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CHLORINATION OF ACETYLENE

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This invention relates to a method for the chlorination of acetylene and particularly to such a process wherein the danger of combustion and explosion incident to most such processes may be avoided, and from which tetrachloroethylene may be obtained as the principal product.

It is well known that the monochloro-acetylene which may be produced constitutes a definite explosion hazard in the direct chlorination of acetylene. Other of the possible acetylene chlorination products, however, are desirable articles of commerce. Among the products which may be produced by the direct chlorination of acetylene are dichloro-acetylene, acetylene dichloride (symmetrical dichloroethylene), acetylene tetrachloride, trichloroethylene, and tetrachloroethylene. It is possible under some conditions to produce hexachloroethane, and if the acetylene molecule is disrupted during the chlorination process, carbon tetrachloride may be produced. Among the most valuable of these products is tetrachloroethylene. It is, therefore, much to be desired that a process be provided whereby acetylene may be chlorinated directly under conditions which will produce tetrachloroethylene or other valuable products without encountering the explosion hazard previously mentioned. Such is the object of the present invention.

I have now found that acetylene may be chlorinated principally to tetrachloroethylene without danger of combustion or explosion by passing a stream of acetylene into contact with gaseous chlorine, in the presence of the vapors of a chlorinated aliphatic hydrocarbon, under the surface of and in contact with a bath of molten metal chlorides maintained at a temperature from about 175° to 250° C. and preferably between about 190° and 210° C. The weight ratio of chlorine to acetylene is preferably between 4:1 and 6:1 although other proportions may be employed without materially affecting the nature of the chlorinated products obtained.

The chlorinated aliphatic hydrocarbons used as diluents to suppress combustion and prevent explosions in the chlorination of acetylene may be selected from a rather large group, suitable examples of which are chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and similar readily volatile, substantially nonflammable, chlorinated lower aliphatic hydrocarbons.

The molten metal chloride bath in which the reaction is carried out may consist of one or more of the chlorides of aluminum, potassium, sodium, iron, bismuth, zinc, or other metals, provided that such chloride or mixture of chlorides are properly fluid at the reaction temperature.

The eutectic mixture of 60 parts of aluminum chloride, 30 parts of sodium chloride, and 10 parts of ferric chloride by weight is especially suitable since it has a melting point of about 150° C. and a boiling point above 1000° C. Another satisfactory salt bath comprises 30 parts of sodium chloride, and 70 parts of aluminum chloride by weight.

Owing to the heat generated in the chlorination of acetylene it is seldom necessary to employ an external source of heat after the reaction has started. It may become necessary to cool the reaction vessel when high rates of flow of the reactants are employed.

The following examples illustrate the practice of my invention:

Example 1

A mixture of 0.015 pound per minute of acetylene and 0.125 pound per minute of carbon tetrachloride vapor was led under the surface of a bath consisting of the eutectic mixture of aluminum chloride, sodium chloride and ferric chloride at a temperature between 220° and 250° C. Chlorine in the amount of 0.07 pound per minute was led through a separate tube to an equal depth in the same bath where it was released so as to contact and mix with the aforesaid mixture of acetylene and carbon tetrachloride vapor. The reaction products flashed from the bath, were collected, condensed, washed to remove hydrogen chloride, dried, and fractionally distilled. Analysis, based on boiling point and specific gravity of the fractions of the distillate, showed the product of reaction to contain 23.2 per cent carbon tetrachloride, 2.8 per cent ethylene chloride, 54 per cent tetrachloroethylene, and a small amount of a high boiling residue which was not analyzed. About 10 per cent of the gaseous reactants were unaccounted for in this particular run. The amount of carbon tetrachloride recovered was almost identical with that originally employed as a diluent of the acetylene. It appears, therefore, that by far the largest proportion of the acetylene entering into the reaction is converted into tetrachloroethylene.

Example 2

A mixture of 0.05 pound per minute of acetylene, and 0.056 pound per minute of carbon tetrachloride vapor was reacted in a manner analogous to that described above with 0.07 pound per minute of chlorine under the surface of a molten metal chloride bath at a temperature in the range from 190° to 210° C. Chlorine constituted 53.6

per cent by weight of the reaction mixture, acetylene 11.5 per cent, and carbon tetrachloride 42.9 per cent. An analysis of the collected condensate from the reaction mixture showed it to consist of carbon tetrachloride, tetrachloroethylene, and a small amount of a high boiling residue. The weight of carbon tetrachloride recovered was 60 per cent of the original weight of reactants, and tetrachloroethylene accounted for 25 per cent of the weight of reactants. It is seen that 17 per cent more carbon tetrachloride was recovered from the reaction than was employed as the diluent. The conditions employed appear to favor the formation of tetrachloroethylene and carbon tetrachloride from acetylene.

Example 3

In a manner similar to that described in the preceding examples, acetylene tetrachloride was employed as the chlorinated aliphatic hydrocarbon diluent in place of the carbon tetrachloride previously employed. 66 per cent by weight of the reaction mixture consisted of chlorine supplied at a rate of 0.07 pound per minute. 14 per cent of the reactants was acetylene supplied at the rate of 0.015 pound per minute and diluted with 0.021 pound per minute of acetlyene tetrachloride, which represented 20 per cent of the weight of the ternary reaction mixture. The temperature of the molten metal chloride bath was held at or near 210° C. Analysis of the condensed reaction products showed them to contain carbon tetrachloride 8 per cent, trichloroethylene 21.6 per cent, tetrachloroethylene 34 per cent, and acetylene tetrachloride 15.4 per cent. About ¼ of the acetylene tetrachloride employed as a diluent in the reaction was converted to other chlorination products. The largest proportion of the acetylene employed was converted to tetrachloroethylene while smaller amounts were converted to trichloroethylene and carbon tetrachloride.

In no instances have I found evidence of the formation of any appreciable amount of acetylene tetrachloride under the conditions herein employed. The principal product in all cases appears to be tetrachloroethylene. Regardless of the chlorinated aliphatic hydrocarbon employed as the diluent in the reaction, some carbon tetrachloride appears to be formed in every instance. Carbon tetrachloride is the preferred diluent during the reaction because, next to the more expensive chloroform, it is the lowest boiling of the completely nonflammable chlorinated aliphatic hydrocarbons and may be most readily separated by distillation from other volatile products of the reaction.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the process herein disclosed, provided the step or reagents stated by any of the following claims or the equivalent of such stated step or reagents be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. The process which comprises reacting chlorine with acetylene in the presence of the vapors of a nonflammable chlorinated lower aliphatic hydrocarbon, and in contact with molten metal chlorides at a temperature between about 175° and 250° C.

2. The process which comprises diluting acetylene with the vapors of a nonflammable chlorinated lower aliphatic hydrocarbon, and passing the mixture in contact with gaseous chlorine under the surface of a molten metal chloride bath at a temperature between 175° and 250° C.

3. The process which comprises diluting acetylene with the vapors of carbon tetrachloride, and passing the mixture in contact with gaseous chlorine under the surface of a molten metal chloride bath at a temperature between 175° and 250° C.

4. The process which comprises diluting acetylene with the vapors of a nonflammable chlorinated lower aliphatic hydrocarbon, passing the mixture under the surface of a molten metal chloride bath at a temperature between 175° and 250° C., there chlorinating the mixture with gaseous chlorine, and separating tetrachloroethylene from the reaction product.

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