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Hydrogenation of Ethylacetylene over Nickel

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The hydrogenation of ethylacetylene has been studied in a constant-volume static system over a nickel-pumice catalyst between 20° and 60°C. Kinetics and products analyzed are reported. The percentage of 1-butene has been measured as a function of initial hydrogen and ethylacetylene pressures, temperature, and conversion. Though the selectivity was found to be independent of ethylacetylene and hydrogen pressures at 40°C, it decreased with initial hydrogen pressure at 50° and 60°C. An activation energy of 10.0 ± 0.05 kcal/g mole was determined. A mechanism for the reaction is developed.

INTRODUCTION

Recently several papers have appeared describing the kinetics of catalytic hydrogenation of acetylene (*1*) and methylacetylene (*2–4*). However, 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 at room temperature using alcohol as a solvent and barium sulfate supported palladium as catalyst. The only products observed were 1-butene (98%) and *n*-butane (2%). Meyer and Burwell (*6*) studied the gas-phase reaction between deuterium and ethylacetylene, using 0.3% palladium on alumina as a catalyst. They reported 1-butene (99.1%), *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 ethylacetylene remained unreacted. Isomerization and hydrogenation of 1-butene occurred only after the alkyne was completely removed. Ethylacetylene was found to displace 1-butene from the surface prior to its isomerization and to prohibit the reentry of 1-butene into the reacting surface layer.

In this paper, we report the kinetics of ethylacetylene hydrogenation over nickel-pumice catalyst and the yields of the various products over a wide range of conditions.

EXPERIMENTAL

The apparatus, preparation of the catalyst, experimental procedure, and analytical technique have been described fully previously (*2, 4*). A constant temperature water bath, the temperature of which was controlled to within ± 0.05C° surrounded the reaction vessel instead of the adjustable electrically heated furnace. Cylinder ethylacetylene (Matheson Co.) was passed through a bed of anhydrous silica gel and subjected to bulb-to-bulb distillation through traps immersed in liquid nitrogen and Dry Ice, with generous rejections of head and tail products, until no impurities were detected by a gas chromatography.

The reaction products were analyzed by a Fisher gas partitioner employing two columns, a 12 ft long column packed with 30% hexamethylphosphoramide on 60–80 mesh Columpak and a 13-ft. column packed with 30–60 mesh activated 13x Molecular Sieve. Polymers were determined by difference.

RESULTS AND DISCUSSION

a. Pressure fall–time curves. The pressure fall–time (*P–t*) curves observed in the hydrogenation of acetylene (*7, 8*) and methylacetylene (*4*) over nickel-pumice catalyst

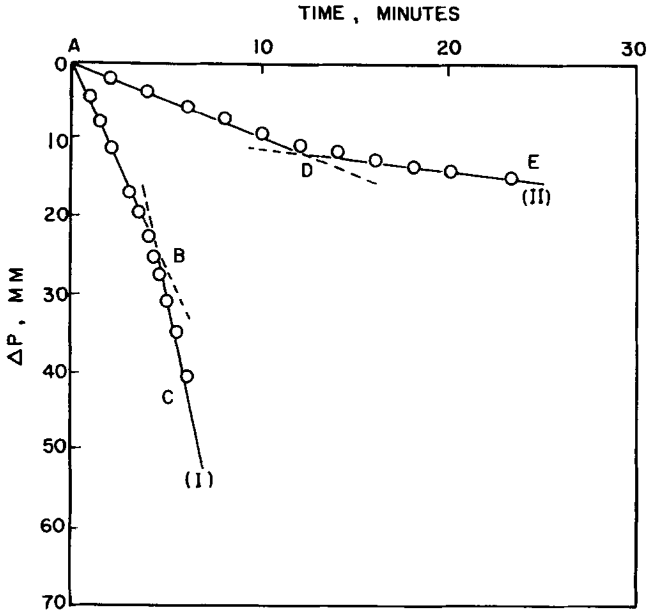


FIG. 1. Pressure-time curves; ethylacetylene, 50 mm. I, curve ABC: P_{H_2} = 125 mm, temperature, 50° C; II, curve ADE: P_{H_2} = 50 mm, temperature, 40°C.

have been discussed in detail previously. The pressure-time curves observed in the hydrogenation of ethylacetylene over nickel-pumice catalyst consisted of two linear portions of different rates (Fig. 1, curve ADE, Type I), when the initial hydrogen/ethylacetylene ratio was 2 or less than 2. At higher hydrogen/ethylacetylene ratios, a different type of curve (Fig. 1, curve ABC, Type II) was observed. This curve was similar to the one observed by Bond and Wells (*8*) for acetylene hydrogenation over platinum, and by Mann and Khulbe (*2*, *3*) for methylacetylene hydrogenation over unsupported cobalt and nickel-copper alloys. In the region AB, the reaction was first order with respect to hydrogen and the main product was α-butylene (1-butene) whereas after the rapid acceleration, the main process occurring was the further hydrogenation of 1-butene to butane.

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 pressures (45–150 mm), orders in hydrogen were determined at several temperatures. Similarly orders in ethylacetylene were 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 1.

TABLE 1

ORDER OF REACTION WITH RESPECT TO HYDROGEN AND ETHYLACETYLENE

Temp. (°C)	Order of reaction with respect to— Hydrogen	Ethylacetylene
23°	1.10 ± 0.02	0.00 ± 0.01
30°	1.03 ± 0.02	0.00 ± 0.01
36°	1.00 ± 0.02	−0.01 ± 0.01
45°	1.00 ± 0.02	−0.23 ± 0.01
55°	1.00 ± 0.02	−0.30 ± 0.01

The order with respect to hydrogen (Table 1) was always about one and did not depend on temperature. However, the order of reaction with respect to ethylacetylene was temperature-dependent and became negative with increased temperatures.

c. Temperature dependence of rate constants. Specific reaction rates were obtained from initial rate measurements for reaction of 50 mm of ethylacetylene with 45–150 mm of hydrogen between 20° and 60°C. An activation energy of 10.0 ± 0.05 kcal/g mole was obtained.

d. Dependence of selectivity upon pressure fall. The course of the reaction for hydrogen/ethylacetylene ratios of 1 (P_{H_2} = 50 mm and $P_{C_4H_6}$ = 50 mm) and 2.5 (P_{H_2} = 125.5 mm and $P_{C_4H_6}$ = 50 mm) was followed by analyzing the reaction products after various falls in pressure. The selectivity (S) defined as the ratio of α-butylene to α-butylene plus n-butane

$$P_{\alpha\text{-butylene}}/(P_{\alpha\text{-butylene}} + P_{n\text{-butane}})$$

was independent of pressure fall for equimolal quantities of the reactants. However, for the hydrogen/ethylacetylene ratio of about 2.5, the selectivity was dependent on the pressure fall (Fig. 2). This was due to the readsorption of α-butylene on the surface and its further hydrogenation to n-butane.

e. Dependence of selectivity upon initial pressures of hydrogen and ethylacetylene. Measurements were made of the selectivity of nickel 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 results are shown in Fig. 3. The selectivity was nearly independent of hydrogen pressures at 40°C. However, at 50° and 60°C, the 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, whereafter it rapidly decreased. No significant variation of selectivity with initial ethylacetylene pressures (45–150 mm) for a fixed initial hydrogen pressure (50 mm) was noted.

f. Dependence of selectivity and polymerization upon temperature. The temperature dependence of selectivity for hydrogen ethylacetylene ratios of 1 and 3 was studied by analyzing the reaction products at several temperatures for a total pressure fall of 20 mm. The results are given in Table 2. Though the selectivity increased slightly with increasing temperature for a hydrogen/ethylacetylene ratio of 1, it

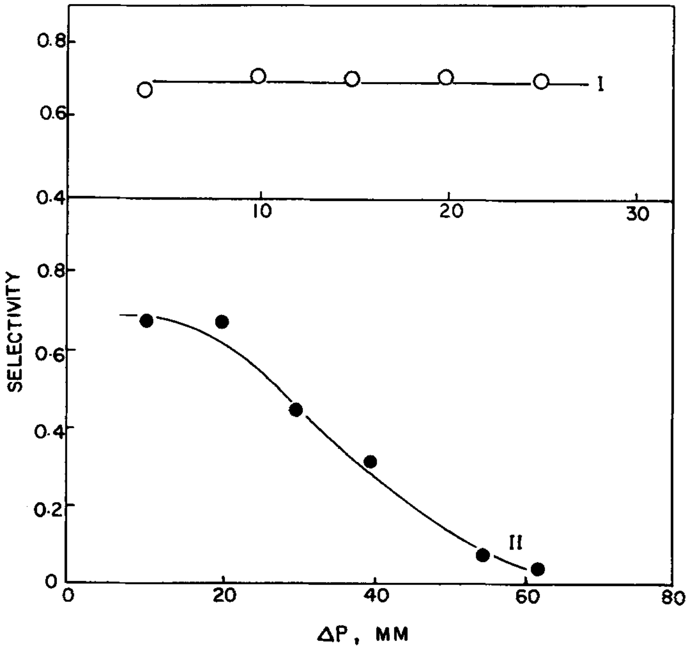


FIG. 2. Selectivity dependence upon pressure fall; ethylacetylene, 50 mm. I, P_{H_2} = 50 mm, temperature 30°C; II, P_{H_2} = 125 mm, temperature, 50°C.

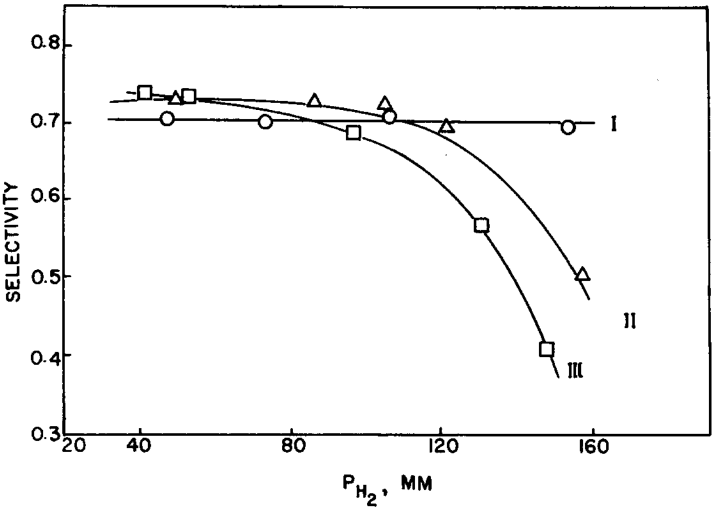


FIG. 3. Selectivity dependence upon initial hydrogen pressure; ethylacetylene, 50 mm, temperature (°C): I, 40°C; II, 50°C; III, 60°C.

decreased very rapidly for a ratio of 3. Small amounts of polymers were observed.

g. General discussion. Though the shape of the pressure–time curves has been studied in detail by Bond (*7*) for acetylene hydrogenation and by Mann and Khulbe (*2*, *3*) for methylacetylene hydrogenation over nickel, and nickel-copper alloys, no such studies are reported for ethylacetylene hydrogenation. Hence no direct comparison of the results obtained in this investigation can be made with those of Bond or Mann and Khulbe, or any other published work.

The pressure–time curves obtained by Mann and Khulbe for methylacetylene hydrogenation were different from those obtained by Bond for acetylene hydrogenation. This may be due to the difference in the method of preparation and activation of the catalyst.

For hydrogen/ethylacetylene ratios of 2 or less than 2, the pressure–time curves obtained in ethylacetylene hydrogenation over nickel-pumice catalyst were similar to those (Type I) obtained by Mann and Naik (*4*) and Mann and Khulbe (*2*) for methylacetylene hydrogenation over nickel. However, for ratios greater than 2, the curves were unlike those obtained for methylacetylene hydrogenation in the sense that no acceleration in the rate (curve ABC, Fig. 1) was observed. A similar type (curve ABC) of curve was observedby Bond and Wells (*8*) for acetylene hydrogenation

TABLE 2

TEMPERATURE DEPENDENCE OF SELECTIVITY

Temp. (°C)	Initial pressure of reactants, (mm)		Products, (mm)			Percent polymer[a]	Selectivity
	H_2	C_4H_6	C_4H_6	1-C_4H_8	C_4H_{10}		
30°	49.0	49.0	34.5	10.0	4.0	1.0	0.714
40°	48.0	48.0	35.0	8.5	3.5	2.0	0.708
50°	47.5	47.5	31.0	13.0	4.5	—	0.742
60°	47.0	47.0	30.5	13.0	4.5	—	0.742
30°	147.0	49.0	34.0	11.0	4.5	—	0.710
40°	144.0	48.0	33.5	9.0	4.0	3.0	0.693
50°	142.5	47.5	32.0	6.5	7.5	3.1	0.464
60°	141.0	47.0	31.0	6.0	9.0	2.2	0.400

[a] Includes traces of *cis*- and *trans*- 2-butene.

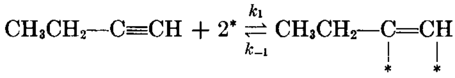
over platinumand by Mann and Khulbe (*2*, *3*) for methylacetylene hydrogenation over cobalt and nickel-copper alloys. Since ethylacetyene is more strongly adsorbed than 1-butene or hydrogen, an increase in the initial pressure of 1-butene or hydrogen would facilitate the entry of 1-butene into the reactive layer, and further hydrogenate 1-butene to *n*-butane. This would result in an acceleration of the reaction. *n*-Butane formed in the early stages, must have, therefore, come from the further hydrogenation of ethylacetylene without the readsorption of gaseous 1-butene on the surface. The increase in the rate of reaction in the region BC (acceleration) was much less in ethylacetylene hydrogenation as compared to methylacetylene hydrogenation.

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 low.

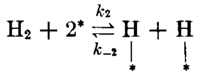
The order with respect to ethylacetylene was temperature-dependent and became more negative with increasing temperature. An increase in the temperature decreases the concentration of reactants in the reactive layer. Since ethylacetylene is more strongly adsorbed on the surface than hydrogen, with increasing temperatures, the desorption of the former would be less than the later. This would result in decreased hydrogen/ethylacetylene ratios on the surface. Hence the order with respect to ethylacetylene becomes more negative with temperature.

Unlike the findings of Meyer and Burwell (*6*) for ethylacetylene hydrogenation over alumina-supported palladium, and of Bond (*9*) for 1-butene hydrogenation over several catalysts, no *cis*- and *trans*- 2-butene were observed in the products. This is probably due to 1-butene not being readsorbed at low hydrogen/ethylacetylene ratios (*2*). On the whole, there is a general similarity between methylacetylene hydrogenation over nickel pumice and nickel powder and ethylacetylene hydrogenation over nickel-pumice.

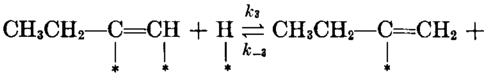
We suggest the following mechanism for ethylacetylene hydrogenation:



$$CH_3CH_2\text{—}C\equiv CH + 2^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CH_2\text{—}\underset{*}{\underset{|}{C}}=\underset{*}{\underset{|}{CH}} \quad (1)$$

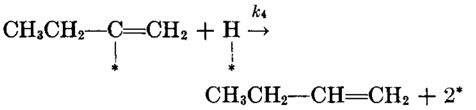


$$H_2 + 2^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{*}{\underset{|}{H}} + \underset{*}{\underset{|}{H}} \quad (2)$$



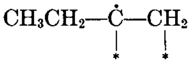
$$CH_3CH_2\text{—}\underset{*}{\underset{|}{C}}=\underset{*}{\underset{|}{CH}} + \underset{*}{\underset{|}{H}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_3CH_2\text{—}\underset{*}{\underset{|}{C}}=CH_2 + 2^* \quad (3)$$

(half-hydrogenated state)



$$CH_3CH_2\text{—}\underset{*}{\underset{|}{C}}=CH_2 + \underset{*}{\underset{|}{H}} \xrightarrow{k_4} CH_3CH_2\text{—}CH=CH_2 + 2^* \quad (4)$$

Step (4) is not shown as reversible since 1-butene produced in the gas phase is not readsorbed due to the presence (strongly adsorbed) of ethylacetylene and any adsorbed 1-butene so formed is rapidly displaced from the surface by adsorbing ethylacetylene or form a free radical



$$CH_3CH_2\text{—}\underset{*}{\underset{|}{\dot{C}}}\text{—}\underset{*}{\underset{|}{CH_2}}$$

by combining with an active site. The free radical then either reacts with adsorbed hydrogen to give adsorbed 1-butene which is further hydrogenated to butane or combines with ethylacetylene to form polymers.

From Eqs. (1) to (4), and equating the rates of half-hydrogenated state formation and removal,

$$k_3\theta_H\theta_{C_4H_6} = k_4\theta_H\theta_{C_4H_7} + k_{-3}\theta_{C_4H_7}[**] \quad (5)$$

the rate of 1-butene formation is given by

$$\frac{dP_{C_4H_8}}{dt} = \frac{k_3k_4\theta_H{}^2\theta_{C_4H_6}}{k_4\theta_H + k_{-3}[**]}$$

where θ_H, $\theta_{C_4H_6}$, and $\theta_{C_4H_7}$, are the fraction of the surfaces covered by hydrogen, ethylacetylene, and half-hydrogenated state.

The fractional surface covered by ethylacetylene ($\theta_{C_4H_6}$) was very high and approached 1. Now if $k_4\ \theta_H >> k_{-3}$ [**], the reaction would be first order with respect to hydrogen pressure. Hence the observed order of nearly one with respect to hydrogen is understandable.

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