THE SYNTHESIS OF ALKYL ACETYLENES FROM CALCIUM ACETYLIDE

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Since Lebeau and Picon[2] prepared methylacetylene by the action of sodium acetylide on methyl iodide in liquid ammonia at —45° C. the general equation,

$$HC\equiv CM + RX \longrightarrow MX + RC\equiv CH,$$

has been illustrated by a number of specific reactions, notably by the original invehtigators but also by others[3]. While the alkyl halide has been represented by a large number of combinations of various alkyl groups with chlorine, bromine, iodine and lately the sulphate radical[4], the metal has been almost exclusively sodium, though occasionally during the last few years potassium has been successfully employed in these laboratories and more recently the alkaline earth acetylides have been used. As early as the end of the last century Moissan[5] prepared the acetylides of lithium, calcium and barium as well as those of sodium and potassium, employing the acetylene to metal method. Moissan, however, considered even the mono-substituted products to be a molecular association of one molecule of carbide and one molecule of acetylene. The acetylide structure, as shown in the above equation, has been assumed throughout this work as most easily and simply explaining the observed reactions.

Although the action of the alkaline earth metal acetylides would in every way be expected to be analogous to that of sodium and potassium acetylide, this has not heretofore been experimentally verified. This paper reports the action of ethyl sulphate, amyl chloride, and butyl and amyl bromides on calcium acetylide in liquid ammonia.

An interesting phenomenon, not heretofore reported in the literature, was noted in connection with the preparation of calcium acetylide by the acetylene to metal method. As the acetylene was bubbled through the ammonia solution of calcium the rate of absorption was followed by means of bubble bottles. As soon as decolorization occurred, indicating that the formation of the acetylide was complete, the rate of the absorption of the acetylene abruptly increased by what was roughly estimated to be three times. This was interpreted as indicating that the rate of solution of acetylene in ammonia (which is quite high in pure ammonia) was decreased by metal solutions but unaffected by acetylide solutions. This chance observation led to the development of a new synthesis of metal acetylides which will be discussed below.

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[1] Now with Union Carbide and Carbon Research Laboratories, Niagara Falls, N. Y.

[2] Lebeau and Picon: Compt. rend. **156**, 1077. 1913.

[3] Picon: Compt. rend. **158**, 1185, 1346. 1914. Mass and Russell: J. Am. Chem. Soc. **43**, 1227. 1921. Hurd, Meinert, and Spencer: Ibid. **52**, 1138. 1930. Heisig: Ibid. **53**, 3245. 1931.

[4] Hurd and Meinert: J. Am. Chem. Soc. **52**. 4540, 1930; **53**, 289, 1931.

[5] Moissan: Compt. rend. **127**, 911. 1898.

Ethyl Sulphate

To avoid the complicating factors of handling large amounts of reagents and products, small amounts of material were finally used. Commercial calcium metal shavings were dissolved in liquid ammonia at atmospheric pressure; acetylene gas was bubbled through the solution until the latter was decolorized (indicating complete conversion of the metal to the acetylide). The excess acetylene was removed and ethyl sulphate was added to the solution, the gaseous products being appropriately collected. It was shown by chemical analysis that the product was all ethyl acetylene. The yield was determined by reducing the volume of collected gas to standard conditions and applying the general gas law. The assumed reaction is

$$HC\equiv CCaC\equiv CH + 2Et_2SO_4 \longrightarrow Ca(EtSO_4)_2 + 2EtC\equiv CH$$

When this synthesis was first carried out, approximately 2/3 gram mole of calcium acetylide was caused to act on 4/3 gram mole of ethyl sulphate. The gaseous product of the reaction, together with the ammonia coming from the boiling solvent's surface, was passed through a large bottle of water and a bottle containing dilute sulphuric acid to insure the removal of all ammonia, then through a tower, the lower half of which contained soda-lime and the upper half calcium chloride. The product was then liquefied by passing through two spiral, ammonia-cooled condensers[5] and was collected in large test tubes which were im-

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[5] Vaughn and Pozzi: J. Chem. Ed. 8, 2433. 1931.

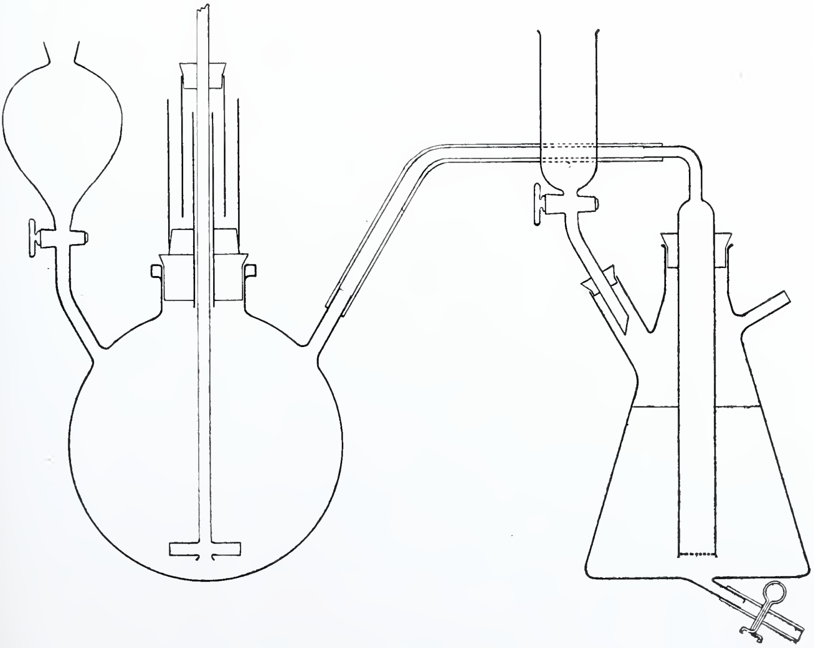

Fig. 1. Apparatus for the Synthesis of Ethyl Acetylene.

mersed in liquid ammonia. Owing to losses in the wash water and to the inefficiency of the condensing and collecting system, yields greater than 75% of the theoretical were not obtained.

In the subsequent experiments, in order to obtain quantitative data, much smaller quantities of accurately weighed material were used in an apparatus of novel design (see Fig. 1), and the purified product was collected and measured as a gas at atmospheric pressure and room temperature, no attempt being made to condense the product.

Alkyl Halides

The experiments in which alkyl halides were used were made on a larger scale than those in which ethyl sulphate was used. The calcium acetylide was prepared by the metal to acetylene method[6] and the reaction was effected in an autoclave. The yields obtained compared very favorably with those resulting from the use of sodium acetylide under identical conditions.

In addition to the acetylenic materials these reactions also yielded amines, alkenes, dialkyl acetylenes, and dialkyl ethers. The nature and origin of these products, which are also obtained when sodium acetylide is employed, will be discussed fully in a later paper.

Calcium Acetylide

Calcium acetylide was prepared by two methods. In the one method the calcium was dissolved in ammonia and acetylene bubbled into the solution. In the other method a solution of acetylene in ammonia was prepared and to this was added calcium metal or, better, a solution of calcium in ammonia. The rate of addition of the metal was carefully controlled in such a way that the entire solution was never blue. The metal to acetylene method is very convenient and requires only about 10% to 20% as much time as the acetylene to metal method.

Experimental Part

Calcium Acetylide (Acetylene to Metal).—Approximately 1.5 grams of calcium metal shavings were placed in a special 500-ml. flask (Fig. 1) bearing a mercury-sealed Bennings stirrer[7] and a dropping funnel. About 250 ml. of liquid ammonia were forced into the flask through the dropping funnel. After stirring for three or four minutes to insure complete solution of the calcium, acetylene from a Prestolite cylinder was passed through a Filtros gas diffuser immersed in a concentrated sulphuric acid, a bubble bottle containing the same liquid, a U-tube containing soda-lime, and into the reaction flask through the dropping funnel. The passage of acetylene was continued until decolorization occurred. A water bath was placed under the reaction flask and the solution of calcium acetylide was evaporated to dryness to insure complete removal of excess acetylene. During the preparation of calcium acetylide all waste ammonia and acetylene was conducted to a suitable fume hood. The dry cake of calcium acetylide was redissolved in about 200 ml. of liquid ammonia.

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[6] Vaughn, Vogt, Sartoretto, and Nieuwland: To be published.

[7] Bennings: Proc. Ind. Acad. Sci. 37, 263. 1927.

Reaction with Ethyl Sulphate.—An accurately weighed sample (5.852 grams) of ethyl sulphate was then introduced through the dropping funnel. The weighing bottle was rapidly rinsed out with successive small portions of liquid ammonia, and these rinsings were washed into the flask with more ammonia. Just before the addition of the ethyl sulphate the other flask opening was connected by a short piece of gum tubing to the special washing flask shown in Figure 1. The inlet tube of this flask was terminated by a perforated porcelain disc which served to break up the gas stream and thus facilitate washing. The washing flask was filled to the level in the figure with 50% sulphuric acid. The washed gases were collected over a solution almost saturated with respect to sodium sulphate[8], and quite saturated with respect to ethylacetylene after the numerous trial runs. The mixture of gases from the reaction flask was forced, by the boiling ammonia, through the washing flask where the ammonia was removed and the residue was collected by displacement in a 1,000-ml. cylinder. When all evolution of gas had ceased, the contents of the flask and the inverted cylinder were brought to room temperature. The gas was brought to atmospheric pressure and its volume was found to be 930 ml. at 748.9 mm. and 22° C. By means of a Broensted-Richards differential manometer[9] the vapor pressure of the sodium sulphate solution was estimated to be 11 mm. The pressure exerted by the collected gas was therefore 737.9 mm. Applying the gas laws and assuming the gas to be pure ethylacetylene, the weight of evolved gas was 2.01 grams. The theoretical yield is 2.05 grams. Thus, within the limits of accuracy of the volumetric method employed, the yield was theoretical.

Purity of Ethylacetylene.—A preparation was made with a modified apparatus which was designed to exclude all air from the sample of gas collected. This precaution was not taken in the experiment to determine the yield since the air displaced from the apparatus was subject to volumetric measurement, and the volume of air so obtained was equal to that of the gaseous product which took its place. By means of this modified apparatus 99.5 ml. of the gaseous product was drawn into a gas burette. This gas was passed and repassed into a Hempel pipette containing the alkaline mercuric cyanide reagent of Hoffman and Krimreuther[10] until adsorption ceased, 0.5 ml. of unabsorbed gas remained. During the collection of the gas sample the temperature of the sulphuric acid wash solutions was considerably raised. This would tend to lower the solubility of any of the atmospheric gases originally present in the liquid and would throw these gases out of solution, mingling them with the reaction product. Therefore, within the limits of error of the experiment (about 1%), we can assume complete absorption. We may conclude that the product of the reaction is entirely acetylenic. Since the possibility of acetylene had been excluded by dry-

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[8] The gaseous product was collected over sodium sulphate solution in order to obtain the maximum salting out effect; the solution was also slightly acid to insure removal of any possible trace of ammonia; a slight amount of methyl orange was added to act as an indicator.

[9] Broensted and Richards: J. Am. Chem. Soc. 50, 3030. 1928.

[10] Hoffman and Krimreuther: Ber. **41**, 314. 1908.

ing the calcium acetylide before the addition of the alkylating reagent, we may assume that the product of the reaction is entirely ethylacetylene and that the equation given above represents the reaction.

Calcium Acetylide (Metal to Acetylene).—Approximately 750 ml. of ammonia were placed in a 4-liter beaker, and a rapid stream of acetylene was bubbled in. After about 2 minutes, a solution of 208 g. of calcium in 3 liters of ammonia was added as rapidly as possible without turning the entire solution blue. The reaction was usually complete in 20 to 40 minutes.

Reaction With Alkyl Halides.—The liquid ammonia-acetylide mixture was poured into a cadmium-lined autoclave of about 8 liters capacity. Five moles of the alkyl halide were cooled by pouring rather slowly into 250 ml. of ammonia. This mixture was quickly poured into the autoclave and the head made up as quickly as possible. The pressure rose rather rapidly to 170-190 lb. per sq. in. and then slowly dropped to 140-150 lb.

After standing overnight, the pressure was released, the head removed and water added to the liquid ammonia mixture in a fine stream until bubbling had ceased. The upper layer of crude alkyl acetylene was separated and washed with dilute hydrochloric acid until no longer ammoniacal. The crude acetylene was then fractionated in a 1-m. jacketed Vigreaux column. The properties and yields of the acetylenes prepared are given in Table I.

TABLE I

Properties and Yields of Alkyl Acetylenes

Prepared from	% Yield	b.p.	m.p. of Hg Derivative[11]
Amyl chloride	56%	98-101°	60.8-61.3°
Amyl bromide	31%	97-100°	60.9-60.1°
Butyl bromide	45%	70-72°	96.0-96.3°

Conclusion

1. Calcium acetylide is obtained either by the passage of acetylene into calcium-ammonia solutions or by the addition of calcium-ammonia solutions to acetylene-ammonia solutions, the second scheme being the more rapid.

2. Ethyl sulphate reacts vigorously with calcium acetylide in ammonia and gives a theoretical yield of pure butyne-1.

3. Butyl bromide, amyl chloride, and amyl bromide react with calcium acetylide in ammonia producing the corresponding acetylene in yields which compare favorably with those obtained from sodium acetylide.

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[11] Vaughn: J. Am. Chem. Soc. 53, 3453. 1933.