

of the surface in defining the paint performance characteristics of carbon black.

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# Thermal Reaction of Ethylene with Acetylene

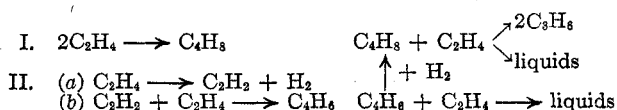
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Following the indications of earlier work of Burk, Baldwin, and Whitacre, acetylene has been shown to react more readily with ethylene than the latter reacts with itself. In this cross reaction butadiene is the preponderant gaseous product although the liquid product exceeds the gaseous. While conditions were chosen to favor the cross reaction, no attempt was made to ascertain the optimum yield of butadiene by this procedure; our aim was to establish with certainty the existence of the cross reaction.

No butadiene is formed when acetylene reacts with itself under conditions used in these experiments. Diolefins and aromatics were prominent in the liquid products.

BUTADIENE has been obtained as a thermal reaction product of ethylene (4, 12) and also of mixtures of ethylene and acetylene (1, 4, 5, 8, 11). Burk, Baldwin, and Whitacre (4) summarized the various mechanisms proposed for the pyrolysis of ethylene and pointed out that the experimental observations upon which they are based do not always agree. They studied the pyrolysis of deoxygenated ethylene at 625° C. and from their results, together with previous work, proposed a dual mechanism:



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The reaction between ethylene and acetylene to form butadiene, first proposed by Berthelot (1), was supported by the fact that the addition of small amounts of acetylene (1.85–3.3 per cent) to the ethylene increased the amount of butadiene formed, affected only slightly the general distribution of products, and was consistent with the order of the reaction under conditions where butadiene is observed. A full investigation of the reaction was not made, however.

The present work is designed to study the reaction between ethylene and acetylene as it pertains to the formation of butadiene and also to liquid hydrocarbons which might be formed from butadiene as an intermediate.

### Experimental Procedure

A mixture of deoxygenated ethylene-acetylene, containing a trace of carbon monoxide added for the purpose and diluted with deoxygenated steam, was heated to 610° C. at atmospheric pressure for reaction times varying between 16.5 and 24.47 seconds. From 12 to 85 liters of ethylene-acetylene were used in each experiment, and the extent of reaction varied between 4.13 and 12.2 per cent for the mixture.

Anesthetic grade ethylene was employed. Analysis showed it to be 99.7 per cent pure. The acetylene was generated from calcium carbide and purified by passage through a series of absorption pipets containing reagents for the removal of the various impurities. The ethylene-acetylene mixture was deoxygenated by the method of Burk, Baldwin, and Whitacre (4). The carbon monoxide for the purpose was prepared by the method suggested by Thompson (15). The water for the steam diluent was deoxygenated by the method of Kobe and Gooding (9). Deoxygenated nitrogen was used to displace the air from the reaction system.

The flow system consisted of a feed system, a reaction vessel, and traps for collecting the products. The feed system was divided into two parts, one for feeding the gaseous mixture and the other for simultaneously feeding the steam.

TABLE I. EXPERIMENTAL DATA AT 610° C. AND ATMOSPHERIC PRESSURE

Expt. No.	Reaction Time, Sec.	Duration of Expt., Hours	Gas Used, Liters		Feed Mixture, Mole %		% Reaction of Mixture	Carbon Formed	Moles C <sub>2</sub> H <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> Converted to Products/100 Moles C <sub>2</sub> H <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> Reacting		Liquids				
			C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>			CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>
2	16.5	3/4	9.05	44.61	25.96	0.32	4.13	Trace	Trace	5.05	2.34	31.06	5.10	0.90	55.0
3	23.4	9	12.19	64.78	40.04	0.51	6.89	1.8	7.2	5.7	1.0	13.5	5.14	0.50	65.2
4	20.9	10 1/3	11.78	...	5.55	0.34	15.70	Trace	7.5	0.4	11.7	...	1.1	0.3	78.9
5	24.47	11 1/4	28.14	56.38	14.42	0.55	12.20	Slight	0.2	1.8	1.4	16.6	3.5	0.2	69.2
6	24.1	12	...	56.83	27.4	0.62	1.1	Trace	3.0	2.2	...	14.9	41.6	Trace	9.5

The reaction vessel was made of heavy, combustion Pyrex glass, 19 mm. inside diameter. It consisted of three vertical spirals fitted into a cylindrical space in the electric furnace, 4.5 inches (11.4 cm.) i. d. and 10 inches (25.4 cm.) long. The inlet and outlet arms were made of smaller tubing, 15 mm. i. d., and extending 3 inches (7.6 cm.) outside the furnace. Each arm contained a thermocouple well. The temperature of the reaction vessel was measured by a platinum and platinum-rhodium thermocouple and a Leeds & Northrup Micromax recorder, and was controlled with a Leeds & Northrup Micromax controller. A stirrer circulated the atmosphere surrounding the reaction vessel. It was possible to hold the temperature at all points in this zone at 610° C. ± 2°. The gases from the reaction vessel passed through a water condenser, an ice-cooled trap, and two absorption traps cooled with solid carbon dioxide and acetone, containing *n*-heptane. The exit gases passed through a calibrated wet test meter. Samples for analysis were taken periodically. The analytical apparatus consisted of a low-temperature distilling column for fractionating the gaseous products, an absorption-combustion apparatus for analyzing the gaseous fractions, and a high-temperature microdistilling column for fractionating the liquid products.

The low-temperature column was of the Podbielniak type. The products collected in the last three traps were distilled into a trap cooled with liquid nitrogen. This distillate was redistilled through the low-temperature column and separated into the following four fractions: ethylene, ethane and acetylene, C<sub>3</sub> hydrocarbons, and C<sub>4</sub> hydrocarbons.

The absorption-combustion apparatus for the analysis of the gases was the standard Orsat type. The

technique was the same as that described by Burk, Baldwin, and Whitacre (4). Following the fractional distillation of the gases, the fractions were further analyzed by this method.

The high-temperature microdistilling column was of the type suggested by Craig (6). It consisted of a 5-mm. i. d. glass tube 31.5 cm. long, with a 3-mm. o. d. inner tube (sealed at both ends) and a 29-cm. silvered vacuum jacket, surrounded with an air jacket wrapped with Nichrome wire for heating. It was fitted with a still head of the type described by Selker, Burk, and Lankelma (13). Using a test mixture of carefully purified *n*-heptane and methylcyclohexane, this column gave an efficiency of sixty-four theoretical plates, calculated by Smoker's formula (14), with a take-off rate of 0.1 cc. per hour. This column was employed for fractionating the liquid products.

### Reaction Products

The results of five experimental runs are summarized in Table I. The following two exceptions to the prescribed mode of procedure should be noted: (a) The uncondensed gas from experiment 2 was collected over water and was analyzed directly in the absorption combustion apparatus without previous distillation. (b) The uncondensed gas from experiments 4 and 5 was also analyzed directly since the high percentage of acetylene with the narrow range between its boiling and melting points made distillation impracticable.

The liquids from experiment 5 were carefully fractionated and certain of the constituent hydrocarbons identified. The distillation curve is shown in Figure 1.

From properly selected fractions, benzene was identified as the *m*-dinitro derivative and toluene as the 2,4-dinitro derivative; and 1,3-cyclohexadiene although not positively identified, was indicated by the formation of a product melting at 141–145° C. by a Diels-Alder reaction with maleic anhydride. Birch and Scott (3) reported 147° C. as the melting point of the cyclohexadiene derivative. Insufficient quantities of material, however, prevented further identification of this product.

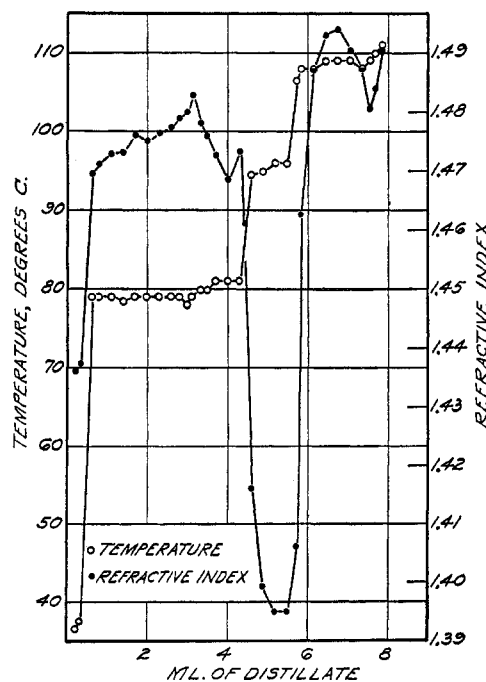


FIGURE 1. DISTILLATION OF LIQUID PRODUCTS FROM EXPERIMENT 5

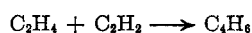
TABLE II. YIELD OF BUTADIENE PER 100 LITERS OF ETHYLENE PASSED

Expt. No.	Reaction Time, Sec.	Feed Mixture, %				% Reaction	Co. C <sub>4</sub> H <sub>6</sub> /100 L.
		C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	Steam		
2	16.5	5.27	25.96	0.32	68.45	4.13	782
3	23.4	7.53	40.04	0.51	51.92	6.89	891
5	24.47	14.42	28.90	0.55	56.13	12.20	2958
6	24.1	0.0	27.4	0.62	71.98	1.10	171.5

TABLE III. PER CENT REACTION OF ACETYLENE (ASSUMING NO INTERACTION OF ETHYLENE AND ACETYLENE)

Expt. No.	Reaction Time, Sec.	Feed Mixt., %		% Reaction	
		C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	Total	Of C <sub>2</sub> H <sub>2</sub>
3	23.4	7.53	40.04	6.89	1.1
4	20.9	5.55	0.0	15.70	0.0
5	24.47	14.42	28.90	12.20	1.1

As previously stated, Burk, Baldwin, and Whitacre (4) presented evidence for the reaction,



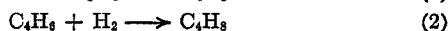
first proposed by Berthelot in 1866. Further evidence in support of this mechanism has been obtained in the present investigation. Since no butadiene was formed from acetylene in experiment 4, one would suspect that the butadiene formed in experiments 2, 3, 5, and 6 arose either from ethylene alone or by the interaction of ethylene and acetylene. If it was formed entirely from the ethylene, however, its yield per unit volume of ethylene passed would be approximately constant in each experiment. Table II indicates that the contrary is the case. Butadiene formation is dependent upon the percentage of acetylenes in the feed mixture.

Further evidence on this point is given by the per cent of reaction of the various mixtures. Assuming that there was no interaction of ethylene and acetylene and that ethylene reacted to the extent of 1.1 per cent as in experiment 6, the per cent reaction of acetylene in experiments 3 and 5 may be calculated. These results, compared with the per cent reaction of acetylene alone in experiment 4, are shown in Table III.

These results show that if there was no interaction of ethylene and acetylene in experiments 3 and 5, the per cent reaction of acetylene would have to be more than twice the value found in experiment 4.

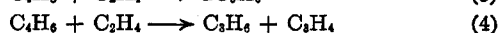
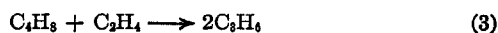
In experiment 6 (pyrolysis of ethylene) propylene, butylene, and butadiene were the principal products; in experiment 4 (pyrolysis of acetylene) vinylacetylene was the principal gaseous product. This suggests that, in the pyrolysis of ethylene-acetylene mixtures (experiments 2, 3, and 5), most of the butylene and propylene was formed from the ethylene and the vinylacetylene from the acetylene. This is brought out in Table IV.

The formation of butylene may be accounted for in two ways (4):

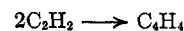


Reaction 1 is supported by the results in experiments 3 and 6 (Table IV). Approximately the same amount of butylene was formed, although no acetylene was present in experiment 6. However, the amount of butylene formed in experiment 5 suggests that reaction 2 may take place to an appreciable extent in the presence of relatively large amounts of butadiene.

Burk, Baldwin, and Whitacre (4) presented evidence to show that propylene is a secondary reaction product. They favored the first of the following two reactions which could be used to account for its formation:



The data of Table IV suggest that most of the propylene was formed according to reaction 3. However, since its yield was increased by the presence of acetylene, which formed butadiene, it is probable that reaction 4 occurs to some extent. This is supported by the fact that propylene was identified in the reaction products of experiment 5. The formation of vinylacetylene in experiment 4 may be accounted for by dimerization:



This mechanism is in agreement with Pease's observation (10) that the polymerization of acetylene is bimolecular.

The data in Table IV indicate that the yield of vinylacetylene was less in experiments 3 and 5 in which ethylene was present. This suggests the possible interaction of ethylene and vinylacetylene to form higher polymers according to the equation:



Two principal mechanisms have been proposed to account for the formation of liquid products from the pyrolysis of ethylene. The first involves the primary formation and subsequent polymerization of acetylene (2). The second involves the formation of butadiene followed by condensation with ethylene to form the higher polymers (7). Evidence that butadiene is an intermediate in the formation of liquid products is obtained by comparing the yield of liquid per 100 liters of acetylene passed in experiments 3, 4, and 5 (Table V).

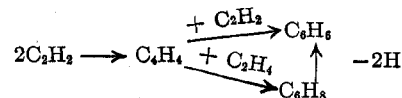
TABLE IV. YIELD OF PRODUCTS PER 100 LITERS OF GAS PASSED

Expt. No.	Reaction Time, Sec.	Feed Mixt., %		Co. of Product/100 L.		
		C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>
3	23.40	7.53	40.04	210	309	221
4	20.90	5.55	0.0	...	...	925
5	24.47	14.42	28.90	321	447	263
6	24.10	0.0	27.4	231	213	...

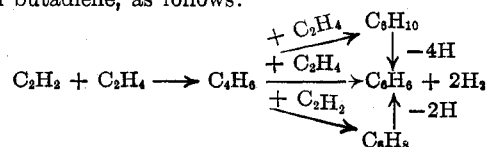
TABLE V. YIELD OF LIQUID PER 100 LITERS OF ACETYLENE PASSED

Expt. No.	Reaction Time, Sec.	Feed Mixt., %		% Reaction	Grams of Liquid/100 L.
		C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>		
3	23.4	7.53	40.04	6.89	33.96
4	20.9	5.55	0.0	15.70	14.43
5	24.47	14.42	28.90	12.20	30.63

Since in the presence of ethylene more than twice as much liquid was formed, it appears that at least half of the liquid was formed as a result of the interaction of ethylene and acetylene. This is further supported by the fact that the composition of liquid products from experiment 4 varied considerably from that of experiments 3 and 5. Whereas the former boiled between 75° and 85° C., the latter boiled between 30° and 111° C. and left a relatively large residue. The formation of cyclo-olefin and aromatic hydrocarbons may result from either of the two mechanisms previously referred to. If from acetylene, the mechanism would be as follows:



If from butadiene, as follows:



The C<sub>6</sub> hydrocarbons and toluene may be accounted for by reaction between unsaturated units of C<sub>2</sub> and C<sub>2</sub> and of C<sub>3</sub> and C<sub>4</sub>, respectively.

### Summary

The synthesis of butadiene by the interaction of ethylene and acetylene was studied in an all Pyrex glass flow system at 610° C. at atmospheric pressure and with a short reaction time. Steam was used as a diluent. Special precautions were taken to remove traces of oxygen from the reacting gases.

The results of this investigation indicate that ethylene and acetylene combine in equimolecular proportions to form butadiene. Side reactions which occur are the dimerization of ethylene and of acetylene. From these primary products both gaseous and liquid secondary products are formed.

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# Recovery of Oil from Whole Cotton

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**Objectionable coloring matter in the stems and cusps can be removed from whole cotton by aqueous solutions of sulfides or sulfites. After treatment with a sulfide, organic solvents recover the oil in a form easily bleached by standard adsorbents. A refined oil can be obtained from whole cotton which meets standard specifications and the requirements of the American market.**

THE term "whole cotton" connotes plants grown under forcing conditions of close planting and harvested by mowing the whole plant after it has attained a maximum content of oil and cellulose. In the season of 1940 a grant from the International Harvester Company made it possible to grow whole cotton on a farm near Chapel Hill in a study of production costs. Shortly after harvesting, a number of bales were selected at random and a composite sample was prepared. Analysis showed 53.5 per cent cellulose and 8.4 per cent oil (ether extract), and the product appeared suitable for a study of oil recovery.

Whole cotton is prepared for processing by pulverizing the air-dried material. The oil can then be removed by solvent extraction, the residue being subsequently pulped. In the solvent extraction not only is the cottonseed oil dissolved, but there are removed from the mass some waxes (from the lint) and a complex of highly colored substances (from the bark of the stems). To separate these coloring matters from the oil is sometimes so difficult as to prejudice the use of whole cotton as a practicable source of oil. The difficulty can be

resolved, however, by removing the coloring matters before solvent extraction, and an oil is obtained which meets American requirements of color and standard properties.

### Solvent Extraction of Oil

The pulverized whole cotton is a fluffy mass of lint interspersed with fragments of wood particles from stems and cusps and broken seed meats. By weight the lint comprises a quarter of the mass and the seed meats about 35 per cent, the remainder is divided about equally between stems and cusps. It is impracticable to extract the oil by pressing—hence, recourse to solvent extraction. Practically, a low-boiling hydrocarbon (boiling at 60-70° C.) is suitable. Ether, carbon disulfide, carbon tetrachloride, and other fat solvents are available for laboratory work only. Solvent extraction in itself presents no difficulties; it has long been established practice in Europe and is receiving increased attention in this country. The amount of oil recovered is thought to be more efficient, with costs on a par with those of the press in American operations (2, 5, 6, 7).

If the pulverized mass is extracted with any of the solvents cited and the solvent evaporated from the extract, the residue is a dark brown, almost black, viscous paste. The

TABLE I. COMPARISON OF OILS FROM WHOLE COTTON WITH STANDARD A. O. C. S. SPECIFICATIONS<sup>a</sup>

Constant	Standard	Crude Oil from Whole Cotton	Oil after Pre-treatment with Na <sub>2</sub> S	Refined Oil from Pretreated Whole Cotton
d <sub>4</sub> <sup>25</sup>	0.916, 0.918	0.885, 0.890	0.893, 0.900	0.908, 0.912
n <sub>D</sub> <sup>25</sup>	1.468, 1.472	1.475, 1.479	1.474, 1.476	1.473, 1.475
Saponification No.	190, 198	178	188	198, 201
Iodine No.	106, 113	88	.....	101, 105

<sup>a</sup> Determinations of iodine numbers as recommended by Rosenmund and Kuhnemann (8), other determinations as recommended by Griffen (3).