

**SOME REACTIONS  
OF ACETYLENE.  
DISSERTATION**

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Some Reactions of Acetylene. Dissertation by Julius A. Nieuwland

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**JULIUS A. NIEUWLAND**

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SOME  
REACTIONS OF ACETYLENE

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DISSERTATION

SUBMITTED TO THE FACULTY OF PHILOSOPHY OF THE CATHOLIC  
UNIVERSITY OF AMERICA FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

BY

*Julius*  
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## THE HYDROGENATION OF ACETYLENE.

### THE HISTORY OF THE SYNTHESIS OF ETHYLENE.

Numerous attempts have been made to unite acetylene with hydrogen to form ethylene or ethane. The first combination of acetylene with hydrogen was effected by Wilde,<sup>1</sup> who united them by passing the gases over platinum black, ethylene being formed. The residual gas did not give the acetylene reaction with ammoniacal cuprous chloride, and was absorbed by fuming sulphuric acid.

Berthelot<sup>2</sup> succeeded in obtaining ethylene from acetylene given off from copper acetylide in the presence of nascent hydrogen. The gases were obtained from zinc and from copper acetylide in ammonia water. Hydrogen from an acid solution did not give a good yield of ethylene. The ethylene was separated from the acetylene with difficulty, as the two hydrocarbons dissolved in the ammoniacal cuprous chloride. The latter gas, however, formed a precipitate of copper carbide, from which the acetylene could be determined gravimetrically, and the ethylene could be calculated volumetrically by boiling the solution of the cuprous chloride, when the gas was evolved from the solution, and measured after washing free from ammonia.

<sup>1</sup> Ber. 7. 353. (Bull. d' Acad. Royal de Belg. 2, XXI., No. 1. (1864).)

<sup>2</sup> Ann. Chim. Phys. 3, LXVII., 51, (1863.)

Berthelot<sup>1</sup> likewise showed that when a mixture of hydrogen and acetylene was heated, ethylene was one of the products. He accounted for the formation of the ethylene in two ways, first by direct addition, when the action represented by the equation,  $C_2H_2 + H_2 = C_2H_4$ , took place. As, however, the yield of the ethylene was too small to correspond to this reaction, another mode of formation was suggested, namely:  $2C_2H_2 = C_2H_4 + 2C$ . Ethylene likewise underwent decomposition into acetylene and ethane:  $2C_2H_4 = C_2H_2 + C_2H_6$ . If hydrogen were present it united with the ethylene to form ethane.

In 1895, N. Caro<sup>2</sup> claimed that he had obtained alcohol from acetylene. This gas and hydriodic acid gave ethylene di-iodide, or ethylidene di-iodide, and this product being boiled with a concentrated solution of caustic potash gave potassium acetate, acetylene and alcohol. Seventy grams of alcohol were said to have been obtained in one operation. When the di-iodide was decomposed with silver hydroxide, only small quantities of acetylene were obtained, together with 90 per cent. potassium acetate and alcohol. (!) The di-iodide of ethylene heated in closed tubes with water gave a yield of alcohol that amounted to 40 per cent. of the theoretical.

Krüger and Pneckert<sup>3</sup> repeated Caro's work, and found that they could make 50 grams of di-iodide in three months and from this no alcohol could be obtained, though aldehyde was shown to be present.

<sup>1</sup> Ann. Chim. Phys. 4, IX., 431.

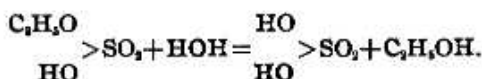
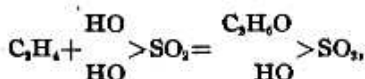
<sup>2</sup> Cent. (1895) 2, 437. Chem. Ind. 18, 226.

<sup>3</sup> Chem. Ind. 18, 454.



Caro repeated his work, but could not obtain his previously published results and acknowledged his mistake.

Krüger<sup>1</sup> could not, moreover, succeed in uniting acetylene with nascent hydrogen, as Berthelot<sup>2</sup> had claimed. In 1894, an article was published by Frank<sup>3</sup> advocating the commercial manufacture of alcohol thus prepared by the action of acetylene on nascent hydrogen. The ethylene formed was to be led into ordinary strong sulphuric acid. This, diluted and boiled with water, would give alcohol. The acid would be again concentrated and used. This process was represented by the following reactions:



In 1899 and 1900, Sabatier and Senderens<sup>4</sup> studied the action of finely divided metals such as nickel, cobalt, copper, and iron on a mixture of hydrogen and acetylene, and found that under certain conditions of temperature and time, ethylene, ethane and

<sup>1</sup> Chem. Ind. 18, 459.

<sup>2</sup> Compt. Rend. 54, 515.

<sup>3</sup> Chem. Ind. 18, 74. (1894).

<sup>4</sup> Compt. Rend. 128, 173, and 130, 1559, 1628, 1762.

other hydrocarbons of the aliphatic and aromatic series were obtained.

In 1902, the addition of hydrogen to acetylene was effected electrolytically by Bilitzer.<sup>1</sup> He electrolyzed acetylene gas dissolved in a solution of sodium potassium and ammonium hydrates, and in sulphuric acid. In the alkaline electrolytes depolarization with the union of acetylene and the electrolytic hydrogen took place with a platinized platinum cathode, but not with plates of platinum or nickel. In sulphuric acid solutions of acetylene with platinized platinum electrodes the products were ethylene, ethane, and hydrogen, according to the strength of the current used. The hydrogenation of the acetylene was effected only when very weak currents were employed. This seems to show that the action was entirely a mechanical one, for when strong currents were used the platinum electrodes would become coated with gas and prevent the access of the acetylene to the finely divided platinum on the surface of the electrode. The acetylene was absorbed with ammoniacal silver nitrate, the ethylene with fuming sulphuric acid. Hydrogen and ethane were determined by explosion. Bilitzer worked with very small quantities and claimed yields of ethylene and ethane entirely quantitative, measured by the law of electrochemical equivalents.

In a solution of normal sulphuric acid, alcohol was supposed to be formed at the mercury cathode, presumably due to the reduction of aldehyde formed by

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<sup>1</sup> *Monats. f. Chem.* XXIII, 203.

the action of the sulphuric acid on the acetylene. Traces of alcohol were vouched for. The alcohol was indicated by the potassium bichromate and iodoform reactions. The author wished to obviate any mistake and passed acetylene into a portion of the acid without using any current. Only the odor of iodoform was noticed. When the current was passed through the solution for the same length of time as in the previous experiment, a fine but perceptible precipitate of iodoform was obtained. Therefore the author concluded that in the second instance the precipitate of iodoform was due to the alcohol formed at the cathode. The author did not suppose that acetylene was changed to ethylene in an acid solution, but thought that the aldehyde present, especially at the mercury cathode was reduced to alcohol at that pole. Now this presupposes that the aldehyde was present before the alcohol was formed. Alcohol may have been present, but the iodoform test does not demonstrate its presence when a primary aldehyde is in solution with it. Acetaldehyde will give the iodoform reaction far more readily than alcohol,<sup>1</sup> and so no reliance can be put in this test. Bilitzer accordingly concluded that with platinized platinum electrodes depolarization takes place at the cathode, and that the products in an alkaline solution are ethylene, and ethane when low potentials are used. In a sulphuric acid solution with a cathode of mercury, small quantities of acetylene are changed to traces of alcohol. The improbability of this conclusion will be

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<sup>1</sup> Lieben,—Ann. Supp. 7, 218 and 377.