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PROCESS OF CONVERTING COMPOUNDS OF
THE ACETYLENE SERIES INTO COM-
POUNDS OF THE ETHYLENE SERIES

Walter Reppe and Alexander Rothhaas, Lud-
wigshafen-on-the-Rhine, Germany, assignors,
by mesne assignments, to Jasco, Incorporated,
a corporation of Louisiana

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The present invention relates to a process of converting compounds of the acetylene series into compounds of the ethylene series.

It has already been proposed to convert acetylene derivatives into ethylene derivatives by treating them with aqueous suspensions of zinc dust to which copper sulphate solution has been added. The zinc activated by precipitated copper thus reacts with water with the formation of hydrogen. This process has the objection that the hydrogenation proper requires a multiple of the calculated amount of zinc because on the one hand the reaction proceeds incompletely and on the other hand a considerable part of the zinc is used up by the activation, passing into solution as zinc sulphate, and is thus consumed without being used for the hydrogenation. In order to obtain a satisfactory utilization of zinc, about one third of the zinc must be replaced by copper.

We have now found that compounds of the acetylene series can be converted into compounds of the ethylene series in a considerably simpler and more advantageous manner by treating compounds of the acetylene series in aqueous medium in the presence of basic reacting nitrogen compounds with metallic zinc, preferably in fine dispersion, as it is obtained, for example, in the electrolytic production of zinc. There may also be added as activators metals capable of forming galvanic elements with the zinc.

Basic nitrogen compounds of the said kind are for example ammonia, hydroxylamines and hydrazines and organic amines, especially those soluble or easily dispersible in water such as primary, secondary and tertiary aliphatic monoamines and polyamines, alkylamines, such as benzylamine, cycloaliphatic amines, aromatic amines, heterocyclic nitrogen compounds such as pyridine or piperidine, and quaternary ammonium hydroxides derived from these compounds.

Contrary to expectation, only relatively small amounts of free hydrogen are formed in the hydrogenation by the present process, so that the utilization of the zinc is very favorable. Moreover, the hydrogenation of the acetylene linkage proceeds only to the formation of the ethylene linkage without any appreciable formation of the corresponding saturated compounds. Even when acetylene compounds which contain olefinic double linkages in addition to the triple linkages are hydrogenated, the hydrogenation is limited to the triple linkages. The present invention, therefore, can most advantageously be used for the conversion of vinylacetylene into butadiene.

capable of forming galvanic elements with zinc there may be mentioned for example copper, manganese, iron, cobalt and nickel. The addition necessary for the activation is usually very small. It can be established without trouble by a simple preliminary experiment which combination is most suitable for the hydrogenation to be carried out. In most cases, the addition of an activating metal can entirely be dispensed with.

It is preferable to effect the regeneration of the zinc by electrolysis of the zinc compounds formed because in this way the zinc is obtained in so finely divided a form that it is suitable for direct re-use without further treatment. At the end of the hydrogenation the zinc employed is mainly obtained in the form of a zinc hydroxide suspension.

The basic reacting nitrogen compounds are especially suitable for the reduction of acetylene compounds which are immiscible or difficultly miscible with water because they act as solvent agents for the acetylene compounds and considerably accelerate the reaction. They may be used in various concentrations, for example in 20 per cent or preferably in from 4 to 6 per cent solutions or suspensions. If desired, organic solvents which have a good solvent power for the acetylene compounds and which are not attacked under the reaction conditions may be added to the aqueous solutions, as for example aliphatic alcohols. The hydrogenation may also be carried out in the presence of indifferent substances, as for example indifferent gases. It is often advantageous to work in the presence of dispersing or wetting substances, for example of alkyl naphthalene sulphonic alkali salts or the addition products of 20 molecular proportions of ethylene oxide to fatty alcohols of high molecular weight, in order to produce the most intimate possible contact between all the reactants.

Generally speaking it is sufficient to work at atmospheric pressure and at ordinary or slightly elevated temperature, but any other pressures may be used within a wide range of temperatures. The process may be carried out continuously, discontinuously or in a cycle.

The process according to this invention may be used for practically all compounds having triple carbon linkages, as for example for acetylene, phenylacetylene, vinylacetylene, diacetylene, divinylacetylene, methylbutinol, propiolic acid, phenylpropiolic acid and many other acetylene derivatives.

The following examples will further illustrate how the said invention may be carried out in

Among suitable activating metals which are

practice but the invention is not restricted to these examples.

Example 1

- 5 3 liters of vinylacetylene are shaken with a suspension of 50 grams of about 77 per cent electrolytic zinc dust, 1 gram of the condensation product of 1 molecular proportion of oleyl alcohol and 20 molecular proportions of ethylene oxide as a wetting agent and 23 grams of ethylamine in 10 200 cubic centimeters of water for several hours. Pure butadiene, containing only traces of unchanged vinylacetylene and butylene in addition to a little hydrogen, is obtained in almost the 15 quantitative yield.

In an otherwise identical manner, butadiene is obtained in practically the quantitative yield from vinylacetylene when using the following mixtures:

- 20 (1) 3 liters of vinylacetylene, 50 grams of 77 per cent electrolytic zinc dust and 36 grams of diethylamine.
 25 (2) 2 liters of vinylacetylene, 50 grams of 77 per cent electrolytic zinc dust and 36 grams of butylamine or 65 grams of dibutylamine,
 (3) 2 liters of vinylacetylene, 20 grams of about 70 per cent electrolytic zinc dust and 43 grams of piperidine,
 30 (4) 3 liters of vinylacetylene, 20 grams of 70 per cent electrolytic zinc dust, 23 grams of ethanolamine or 53 grains of diethanolamine or 75 grams of triethanolamine.
 (5) 3 liters of vinylacetylene, 12 grams of about 35 70 per cent electrolytic zinc dust and 40 grams of pyridine,
 (6) 2 liters of vinylacetylene, 20 grams of about 83 per cent electrolytic zinc dust and 50 grams of hydrazine hydrate,
 40 (7) 3 liters of vinylacetylene, 20 grams of about 83 per cent electrolytic zinc dust and 91 grams of tetramethyl ammonium hydroxide or
 (8) 3 liters of vinylacetylene, 40 grams of about 83 per cent electrolytic zinc dust and 47 grams 45 of aniline.

Example 2

- 3 liters of vinylacetylene are shaken for some hours with a suspension of 50 grams of 77 per cent electrolytic zinc dust and 1 gram of the sodium salt of butylnaphthalene sulphonic acid 50

in 200 cubic centimeters of about 5 per cent ammonia in a shaking flask. The gas obtained consists almost exclusively of butadiene with which a few per cent of hydrogen and vinylacetylene and only traces of butylene are mixed.

Example 3

2 liters of acetylene are shaken for several hours with a suspension of about 100 grams of 80 per cent electrolytic zinc dust and 1 gram of the sodium salt of butylnaphthalene sulphonic acid in a 5 per cent ammoniacal solution. The resulting gas consists of ethylene, unchanged acetylene, a little hydrogen and traces of ethane.

Example 4

15 grams of phenylacetylene are shaken with a suspension of 100 grams of about 80 per cent electrolytic zinc dust in 5 per cent ammonia solution containing dissolved therein a small amount of the sodium salt of butylnaphthalene sulphonic acid until a sample withdrawn is free from phenylacetylene, which is the case after some hours. Styrene is mainly obtained.

What we claim is:

1. A process for the conversion of compounds of the acetylene series into those of the ethylene series which consists in treating compounds of the acetylene series in an aqueous medium in the presence of basic reacting nitrogen compounds with metallic zinc.

2. A process for the conversion of compounds of the acetylene series into those of the ethylene series which consists in treating compounds of the acetylene series in an aqueous medium in the presence of basic reacting nitrogen compounds with zinc dust.

3. A process for the conversion of compounds of the acetylene series into those of the ethylene series which consists in treating compounds of the acetylene series in an aqueous medium in the presence of basic reacting nitrogen compounds with zinc dust in the presence of a dispersing agent.

4. A process for the conversion of vinylacetylene into butadiene which consists in treating vinylacetylene in an aqueous medium in the presence of basic reacting nitrogen compounds with zinc dust.

WALTER REPPE.

ALEXANDER ROTHHAAS.