ENCLOSURE (B) 11

SYNTHESIS OF BUTENE FROM ACETYLENE

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Butene was synthesized from vinyl acetylene by partial hydrogenation. Palladium and nickel catalysts for this reaction were compared, and the exact conditions for obtaining high yields of butene and suppressing the formation of butadiene and butane were investigated.

I. INTRODUCTION

Isooctane is synthesized from acetylene through eight steps, acetylene, acetaldehyde, aldol, crotonaldehyde, butanol, butene, isobutene, isooctene and isooctane. This method is troublesome not only because of the long course but also the loss of mercury is unavoidable during the synthesis of acetaldehyde from acetylene. Hence, the manufacture of butene from acetylene through vinyl acetylene was investigated. Butene was prepared by the hydrogenation of vinyl acetylene which was obtained by the catalytic polymerization of acetylene. The catalytic polymerization of acetylene was reported by Niewland, *J.A.C.S.* 4197 (1931); Klebbanskii, *India Rubber J.*, 10, 16; and Schmidt, *Z. Elect. Chem.*, 45, 503 (1931). Since no additional data of importance were obtained in regard to the preparation of vinyl acetylene from acetylene, this report is only concerned with the partial hydrogenation of vinyl acetylene to butene.

II. DETAILED DESCRIPTION

A. Apparatus and Procedure

A mixture of vinyl acetylene and hydrogen was passed through a glass tube which was heated in an electric furnace. The catalyst was placed in the reaction tube and the temperature was measured at the center of the reaction tube. Vinyl acetylene used was prepared by the catalytic polymerization of acetylene using a well-known cuprous chloride complex salt solution and was purified by redistillation.

B. Analytical Method

The hydrogenated product which contains vinyl acetylene, butadiene, butene, octane, hydrogen, oxygen, and nitrogen was analyzed by the following method. Vinyl acetylene in 100cc of the sample gas was measured by absorption in an alkaline mercurous cyanide solution. A 25cc portion of the remainder was mixed with 500cc of pure hydrogen and was repeatedly passed through a capillary tube packed with palladium asbestos maintained at 120°C until there was no volume change. The volume of the hydrogen consumed by the hydrogenation of butadiene and butene, and by the combustion with oxygen was measured. Separately, butene and butadiene in another 25cc portion of the remainder from the vinyl acetylene analysis was passed through bromine water, and then the bromine vapor mixed in the sample was removed by a caustic potash solution. The oxygen content was then determined on this sample by absorption in pyrogallol. The percentages of butene, butadiene and oxygen were calculated from the results of the hydrogenation, the bromine absorption and the absorption of oxygen in the pyrogallol solution. Hydrogen was determined by the ordinary combustion method on palladium asbestos. Since the vinyl acetylene used was well purified and the air in the apparatus was replaced carefully by the charging gas, it was regarded that the oxygen and nitrogen in the product came from the atmospheric air after the hydrogenation reaction. Therefore, the amount of the nitrogen in the product was calculated as four times that of the oxygen in the sample. Butane in the product was calculated by the difference of the total volume of the sample taken and the volume of the other components previously measured. These methods were checked exactly with mixed gases having known compositions.

C. Experimental Results

1. Partial Hydrogenation of Vinyl Acetylene to Butene by Palladium Catalyst

The palladium catalysts, supported on diatomaceous earth having various compositions, were prepared by Willstatter's method.

a. Effect of the concentration of palladium in the catalysts

Table I(B)11 shows the effect of varying concentrations of palladium in the catalysts on the yield of butene

TABLE I(B)11

Pd. Conc. in Cat. (%)	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
5	17	8.0	11.7	79.8	0.5	66.3
0.66	17	3.8	10.4	79.8	6.0	65.9
0.4	11	3.1	8.8	88.1		78.2
0.3	11	7.7	20.0	72.3		64.3
0.2	15	7.0	20.5	72.5		61.4
0.1	9	10.0	11.6	78.4		71.5
0.05	15	5.6	21.7	72.7		61.7
0.025	14	4.6	15.9	79.5		68.0

Wt. of the cat. used .... 2 grams
Reaction temperature .... 100°C
Gas velocity ....6 lit/hr/gm of cat
Ratio of hydrogen to vinyl acetylene 2

b. Effect of the reaction temperature

Table II(B)11 shows the effect of the reaction temperature on the yield of butene.

TABLE II(B)11

React. temp. °C	C_4H_4 polymerized	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
30	0	82.8	14.7	2.5		
50	19	3.1	10.8	86.8		70.4
80	12	5.8	12.6	79.5	2.1	70.2
100	15	5.6	21.7	72.7		61.8
145	16	3.6	22.4	74.0		62.3

Pd. in cat. percent 0.05
Wt. of cat. .... 2 grams
Gas velocity ....6 lit/hr/ gm of cat
Ratio of hydrogen to vinyl acetylene 2

c. Effect of the ratio of the amount of hydrogen to vinyl acetylene on the yield of C_4H_8

The effect of varying amounts of hydrogen to vinyl acetylene is shown in the Table III(B)11.

TABLE III(B)11

H_2/C_4H_4	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
1.2	20	39.9	40.7	14.2	11.3	11.3
2.0	9	10.0	11.6	78.4		71.5
2.3	1	2.0	2.0	88.5	7.6	87.8
2.9	23	1.1		81.9	17.0	63.5
3.9	34	0.7	4.8	69.3	25.2	48.4

Pd. content in cat. percent 0.1
Wt. of cat. .... 2 grams
Reaction temperature .... 100°C
Gas velocity .... 6 lit/hr/gm of cat

d. Effect of the gas velocity

The effect of the gas velocity on the yield of butene is shown in Table IV(B)11.

TABLE IV(B)11

gas. vel. lit/hr/gm of cat.	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
12	12	33.7	33.5	32.8		28.5
6	20	12.0	18.9	69.1		55.2
3	14	4.6	15.9	79.5		67.9
1	22	3.4	6.6	83.9	6.3	65.3
0.5	26	6.8	9.6	68.5	15.1	50.7

React. temp. .... 100°C
H_2/C_4H_4 2
Pd. conc. in cat. percent 0.05

e. From these experimental results the following conclusions were derived

(1) There was no pronounced effect of the concentration of palladium in the catalyst on the reaction within the limit of the experiments.

(2) No reaction occured below 30°C. The temperature of the reaction must be above 50°C.

(3) The unreacted vinyl acetylene could be decreased to less than 1% when approximately three times as much hydrogen as vinyl acetylene was used.

(4) The formation of butene could be completely suppressed.

(5) In view of the formation of butene at higher ratios the best ratio of the amount of hydrogen to vinyl acetylene appears to be 0.25.

(6) At the optimum condition the concentration of butene in the C_4 hydrocarbons of the product was 80-90% and 70-75% of the vinyl acetylene was converted to butene.

2. Partial Hydrogenation of Vinyl Acetylene by Nickel Catalyst

The nickel catalyst was prepared by ignition of purified nickel nitrate at 800°C for three hours, and the catalyst was reduced in an atmosphere of hydrogen for three hours before use.

a. Effect of the ratio of hydrogen to vinyl acetylene

When the palladium catalysts were used the ratio of hydrogen and vinyl acetylene showed a pronounced effect on the yield of butene.

Therefore, the effect of the ratio of hydrogen to vinyl acetylene was first examined. The experimental results are shown in Table V(B)11.

TABLE V(B)11

H_2/C_4H_4	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
1.9	55	1.3	17.6	80.2	0.9	36.1
2.3	54	0.5	2.4	95.6	1.5	44.3
2.6	48	0.5	5.5	91.0		48.9
3.1	48	0.6	3.2	86.6	9.6	45.3
3.8	36	0.7		85.7	13.6	58.8
4.0	46	0.9	8.5	67.0	23.6	36.5
4.3	31			60.3	39.7	41.6

Wt. of cat. used .... 5 grams
Reaction temperature .... [illegible]°C
Gas velocity .... 6 lit/hr/gm of cat

b. Effect of the reaction temperature

Table VI(B)11 shows the effect of the reaction temperature.

TABLE VI(B)11

React. temp. °C	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
150	48	0.5		91.2	8.3	47.6
100	45	0.4	5.5	94.1		48.8
50	50	1.2	10.4	77.3	11.1	38.9
40	30	1.0	10.2	69.8	19.0	48.9

Wt. of cat. used .... 5 grams
Ratio of H_2 to C_4H_4 .... 2.5
Gas velocity .... 6 lit/hr/gm of cat

c. Effect of gas velocity

Table VII(B)11 shows the effect of the gas velocity.

TABLE VII(B)11

Gas vol. lit/hr/gm of cat	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
6	35	16.2	25.7	58.1		37.8
3	41	40.0	4.7	87.1	7.4	51.5
1.2	48	0.4	5.5	94.1		48.9
0.6	50	0.4	37.6	40.8	21.6	20.0

Wt. of cat. used .... 5 grams
Reaction temperature .... 100°C
Ratio of H_2 to C_4H_4 .... 2.5

d. From these results the following conclusions were derived

(1) The unreacted vinyl acetylene was easily kept below 1%.

(2) The formation of butane was very small when the reaction temperature was 100°C and when the ratio of hydrogen to vinyl acetylene was less than 2.6. Increasing the reaction temperature and the hydrogen to vinyl acetylene ratio increases the formation of butane.

(3) At optimum conditions the gas produced contained 90 percent or more butene but half of the vinyl acetylene was polymerized and only the other half was hydrogenated to butene.

3. The Polymerization of Vinyl Acetylene, Butadiene, and Butene on the Catalysts in the Absence of Hydrogen

In order to clarify the polymerization action of the catalysts, the individual unsaturated hydrocarbons mentioned above were passed through the catalysts repeatedly in the absence of hydrogen and the volume decrease was measured at each pass. The relation between the volume decrease and the number of passes are shown in Figure 1(B)11. As the figure shows, vinyl acetylene is most apt to polymerize. The polymerization occured not only on nickel and palladium but also on the diatomaceous earth. Although the palladium-diatomaceous earth catalyst had a greater tendency to polymerize vinyl acetylene than the nickel catalyst, the hydrogenation results indicated the reverse to be true. This fact may be explained by the strong hydrogenation action of the palladium catalyst on vinyl acetylene. On this catalyst vinyl acetylene will be easily hydrogenated, therefore the polymerization of vinyl acetylene will be suppressed. Hence, catalysts having strong hydrogenation activity for the triple bond will be suitable for diminishing the polymerization loss.

4. Comparison of Palladium and Nickel Catalysts

Although from the point of view of the purity of butene in the product, the nickel catalyst is more advantageous than the palladium catalyst; the former has a stronger polymerization action on unsaturated hydrocarbons in the hydrogenation reaction than the latter.

The polymerization action of nickel catalyst might be weakened by reducing its polymerization activity by heat, catalyst poisons, or activity deterers, and maintaining the hydrogenation activity.

III. CONCLUSIONS

This method for manufacturing butene as a raw material of isooctane is difficult to extend to commercial scale for the following reasons:

A. Butene produced contains some vinyl acetylene even when the partial hydrogenation was carried out at optimum conditions.

B. Butene produced by this method is always mixed with butadiene.

C. The elimination or the separation of the above contaminants by fractionation was difficult because of the proximity of boiling points.

D. Vinyl acetylene should be hydrogenated to a mixture of butene and butane, since there should be no butadiene or vinyl acetylene present if the product is to be used for the synthesis of isooctane.

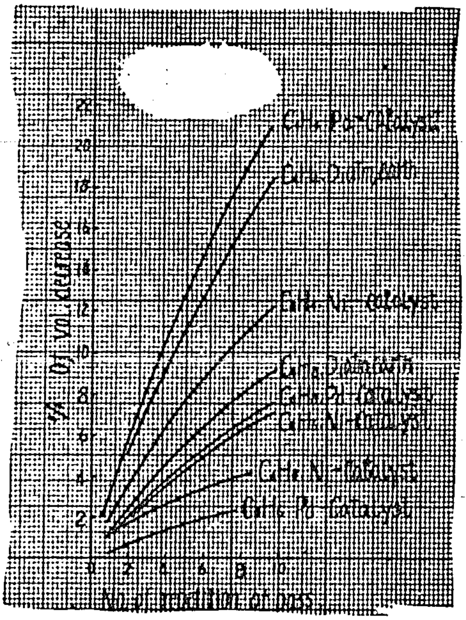

Figure 1(B)11

POLYMERIZATION OF C_4H_4, C_4H_6 AND C_4H_8 ON CATALYSTS