

Dr. H. S. Lukens, to whom he would here express his thanks, and also to the Trustees of the Carnegie Institution in Washington for the grant which has made possible this study and kindred studies now in progress.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY]

## THE FORMATION OF BUTADIENE FROM ETHYLENE

By J. E. ZANETTI, J. R. SUYDAM, JR. AND M. OFFNER

Received June 9, 1922

### Introduction

The action of ethylene at high temperatures has been studied by several investigators.

Marchand<sup>1</sup> who was the first to make a careful study obtained carbon and hydrogen from ethylene at a "white heat."

Magnus<sup>2</sup> working at "red heat" obtained methane, hydrogen, carbon and naphthalene.

Berthelot<sup>3</sup> in several investigations obtained acetylene, ethane, styrolene and naphthalene.

Norton and Noyes<sup>4</sup> had observed that a certain hydrocarbon called crotonylene,  $C_4H_6$  (butadiene) was among the products when ethylene was formed by the action of heat, and that its formation had not been observed where ethylene was absent. They, therefore, passed a current of ethylene through a "red-hot" tube and examined the products. They succeeded in identifying benzene, naphthalene, anthracene (?), propylene, butylene, divinyl (butadiene), methane, ethane and carbon. Only a trace of hydrocarbons of the acetylene series was reported.

Day<sup>5</sup> was the first of the workers on this subject to get away from the use of such indefinite terms as "red heat" and "white heat" to denote the temperature at which he worked. His experiments were carried out at 400°, but he does not report the formation of butadiene.

Bone and Coward,<sup>6</sup> starting with a known volume of ethylene, determined the changes in the partial pressures of the gases; ethylene, acetylene, ethane, methane and hydrogen, present at definite temperatures over certain time intervals. The object of their studies was to throw more light on the much mooted questions regarding the mechanism of the transformations which occur in pyrogenic reactions. The hydrocarbon divinyl (butadiene) is not mentioned by them.

A search of the literature fails to show any other work that has been done on the formation of butadiene by the pyrogenic reaction of ethylene.

Staudinger, Endie and Herold,<sup>7</sup> in an investigation of the thermal decomposition

<sup>1</sup> Marchand, *J. prakt. chem.*, **26**, 478 (1842).

<sup>2</sup> Magnus, *Pogg. Ann.*, **90**, 1 (1853).

<sup>3</sup> Berthelot, *Compt. rend.*, **50**, 805 (1860); **62**, 94 (1866); *Ann. chim. phys.*, [4] **16**, p. 144 (1869), etc.

<sup>4</sup> Norton and Noyes, *THIS JOURNAL*, **8**, 362 (1886).

<sup>5</sup> Day, *ibid.*, **8**, 66 (1886).

<sup>6</sup> Bone and Coward, *J. Chem. Soc.*, **93**, 1216 (1908).

<sup>7</sup> Staudinger, Endie and Herold, *Ber.*, **46**, 2467 (1913).

of isoprene, passed butadiene through a tube heated to 800° and obtained a tar containing 10.2% of unsaturated compounds, 30.6% of benzene, 18.3% of saturated compounds, 24.5% of a fraction consisting mostly of naphthalene and 16.5% of a fraction chiefly composed of anthracene.

Davidson,<sup>8</sup> by freezing the gases coming from the decomposition of natural gas condensates, obtained what appeared to be butadiene, which he identified by preparing tetrabromo-butane.

Staudinger, Endie and Herold, and Davidson have pointed out that butadiene may play an important role in the formation of aromatic from aliphatic hydrocarbons and in continuation of the work which has been carried out in this Laboratory for some years, it seemed of interest to study the formation of butadiene from ethylene from a quantitative standpoint.

### Theoretical

The direct formation of butadiene from ethylene takes place according to the equation,  $2C_2H_4 = CH_2=CH-CH=CH_2 + H_2$ .

It will be noted that there is no change of volume in this reaction, which means that the pressure in the reactor would have no influence on the quantity of butadiene formed.

The heat of combustion of butadiene has not been determined and its heat of formation can, therefore, be obtained only from calculations. These, however, give such divergent values that it is not possible to assign any definite value or even an approximate one to the heat of formation of that compound.

This reaction appears to be favored by high temperatures. As, however, all hydrocarbons become extremely unstable at temperatures in the neighborhood of 1000°, the decomposing tendency begins to be manifest and the decomposition to carbon and gas becomes so rapid that there can no longer be any butadiene formed. The formation of butadiene from hydrocarbons by pyrogenic reactions can at best give only small yields, for it does not form at low temperatures and it decomposes above 900°.

**Material.**—The ethylene was commercial ethylene made from ethyl alcohol and was procured in tanks under 80 atmospheres pressure. It analyzed 99.5% ethylene. This gas was tested for the presence of butadiene by passing about 100 liters into bromine and distilling the ethylene dibromide formed. The solid residue was negligible in amount.

**Apparatus and Procedure.**—Fig. 1 shows the arrangement of the apparatus.

The gas bottle (4) was filled with ethylene from the cylinder and measured under atmospheric conditions. The furnace was brought up to temperature. The pressure in the system was regulated by means of the aspirator bottle so that all pressure due to the head of bromine was counteracted.

The ethylene was then allowed to pass through the furnace, the flow

<sup>8</sup> Davidson, *J. Ind. Eng. Chem.*, 10, 901 (1918).

being regulated by means of stopcocks and a flow meter (7) to a flow of about 0.13 liters per minute. The gases were cooled by a condenser (14) and passed through a small Cottrell precipitator to remove tar "fog." The gases coming from the precipitator were passed into bromine and water in 3 gas-washing bottles (16). When the bromine in the first 2 bottles was decolorized, the run was stopped, the bromine in the third bottle decolorized directly from the tank with ethylene, and the bromides distilled with steam.

The distillation was cut at the point where the dibromo-ethane ceased coming over and the water began to be cloudy. This indicated that tetrabromo-butane had begun to distil with the steam.

The solid from the second cut was filtered out, dissolved in water and crystallized. The mother liquor was heated and diluted with water to precipitate more tetrabromo-butane which was crystallized again from 95% alcohol and added to that from the first crystallization. This was repeated until no appreciable amount of tetrabromo-butane could be recovered from the mother liquors. Evaporation of the mother liquors of the 750°, 800° and 850° runs resulted in about 0.5 cc. of liquid which did not solidify at 0°. The composition of this substance was not determined.

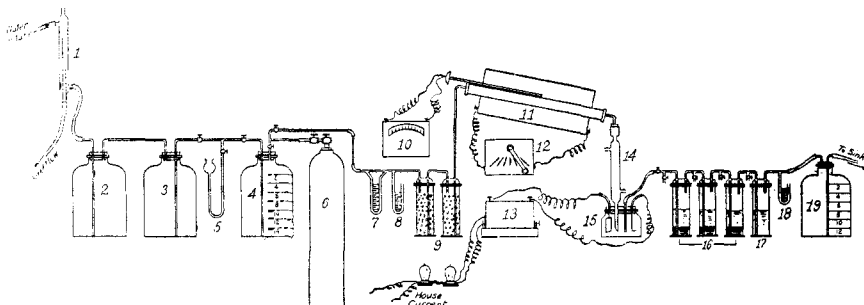


Fig. 1.—Apparatus.

The tetrabromo-butane was dried on a porous plate and then to constant weight in a vacuum desiccator.

In order to have an indication of the extent of the decomposition of ethylene to saturated hydrocarbons and hydrogen the gas, after the absorption in bromine, was passed through sodium hydroxide to remove bromine vapors, was measured in the aspirator, Bottle 19, and analyzed for hydrogen and paraffins.

The values of from 0.10 to 0.15 liters per minute for the speed of ethylene was decided on for the following reasons: (1) this speed would allow the gas to stay in the hot section of the tube about 0.8 minute which, with the time it was in the 10 cm. of the tube which was not in the hot portion of the furnace, was sufficient to bring the gases to the temperature of the walls of the furnace; (2) slower speed, such as would allow the gas to be in

contact with the hot part of the furnace for 3 minutes or longer, would result in a rapid decomposition of ethylene to hydrogen, methane and carbon.<sup>6</sup>

The exact effect of varying the time in the reaction tube on the formation of butadiene remains to be determined.

**Accuracy of Measurements.**—The temperature was controlled by means of a rheostat (12), and a pyrometer (10) having a base metal thermocouple. It was possible to maintain the temperature constant within  $5^{\circ}$ , without any difficulty.

The ethylene can be measured to within 0.2 liter in 19 liters. This is an error of 1.1%. The error in reading the thermometer or barometer is naturally not as great as this. It may be said, therefore, that the error in measuring the ethylene used is less than 2%.

The speed of flow of the ethylene can be regulated within 20.0%, a variation which will have no appreciable effect on the decomposition of the ethylene at a speed of 0.1 liter per minute.

The accuracy in determining the tetrabromo-butane is more difficult to ascertain. In the case of the high point of the curve, where 7.0 g. was recovered from 84 liters of ethylene, a loss of 0.5 g. would mean a reduction of the percentage of ethylene polymerized to butadiene only from 0.960 to 0.890, an error of 7%. Since 0.4 g. of butadiene was easily recovered from 68.0 liters of ethylene in the  $600^{\circ}$  run, the chance of an error of 7% on the high point was probably slight.

**Determination of Butadiene.**—Tetrabromo-butane exists in 2 modifications: one melts at  $118-119^{\circ}$ , boils at  $260-270^{\circ}$ , forms monoclinic crystals which are insoluble in 85% alcohol and in ligroin, and on distilling goes over to the second modification; the latter melts at  $37-39^{\circ}$ , forms rhombic crystals, and is very easily soluble in alcohol, ether and ligroin.

The higher-melting modification is the one obtained by brominating in the proportion 1 : 3.

The first run, for determining whether butadiene was formed by passing ethylene through this apparatus, was made at  $700^{\circ}$ .

Fearing that the presence of water might cause the decomposition of the bromides, we first decided to separate the bromides by dry distillation. However, this method left a tarry residue from which it was impossible to extract the solid tetrabromo-butane completely with boiling alcohol.

The distillation of the bromides with steam proved more effective. The dibromo-ethane distilled in the proportion of about 2 volumes to 1 of water. The water layer was clear until all of the dibromo-ethane had been distilled, when the water coming over became turbid and a yellow solid deposited in the condenser. This solid crystallized from alcohol as pure white needles. On standing for a time, the needles seemed to change their form, and on examination under the microscope, appeared as iridescent plates of irregular outline. The substance was crystallized from hot 95%

alcohol 5 times, dried on a porous plate and then in an oven maintained at about  $100^{\circ}$  for an hour.

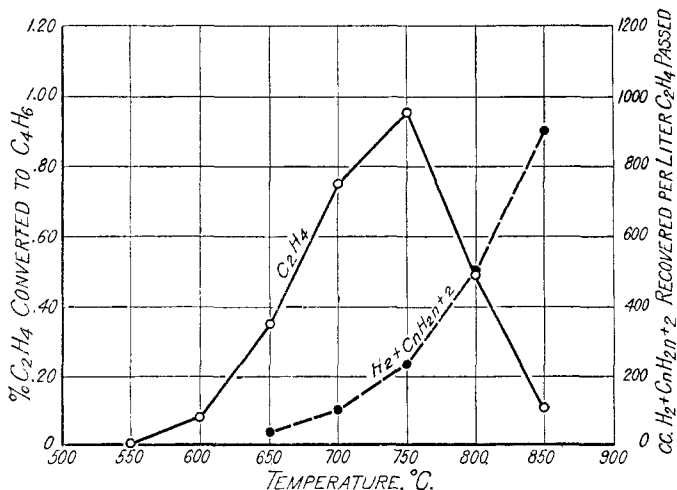
The bromine in the purified solid was determined by the method of Drogin and Rosanoff.<sup>9</sup>

Subs., 0.2805, 0.2358. Calc.: Br, 85.56. Found: 85.58, 85.77.

Our product was found to melt at  $116.8^{\circ}$ . As stated above, the melting point of tetrabromo-butane is  $118-119^{\circ}$ . This is probably due to the fact that the high-melting modification gradually goes over to the low-melting at temperatures above  $100^{\circ}$ .

The bromine content and the proximity of this melting point to the highest yet determined for tetrabromo-butane ( $118-119^{\circ}$ ) is sufficient proof that this material is tetrabromo-butane.

The evaporation of the mother liquor left only a small residue of about 0.5 cc. which stiffened on cooling to  $0^{\circ}$ . On treating this with ligroin and filtering, a small quantity of solid was obtained which probably was tetrabromo-butane. The ligroin was evaporated and the remaining oil chilled, but it did not solidify. These quantities were so small compared to that of tetrabromo-butane recovered that it was not considered worth while to do further work on determining their composition.



After no more of the yellow solid appeared in the condenser, the small quantity of hard, tarry residue remaining in the distillation flask was extracted with alcohol and redistilled with steam. No more yellow solid appeared.

The dibromo-ethane from the distillation with steam was dried and redistilled. It began to boil at  $127^{\circ}$ , and was completely volatilized at  $160^{\circ}$  most of it distilling below  $135^{\circ}$ . The boiling point of dibromo-ethane is

<sup>9</sup> Drogin and Rosanoff, THIS JOURNAL, 38, 711 (1916).

131–132°. Therefore, no tetrabromo-butane came over with the dibromoethane during the distillation with steam.

**Results.**—The curves in Fig. 2 show the relation of yield of butadiene to temperature and the extent of the decomposition of the ethylene to hydrogen and saturated compounds. The yield of butadiene is plotted as percentage by volume of original ethylene, polymerized to butadiene; the hydrogen and paraffins as cubic centimeters of total gas delivered to liters of ethylene passed. The maximum value possible for this latter figure is 2000.

### Discussion of Data

From Fig. 2 it can be seen that butadiene begins to form at 600°, reaches a maximum equivalent to about 1.0% of the ethylene supplied and drops to 0% between 850° and 900°.

It will be noted that the diminution of the amount of butadiene at 750° is coincident with the beginning of the formation of aromatic compounds, which previous results obtained in this and other laboratories have shown to begin at that temperature. Although we are not prepared to say that butadiene is a necessary step in the formation of aromatic substances, it appears to play an important part. The work of Staudinger, Endie and Herold leaves little doubt that this is the case.

It is also interesting to note that we are dealing here with the formation of a compound of higher carbon content from one of lower content by the action of heat. Such reactions are doubtless encountered in the cracking of oils, and although most cracking processes take place below the temperatures of maximum butadiene formation, it is not unlikely that compounds of similar structure may be formed at lower temperatures. It is to be noted that the boiling point of butadiene is around 0°, and very much higher, therefore, than that of ethylene, which is  $-102^{\circ}$ . This, then, is a very good example of building up aliphatic hydrocarbons of higher boiling point from those of lower boiling point by the simple action of heat.

### Summary

1. The formation of butadiene from ethylene has been studied at temperatures varying from 550° to 850°.
2. The temperature of maximum formation has been shown to be 750°, above which the decomposition of ethylene to methane, hydrogen and carbon occurs very rapidly. The maximum quantity of ethylene converted to butadiene was 0.0096 liters per liter of ethylene.
3. It is suggested that the formation of aromatic hydrocarbons from ethylene takes place, at least in part, through the intermediate formation of butadiene.
4. Attention is called to the formation of an aliphatic hydrocarbon of higher boiling point from one of a lower boiling point, and to the possible role of similar reactions in the cracking of oils.