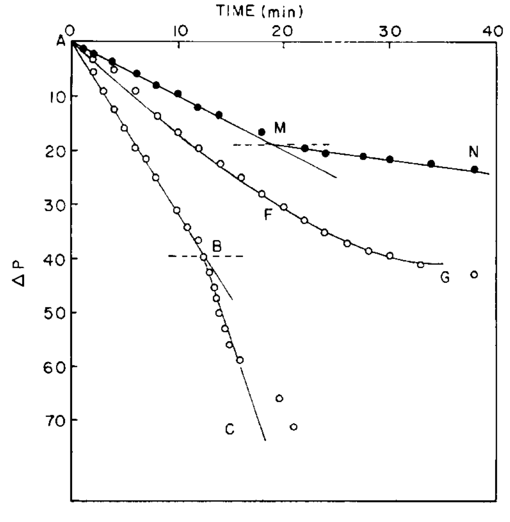


FIG. 1. Pressure fall–time curves; $P_{C_4H_6} = 50$ mm. Curve AFG, Fe-pumice; $P_{H_2} = 161.5$ mm; $T = 115°C$. Curve AMN, Co powder; $P_{H_2} = 54.5$ mm, $T = 35°C$. Curve ABC, Ni powder; $P_{H_2} = 132$ mm, $T = 40°C$.

which had a rate of 56.3 min^{-1} g^{-1} under similar conditions.

a. Pressure fall–time curves. The pressure fall–time (*p–t*) curve observed in the hydrogenation of ethylacetylene over unsupported nickel, cobalt, and iron and supported iron and cobalt for hydrogen/ethylacetylene ratios of less than 2, consisted of two linear portions of different rates (Curve AMN, Type I, bilinear, Fig. 1).

TABLE 1
PRESSURE FALL–TIME CURVES

Catalyst	Kinetics $H_2:C_4H_6 < 2$	 $H_2:C_4H_6 > 2$
Fe powder	Bilinear, Type I	Curve AFG, Type III
Co powder	Bilinear, Type I	Curve ABC, Type IV
Ni powder	Bilinear, Type I	Curve ABC, Type IV
Fe-pumice	Bilinear, Type I	Curve AFG, Type III
Co-pumice	Bilinear, Type I	Curve ABC, Type IV
Ni-pumice	Bilinear, Type I	Curve ABC, Type IV

While for hydrogen/ethylacetylene ratios of 2 or greater than 2, a Type III (Curve AFG) curve was obtained for iron (supported and unsupported), a different type of pressure–time curve (Curve ABC) was observed for other catalysts. Curve ABC is comprised of two linear regions, region AB, in which the reaction was of first order, and region BC, in which the rate of pressure fall accelerated. In the region AB, the main product of the reaction was 1-butene with a small amount of *n*-butane, whereas after the rapid acceleration (region BC) the main process occurring was the further hydrogenation of 1-butene to butane. The kinetic form of the pressure–time curves observed with different catalysts are summarized in Table 1.

b. Order in ethylacetylene and hydrogen obtained by initial rate method. Using a fixed ethylacetylene pressure of 50 mm and a wide range of hydrogen pres-

TABLE 2
ORDER OF REACTION WITH RESPECT TO HYDROGEN AND ETHYLACETYLENE AND ACTIVATION ENERGIES

Temp. (°C)	Order wrt H_2	Order wrt C_4H_6	Energy of activation	Temp. (°C)	Order wrt H_2	Order wrt C_4H_6	Energy of activation
	Iron-pumice, 0.1 g				*Ni powder, 0.075 g*		
90°	1.04	0.0	7.1 kcal	30°	1.00	0.0	12.1 kcal
100°	1.06	0.0		40°	1.00	−0.01	
110°	1.00	0.0		50°	1.01	−0.03	
121°	1.03	0.0		60°	1.01	−0.02	
136°	1.03	0.0					
	Cobalt-pumice, 0.05 g				*Cobalt powder, 0.075 g*		
40°	1.00	0.0	7.5 kcal	30°	0.96	0.0	9.2 kcal
50°	1.00	0.0		40°	1.04	−0.21	
58°	1.01	−0.14		50°	1.05	−0.22	
65°	1.00	−0.09		60°	0.95	−0.280	
73°	1.01	−0.15		68°	1.01	−0.33	

Iron powder, 0.2 g, 130–230°. Reaction very slow and deactivated.

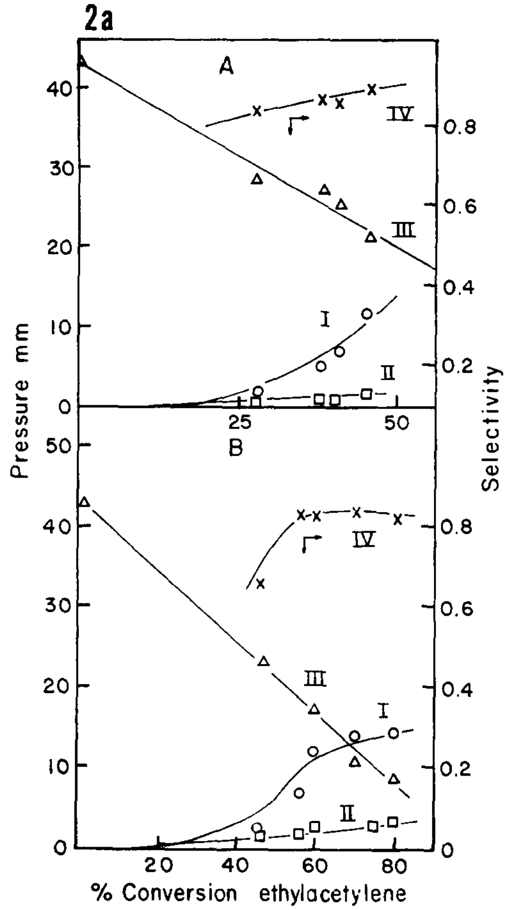


FIG. 2. Course of reaction: I, 1-butene; II, butane; III, unreacted ethylacetylene; IV, selectivity vs. % conversion; V, *trans*-2-butene; VI, *cis*-2-butene. $P_{C_4H_6} = 50$ mm. (a) Fe-pumice, $T = 115$°C. A, $P_{H_2} = 50$ mm; B, $P_{H_2} = 160$ mm.

sures (45–200 mm) the order with respect to hydrogen was determined at several temperatures. Similarly, the order of ethylacetylene was obtained at several temperatures by using a fixed hydrogen pressure of 50 mm and a wide range of ethylacetylene pressures (45–150 mm). The results are given in Table 2. Results for supported nickel have been described in Part I of this series.

The order with respect to hydrogen (Table 2) was about one and was temperature-independent. However, the order of reaction with respect to ethylacetylene was temperature-dependent and became negative with increased temperatures for supported and unsupported nickel and cobalt. But in the case of supported iron it was temperature-independent.

c. Temperature dependence of rate constants. Specific reaction rates were obtained from initial rate measurements for reaction of 50 mm of ethylacetylene with 35–150 mm of hydrogen between 20° and 136°C. Plots of $\log_{10}$ (specific rates) against the reciprocal of absolute temperature were good straight lines over a wide range of temperature for all catalysts satisfying the Arrhenius equation. The derived apparent activation energies are given in Table 2.

d. Dependence of selectivity upon pressure fall or conversion. The course of the reaction for hydrogen/ethylacetylene ratios of $1 (P_{H_2} = P_{C_4H_6} = 50$ mm) and more than 2 ($P_{H_2} =$ more than 100 mm, $P_{C_4H_6} = 50$ mm) was followed by analyzing the reaction products after various falls in pressure. While the selectivity (S) is defined as the ratio of α-butylene to α-butylene plus n-butane plus *cis*-2- and *trans*-2-butene

$$S = \frac{P_{\alpha\text{-butylene}}}{P_{\alpha\text{-butylene}} + P_{n\text{-butane}} + P_{cis\text{-2-butene}} + P_{trans\text{-2-butene}}}$$

conversion (X) is the ratio of ethylacetylene reacted (consumed) to ethylacetylene admitted into the reaction vessel. Figure 2(a), (b), and (c) shows the distribution of products and unreacted ethylacetylene at different percentage conversions of ethylacetylene over the catalysts investigated at equimolal quantities of reactants. While the selectivity increased with increased conversions over iron-pumice it was independent of conversions for all other catalysts. Table 3 gives the selectivity and percentage composition of various reaction products at different hydrogen/methylacetylene ratios. The amount of polymerization was calculated as the difference between the initial pressure of ethylacetylene and the sum of ethylacetylene reacted to form 1-butene, n-butane, and isomers and the unreacted ethylacetylene left in the products. The ploymers may have been in a gaseous form which could not be detected by the hexamethyl phosphoramide or molecular sieve columns under experimental conditions.

The dependence of the selectivity and the

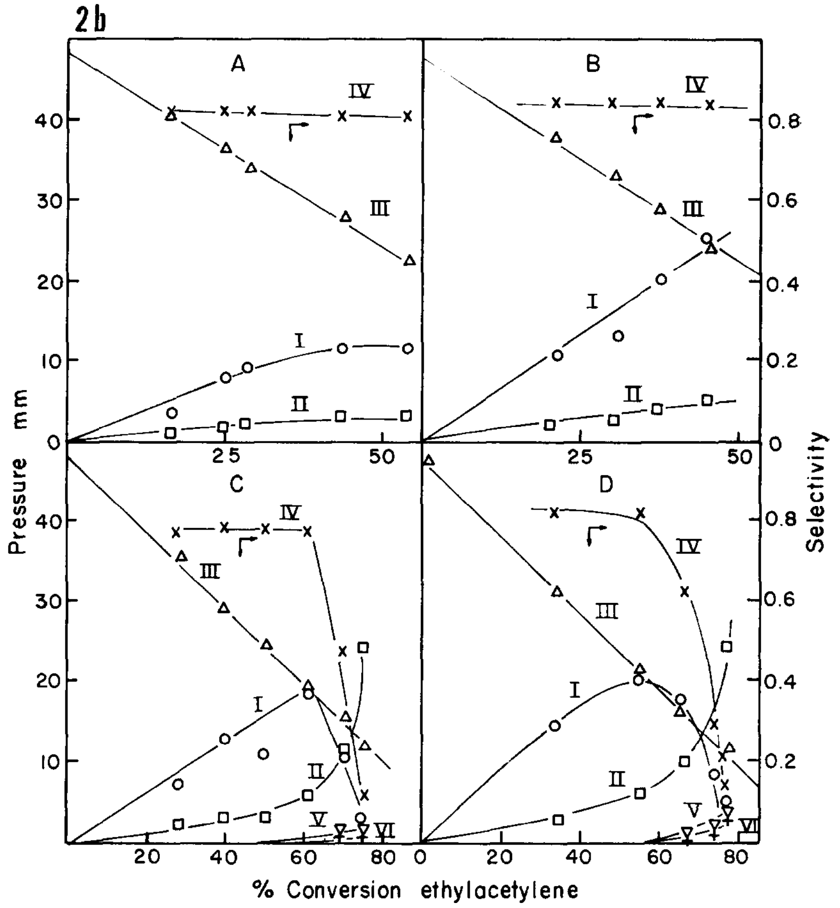


FIG. 2. (*contd.*) (b) (i) Cobalt powder, $T = 35°C$: A, $P_{H_2} = 50$ mm; C, $P_{H_2} = 150$ mm. (ii) Co pumice, $T = 50°C$: B, $P_{H_2} = 50$ mm; D, $P_{H_2} = 130$ mm.

distribution of products upon the percentage conversion of ethylacetylene for hydrogen/ethylacetylene ratios greater than 2 is shown also in Fig. 2(a), (b), and (c) for different catalysts. The selectivity was found to be independent of percentage conversion till about more than half of the ethylacetylene had reacted, after which the selectivity started falling precipitously for all catalysts, except iron-pumice, where it increased in early stages, and then remained constant. It seems that 1-butene did not readsorb on the surface of iron catalyst and no further hydrogenation to form butane took place under experimental conditions.

e. Dependence of selectivity upon initial pressures of hydrogen and ethylacetylene. Measurements were made of the selectivity of metals at different temperatures as a function of initial hydrogen pressure by using a fixed ethylacetylene pressure of 50 mm and varying the hydrogen pressures. Products were analyzed when the total pressure fall was equal to 20 mm of total pressure. The selectivity of unsupported cobalt at 35° and iron-pumice at 117°C was nearly independent of hydrogen pressures (Fig. 3). However, in other cases selectivity was dependent on the initial hydrogen pressures. It decreased slightly initially with increased hydrogen pressures up to a hydrogen/ethylacetylene ratio of about 2, after which it rapidly decreased. No significant variation in the selectivity with initial ethylacetylene pressures (45–160 mm) for a fixed initial hydrogen pressure (50 mm) was observed for all catalysts except for cobalt pumice, where it decreased slightly

2c

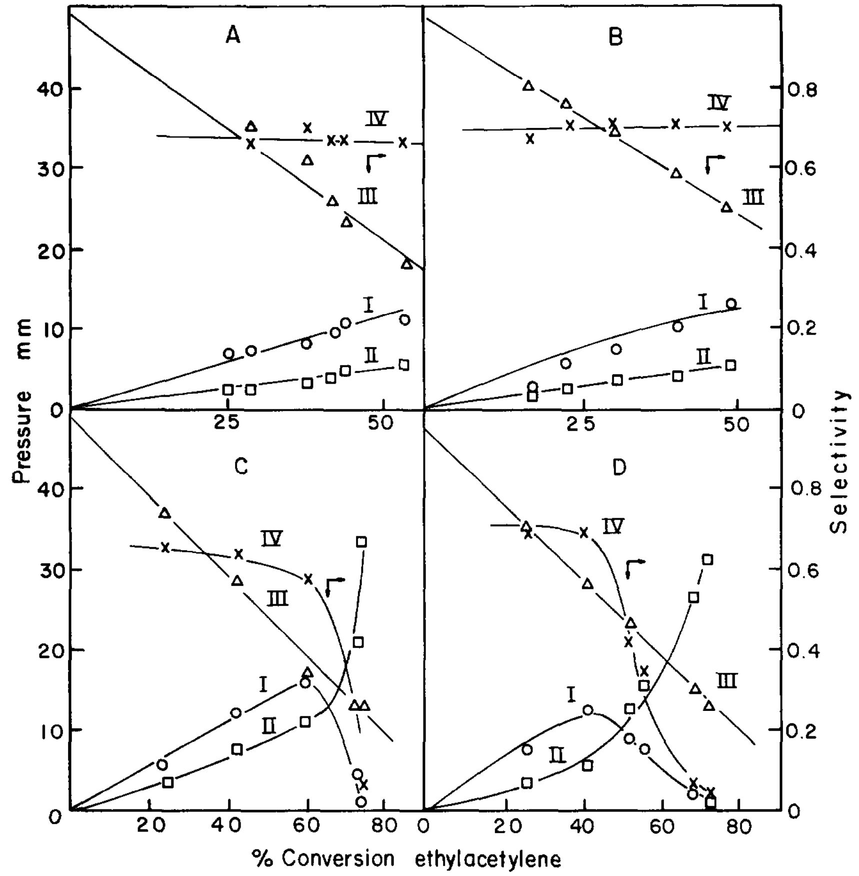


FIG. 2. (*contd.*) (c) (i) Ni powder: A, P_{H_2} = 50 mm, T = 30°C; C, P_{H_2} = 130 mm, T = 40°C. (ii) Ni-pumice: B, P_{H_2} = 50 mm, T = 30°C; D, P_{H_2} = 125 mm, T = 50°C.

with increased initial ethylacetylene pressures (Fig. 4).

f. Dependence of selectivity upon temperature. The temperature dependence of selectivity for hydrogen/ethylacetylene ratio of 1 and more than 2 was studied by analyzing the reaction products at several temperatures for a total pressure fall of 20 mm. The results are given in Fig. 5(A) and 5(B). For equimolal amount of reactants, selectivity decreased with increasing temperatures in the case of nickel powder. However, in other cases, it increased with increasing temperatures. At hydrogen/ethylacetylene ratios of 2 or more, selectivity decreased very rapidly. However, in the case of iron-pumice, it remained constant. Small amounts of polymers were also observed.

DISCUSSION

Very little has been reported about the kinetics of the reaction of ethylacetylene (1-butyne) with hydrogen over metal catalysts. Rieche *et al.* (5) studied the liquid-phase hydrogenation of ethylacetylene and barium sulfate-supported palladium as catalyst. The only products observed were 1-butene (98%) and *n*-butene (2%). Meyer and Burwell (*6*) studied the gas-phase reaction between deuterium and ethylacetylene using 0.3% palladium on alumina as a catalyst. They observed 1-butene (99%), *cis*- and *trans*-2-butene (each 0.2%), and *n*-butane (0.5%) in the products. The reaction was highly selective in the sense that very little butane appeared in the product as long as any ethylacetylene remained unre-

TABLE 3

Dependence of Selectivity and Reaction Products, on Pressure Fall

Catalyst	Temp. (°C)	H_2 pressure (mm)	C_4H_6 at room temp.	Pressure drop (mm)	Products					% Polymers	Selectivity
								Butenes			
					$P_{C_4H_{10}}$	$P_{C_4H_8}$	$P_{C_4H_6}$	*trans*-2	*cis*-2		
Fe-pumice	117°	160	48.0	20.0	1.26	6.5	18.5	0.0	0.0	—	0.838
				43.0	2.75	14.75	10.5	0.25	0.25	—	0.820
Ni-pumice	50°	125	47.5	20.0	5.5	12.5	31.0	0.0	0.00	—	0.695
				62.0	31.0	1.25	13.0	traces	traces	0.52	0.040
Co-pumice	50°	130	47.5	20.0	3.0	14.0	31.0	0.0	0.0	0.0	0.823
				68.5	24.0	5.0	10.0	4.0	2.5	4.2	0.140
Fe powder	130°	102.5		20.0	1.5	11.5	20.0	0.0	—	—	0.884
Ni powder	40°	131	48.0	20.0	7.5	12.0	28.5	0.0	0.0	0.0	0.615
				79.5	33.5	1.0	12.5	traces	traces	2.0	0.029
Co powder	35°	150	48.0	20.0	3.0	10.5	24.5	0.0	0.0	1.03	0.777
				69.5	24.0	3.0	14.0	1.5	0.5	10.3	0.102

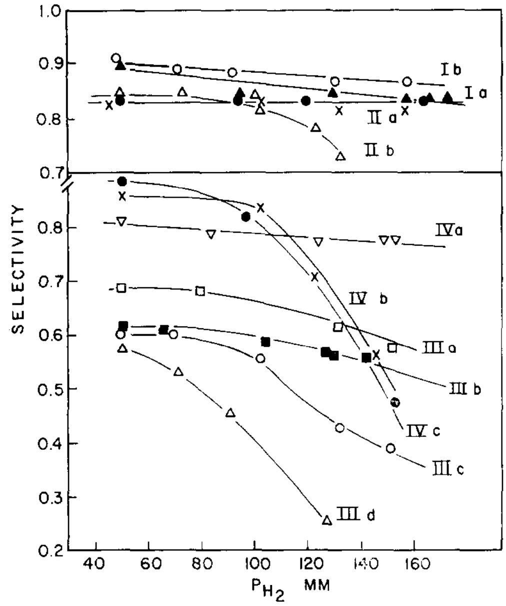


FIG. 3. Dependence of selectivity upon the initial pressure of hydrogen, $P_{C_4H_6}$ = 50 mm. Fe-pumice: Ia, 117°C; Ib, 131°C. Co-pumice: IIa, 70°C (×), 0–60°; ●, IIb, 80°C. Ni powder: IIIa, 40°C; IIIb, 50°C; IIIc, 60°C, IIId, 70°C. Co powder: IVa, 35°C; IVb, 45°C (×); IVc, 55°C (●).

acted. Since no detailed study has been made over nickel, cobalt, and iron, no direct comparison of this work can be made with those of Rieche *et al.* (*5*) and Meyer and Burwell (*6*) or any other published work.

According to Bond (*7*) the kinetic form of the pressure–time curves for acetylene hydrogenation depended on (i) initial hydrogen/acetylene ratio, (ii) the order of the admission of reactants, if added separately, and (iii) the pretreatment of the catalyst, if both the reactants added together. Bond obtained Type I pressure–time curves consisting of two linear portions (Curve AMN, Fig. 1) in acetylene hydrogenation over nickel for initial hydrogen/acetylene ratios greater than 2, when the reactants were premixed before being admitted over activated hydrogen (pretreated surface). For hydrogen/acetylene ratios greater than 2, on adding the reactants successively, he obtained a Type II curve (similar to AB) where the rate was constant up to a pressure fall about equal to the initial pressure of acetylene. A Type III (Curve AFG, Fig. 1) was obtained for hydrogen/acetylene ratios less than 2. Bond and Sheridan (*8*) obtained similar results over nickel-pumice in the hydrogenation of methylacetylene.

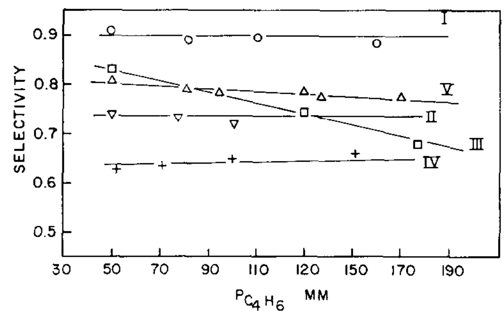


FIG. 4. Dependence of selectivity upon the initial pressure of ethylacetylene; P_{H_2} = 50 ± 1 mm. I, Fe-pumice, 131°C; II, Ni-pumice, 50°C; III, Co-pumice, 60°C; IV, Ni powder, 50°C; V, Co powder, 45°C.

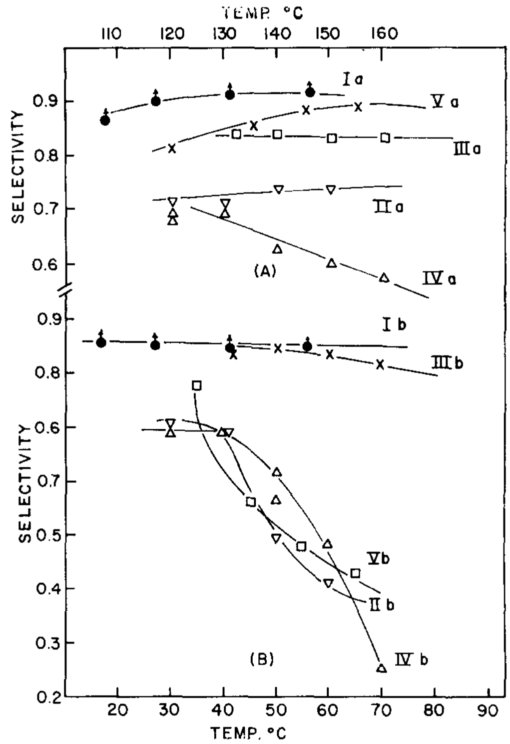


FIG. 5. Dependence of selectivity upon the temperature; $P_{C_4H_6}$ = 50 mm. (A) p_{H_2} = 50 mm; Ia, Fe-pumice; IIa, Ni-pumice; IIIa, Co-pumice; IVa, Ni powder; Va, Co-pumice. (B) Ib, Fe-pumice (P_{H_2} = 130 mm); IIb, Ni-pumice (P_{H_2} = 150 mm); IIIb, Co-pumice (P_{H_2} = 130 mm); IVb, Ni powder (H_2 = 130 mm); Vb, Co powder (H_2 = 150 mm).

The pressure–time curves observed in the hydrogenation of methylacetylene have been discussed in detail by Mann and Khulbe (*2, 3*). In agreement with the previous findings (*2, 3*) for methylacetylene hydrogenation over nickel, cobalt, and iron powder, and the hydrogenation of ethylacetylene over nickel-pumice (*4*), the pressure–time curves observed over supported and unsupported iron and cobalt and unsupported nickel in the present investigations consisted of two linear portions of different rates, (Curve AMN, Fig. 1) for hydrogen/ethylacetylene ratio less than 2. When the hydrogen/ethylacetylene ratio was more than 2, a Type III curve (Curve AFG), was obtained for supported and unsupported iron. Similar pressure–time curves were observed by Bond (*7*) in acetylene hydrogenation over nickel and by Mann and Khulbe (*9*) in methylacetylene hydrogenation over supported iridium and unsupported platinum and iridium. However, over pumice-supported cobalt and unsupported nickel and cobalt, the pressure–time curves were similar to those obtained in the case of nickel-pumice catalyst (*4*) for hydrogen/ethylacetylene ratios of 2 or more.

A similar type of behavior was observed by Bond and Wells (*10*) while investigating the kinetics of acetylene hydrogenation over alumina-supported platinum catalysts and by Mann and Khulbe (*3*) in the case of methylacetylene hydrogenation over nickel-copper alloys.

Sheridan (*11*) obtained a linear pressure–time curve, usually for the first stage of reaction in a hydrogen-acetylene mixture over supported nickel catalysts, though in some cases the rate of fall in the total pressure increased slightly in the early phase of reaction. The early acceleration, though a little more marked at higher temperatures, was not very pronounced in mixtures rich in hydrogen. He found that in all cases the fall in pressure gradually became slower towards the end of the reaction.

The difference in the shape of the pressure-time curves obtained by different investigators as discussed above may be due to (i) differences in the method of preparation and activation of catalysts, (ii) use of hydrocarbon-pretreated catalyst surfaces, (iii) differences in surface coverage by the reactants, (iv) hydrocarbon chain length.

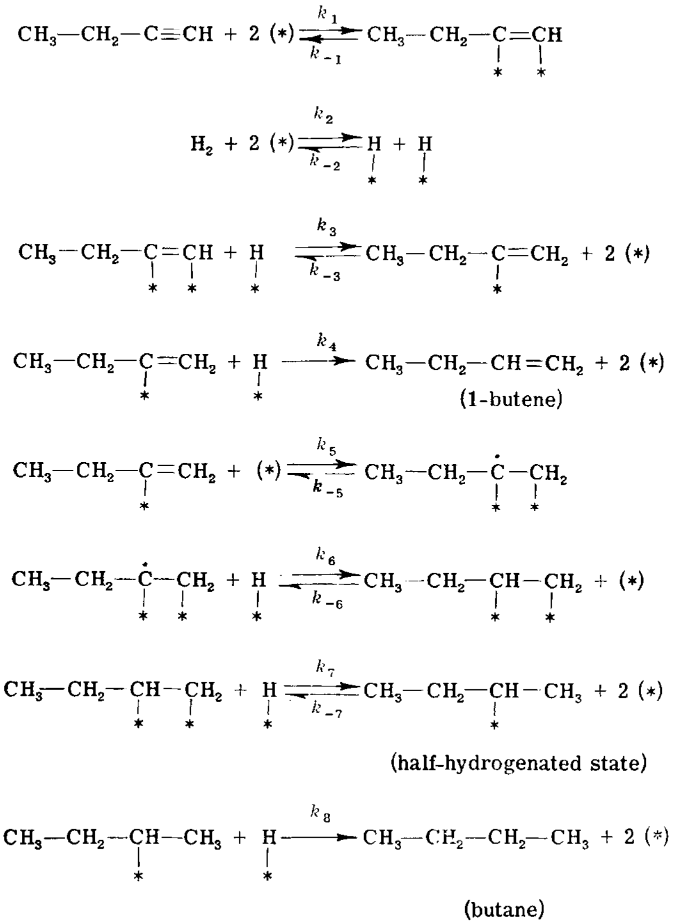
The zero to slightly negative order with respect to ethylacetylene and the positive order with respect to hydrogen indicate that the former was the more strongly adsorbed reactant and its surface coverage was high, whereas hydrogen was weakly adsorbed by comparison and its surface coverage was correspondingly very low.

The order with respect to ethylacetylene was temperature-dependent in the case of cobalt-pumice. However, in the case of supported iron and unsupported nickel and iron it was temperature-independent. An increase in the temperature decreases the concentration of reactants in the reactive layer. Since ethylacetylene is more strongly adsorbed on the surface than hydrogen and the surface is saturated with ethylacetylene, with increasing temperatures, the desorption of the former would be less than the latter. This would result in decreased hydrogen/ethylacetylene ratios on the surface. Hence, the order with respect to ethylacetylene becomes more negative with increasing temperatures.

According to Table 2, both supported and unsupported catalysts yield the sequence Ni > Co > Fe for activity and Table 3 yields the sequence Fe > Co > Ni for selectivity.

Similar to the findings of Meyer and Burwell (*6*) for ethylacetylene hydrogenation over alumina-supported palladium and of Bond (*12*) for 1-butene hydrogenation over several catalysts, *cis*- and *trans*-2-butene were observed in the products when the reactions were carried out over supported and unsupported cobalt and supported iron, at higher ratios of hydrogen/ethylacetylene (2 or greater than 2), and in the latter part of the reaction, that is, when 1-butene is further hydrogenated.

We suggest the following mechanism for ethylacetylene hydrogenation; it is a slightly modified form of the one described earlier (*4*). This mechanism takes into account the formation of butane in the early stages from the half-hydrogenated state rather than from the readsorbed 1-butene.



$$CH_3-CH_2-C\equiv CH + 2\,(*) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3-CH_2-\underset{\underset{*}{|}}{C}=\underset{\underset{*}{|}}{C}H \qquad (1)$$

$$H_2 + 2\,(*) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\underset{*}{|}}{H} + \underset{\underset{*}{|}}{H} \qquad (2)$$

$$CH_3-CH_2-\underset{\underset{*}{|}}{C}=\underset{\underset{*}{|}}{C}H + \underset{\underset{*}{|}}{H} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_3-CH_2-\underset{\underset{*}{|}}{C}=CH_2 + 2\,(*) \qquad (3)$$

$$CH_3-CH_2-\underset{\underset{*}{|}}{C}=CH_2 + \underset{\underset{*}{|}}{H} \xrightarrow{k_4} \underset{\text{(1-butene)}}{CH_3-CH_2-CH=CH_2} + 2\,(*) \qquad (4)$$

$$CH_3-CH_2-\underset{\underset{*}{|}}{C}=CH_2 + (*) \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} CH_3-CH_2-\underset{\underset{*}{|}}{\dot{C}}-\underset{\underset{*}{|}}{C}H_2 \qquad (5)$$

$$CH_3-CH_2-\underset{\underset{*}{|}}{\dot{C}}-\underset{\underset{*}{|}}{C}H_2 + \underset{\underset{*}{|}}{H} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} CH_3-CH_2-\underset{\underset{*}{|}}{C}H-\underset{\underset{*}{|}}{C}H_2 + (*) \qquad (6)$$

$$CH_3-CH_2-\underset{\underset{*}{|}}{C}H-\underset{\underset{*}{|}}{C}H_2 + \underset{\underset{*}{|}}{H} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} CH_3-CH_2-\underset{\underset{*}{|}}{C}H-CH_3 + 2\,(*) \qquad (7)$$

(half-hydrogenated state)

$$CH_3-CH_2-\underset{\underset{*}{|}}{C}H-CH_3 + \underset{\underset{*}{|}}{H} \xrightarrow{k_8} CH_3-CH_2-CH_2-CH_3 + 2\,(*) \qquad (8)$$

(butane)

Step (*4*) is not considered as reversible, since 1-butene produced in the gas phase did not readsorb due to the presence of strongly adsorbed ethylacetylene. Usually the adsorption of 1-butene in the presence of excess ethylacetylene would be less. Any adsorbed 1-butene so formed would be rapidly displaced from the surface by adsorbing ethylacetylene or would be used up in butane formation. This is substantiated by Fig. 2(a), (b), and (c), which shows that the selectivity decreased after the readsorption of 1-butene. At this stage the adsorption of ethylacetylene is negligible.

The rate of disappearance of C_4H_6 is the net rate of this reaction, that is,

$$d(C_4H_6)/dt = k_3(C_4H_6)(H) - k_{-3}(C_4H_7)(^*)^2$$

where all concentrations except those in parentheses are surface species.

From the above scheme, it is clear that there are four intermediates to which the steady state can be applied, i.e., C_4H_7, $\dot{C}_4H_7$, C_4H_8, and C_4H_9.

From (3), (4), and (5)

$$0 = dC_4H_7/dt = k_3(C_4H_6)(H) - k_{-3}(C_4H_7)(^*)^2 - k_4(C_4H_7)(H) + k_{-5}(\dot{C}H_7) - k_5(C_4H_7)(^*) \qquad (9)$$

From (5) and (6)

$$0 = d\dot{C}_4H_7/dt = k_5(C_4H_7)(^*) - k_{-5}(\dot{C}_4H_7) + k_{-6}(C_4H_8)(^*) - k_{-6}(\dot{C}_4H_7)(H) \qquad (10)$$

and from (6) and (7)

$$0 = dC_4H_8/dt = k_6(\dot{C}_4H_7)(H) - k_{-6}(C_4H_8)(^*) - k_7(C_4H_8)(H) + k_{-7}(C_4H_9)(^*)^2 \qquad (11)$$

From (7) and (8)

$$0 = dC_4H_9/dt = k_7(C_4H_8)(H) - k_{-7}(C_4H_9)(^*)^2 - k_{-8}(C_4H_9)(H) \qquad (12)$$

Addition of (10), (11), and (12) yields

$$k_8(C_4H_9)(H) = k_5(C_4H_7)(^*) - k_{-5}(\dot{C}_4H_7) \quad (13)$$

The overall yield of the product is given by (4) and (8), that is

$$k_4(H)(C_4H_7) + k_8(C_4H_9)(H)$$

From (9)

$$k_4(H)(C_4H_7) = k_3(C_4H_6)(H) - k_{-3}(C_4H_7)(^*)^2 + k_{-5}(\dot{C}_4H_7) - k_5(C_4H_7)(^*) \quad (14)$$

Combining (13) and (14) we get

$$k_4(H)(C_4H_7) + k_8(C_4H_9)(H) = k_3(C_4H_6)(H) - k_{-3}(C_4H_7)(^*) \quad (15)$$

which is the rate equation.

Since

$$-d(C_4H_6)/dt = k_3(C_4H_6)(H) - k_{-3}(C_4H_7)(^*)$$

then, if

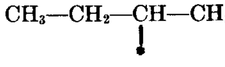
$$k_3\ (C_4H_6)(H) \gg k_{-3}(C_4H_7)\ (^*)$$

the rate equation would be

$$-d(C_4H_6)/dt = k_3(C_4H_6)(H) \quad (16)$$

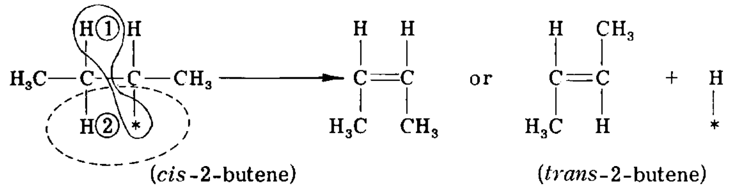
The fractional surface covered by C_4H_6 is generally near saturation, and approaches one. Hence the rate being first order with respect to hydrogen is understandable.

The free radical formed in step (5) may combine with adsorbed butene to form polymers. The formation of *cis*- and *trans*-2-butene may be explained by treating the half-hydrogenated state formed in step (7)



$$CH_3—CH_2—\underset{\overset{|}{*}}{CH}—CH_3$$

as an unstable compound or activated complex which decomposes after an elapse of a certain time. Before the elapse of this time, if there is any H (hydrogen atom) in the vicinity of this complex, it will react and will give butane. Otherwise it will decompose and will give *cis*- or *trans*-2-butene in the following way:



(*cis*-2-butene)
(if H① separate)

(*trans*-2-butene)
(if H② separate)

In our observations (Table 3) the thermodynamically highly favored olefin *trans*-2-butene was formed with high selectivity. But unfortunately we do not have sufficient evidence to support the observations.

Very small amounts of polymers were also obtained at the end of the reaction in comparison to that obtained in acetylene and methylacetylene hydrogenation. This may be due to the steric hinderance by the ethyl group. In general, there is much similarity between the methylacetylene and ethylacetylene hydrogenation over nickel, cobalt, and iron catalysts.

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