2,484,042 HALOGENATION OF ALIPHATIC CONJUGATED DIOLEFINES
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by
The present invention relates to the preparation of chlorinated vinyl compounds and it relates more particularly to the vapor phase chlorination of butadiene to dichlorobutenes.

An object of the present invention is to provide a new and improved process for preparing dichlorobutenes and apparatus therefor. Another object of the present invention is to provide a new and improved process and apparatus for chlorinating conjugated double-bond hydrocarbons in the vapor phase to give partially chlorinated unsaturated compounds. Still another object of the present invention is to provide a novel process and apparatus for low temperature vapor phase chlorination of butadiene to give relatively high yields of dichlorobutenes and to give relatively large proportions of 1,4-dichloro-2-butene.

Other objects and advantages of the present invention are apparent in the following detailed description, appended claims and accompanying drawings.

It has been suggested in the past to chlorinate butadiene in the liquid phase to give dichlorobutenes. This liquid phase chlorination has been carried out in a solvent such as carbon bisulfide or carbon tetrachloride. This process, however, has not been commercially practical because of the high costs of the solvents and because of the costly recovery operations necessary, as well as because of the low yield of dichlorobutenes.

It has also been proposed in the past to produce dichlorobutenes by chlorinating butadiene in the vapor phase at elevated temperatures; that is, at temperatures above 150°C.

This high temperature chlorination is not entirely satisfactory because it requires costly and involved apparatus and gives a preponderance of 1,3-dichlorobutene-3 which is less active and hence less desirable for chemical synthesis than is 1,4-dichlorobutene-2.

It has, in the past, been stated that low temperature vapor phase chlorination of butadiene to give dichlorobutenes is not possible.

I have, however, found that by employing my novel process and apparatus, it is possible effectively to chlorinate butadiene at low temperatures in the vapor phase to give relatively high proportions of 1,4-dichloro-2-butene.

Generally speaking, my present invention contemplates a novel process and apparatus for chlorinating butadiene or other conjugated double-bond hydrocarbons at low and carefully controlled temperature in the vapor phase in such a way that the primary products, namely the dichlorobutenes (or other partially chlorinated olefins), are quickly removed from the excess of reactants thereby preventing side reactions which otherwise lead to undesirable by-products.

For the purpose of illustrating the invention, there is shown in the accompanying drawing one form thereof which is at present preferred, although it is to be understood that the various instrumentalities of which the invention consists can be variously arranged and organized and that the invention is not limited to the precise arrangements and organizations of the instrumentalities as herein shown and described.

The accompanying drawing represents a schematic view of one embodiment of the apparatus of the present invention.

In the accompanying drawing, there is shown one illustrative form of apparatus which has been proven satisfactory in giving relatively high yields of dichlorobutenes and relatively high proportions of 1,4-dichloro-2-butene.

The apparatus includes a generally vertical narrow elongated reactor tube 10 which is provided with a water jacket 11 for the purpose of accurately controlling the temperature during the chlorination; the reaction being exothermic. The relatively narrow elongated reactor tube has been found particularly advantageous in providing a high ratio of cooling surface to reaction volume thereby to give more efficient temperature control.

Butadiene under pressure is admitted at the top of the reactor tube 10 through the line 12. Optionally, a line 13 may also be connected to the top of the reactor tube 10 to permit passage of air or other diluent gas through the tube; the diluent gas serving to aid in temperature control by cutting down the speed of reaction.

Chlorine under pressure is introduced into the reactor tube 10 through the jet tube 14; the tube 14 being telescopically adjustable within the reactor tube 10 so as to permit vertical adjustment of the jet, thereby to vary the position of the mixing zone.

A thermometer 15 extends upward within the lower end of the reactor tube 10; the thermometer being vertically adjustable to permit it to measure the temperature at different parts of the tube.

A thermometer 16 may also be provided for the water jacket 11.

A downwardly-inclined escape tube 17 is provided adjacent the lower end of the reactor tube 10; the escape tube 17 extending within a separatory vessel 18.
The separatory vessel 18 is provided with a bowl 19 and a drainage stop-cock 20 at its lower end.

Water flows continuously into the vessel 18, at generally constant rate-of-flow from the addition funnel 21 which is provided with a vent 22, a water line 23 and a drainage stop-cock 24. The vessel 18 is also provided with a vent 25 having a stop-cock 26 or other suitable pressure-regulating valve in order to control the pressure in the system.

The generally U-shaped arm 28 leads from the upper portion of the bowl 19 to the upper portion of a secondary trap bowl 27 which is provided with a drainage stop-cock 28.

A second U-shaped arm 29 extends from the upper portion of the bowl 27 to waste (or to a recovery system for the water-soluble reaction products). A vent 30 is provided at the top of the U-shaped arm 29 to prevent siphoning through and a similar vent 31 is provided in the top of the U-shaped arm 28; the top of the arm 29 being somewhat lower than the top of the arm 26. The vents 30 and 31 are provided with stop-cocks 29 and 35 respectively (or other suitable pressure-regulating valves) in order to control the pressure in the system.

It can be seen that, with the drainage stop-cocks 20 and 28 closed, water entering the vessel 18 from the addition funnel 21 will flow continuously through the bowl 19, the arm 28, the bowl 27 and the arm 25 to waste. The water level 32 in the vessel 18 is determined by the height of the U-shaped arm 28, while the water level 33 in the arm 25 is in turn determined by the height of the arm 29.

When butadiene and chlorine (and, optionally, air or other diluent gas) are introduced into the reactor tube 10 at predetermined rates-of-flow (suitable flow-meters, not shown, being provided to regulate the rates-of-flow), the reaction takes place within said tube 10 and the reaction products are almost immediately removed from the tube, being swept out through the escape tube 17 into the water system described above.

When the reaction products and the excess reagents enter the water system, a separation occurs. That is, the dichlorobutenes which are insoluble in water separate out in the form of small oily globules which are heavier than water and which thus collect in the bottom of the bowl 15.

The unreacted gas passes upward through the vessel 18 and escapes through the vent 28. From the vent 26, the gas may be passed through any suitable recovery system, if desired.

Dichlorohydrins, which are also formed during the reaction, are water soluble and thus are removed from the dichlorobutenes by the constantly flowing water system which is so arranged as not materially to affect the settling of the oily dichlorobutenes. As stated above, the dichlorohydrins can be recovered from the water if desired.

Any dichlorobutenes which are physically entrained in the water and are carried from the bowl 18 through the arm 28 are trapped in the bowl 21 to prevent their being lost.

The dichlorobutenes which collect in the bowls 19 and 27 can be drawn off from time to time without stopping the reaction which can be carried on continuously.

The apparatus may be of glass or any other suitable inert material which is not attacked by the chlorine and other substances present.

The addition funnel 21 is employed for the purpose of ensuring a steady flow of water into the vessel 18. Where the pressure in the water line 23 is reasonably steady, the funnel 21 may be omitted and the line 23 may be connected directly to the vessel 18.

The following are illustrative examples of the present invention:

**Example 1**

Chlorine and butadiene, in the ratio of 1 to 1.24, were introduced into the reaction tube; no air being added. The temperature of the cooling water was maintained at 13° C. and the maximum temperature in the reaction tube was 78.8° C.

The wet oil collected from the vessels 18 and 21 represented 84% of the theoretical yield. This wet oil was dried with approximately 5-10% of its weight of anhydrous magnesium sulfate and was then fractionated under reduced pressure.

The fractionation yielded 1,2-dichlorobutene-3 and 1,4-dichlorobutene-2; the ratio of the 1,4 isomer to the 1,2 isomer being 1:22:1. The fractionation also yielded a small amount of intermediate fractions and left a higher boiling residue comprising polychlorobutenes.

**Example 2**

The method used was similar to that described in Example 1 except that air also was introduced; the ratio of chlorine:butadiene:air being 1:1:16:4.9. The cooling water was kept at 13.5° C. and the maximum temperature in the reaction tube 10 was 37.5° C.

The weight of wet oil obtained was 62.4% of theoretical yield. On drying this yielded 59.2% of oily products. On fractionation 1,4-dichlorobutene-2 and 1,2-dichlorobutene-3 were obtained in the ratio of 1:27:1; a small amount of intermediate fractions being obtained and a higher boiling residue comprising polychlorobutenes being left.

**Example 3**

In this case, air was again omitted; the ratio of chlorine to butadiene being approximately 1:0:1.1. The temperature of the cooling water was 13.5° C. while the maximum temperature in the reaction tube was 78.8° C.

The yield of wet oil was 80.2% which, upon drying and fractionation, gave 1,4-dichlorobutene-2 and 1,2-dichlorobutene-3 in the ratio of 1:27:1; a small amount of intermediate fractions being obtained and a higher boiling residue comprising polychlorobutenes being left.

The temperature employed within the reaction tube may vary through a relatively small range from approximately 25° C. to approximately 100° C. The optimum temperature in each case is governed by the factors of time and the character of the products obtained. That is, at low temperatures, the reaction time is necessarily increased while at high temperatures, greater proportions of undesirable by-products are obtained. In any case, we have found that it is best to carry out the reaction substantially below 150° C.

While I do not intend to be bound thereby, my theory is that the failure of previous workers to obtain the dichlorobutenes during low temperature vapor-phase reaction was the result of failure to remove the products immediately from the excess of reactants so that side reactions occurred. According to my present process, on the other hand, the dichlorobutenes are sepa-
rated immediately from the excess of reactants and also from the water-soluble reaction products. Thus, the dichlorobutenes formed are preserved and are not modified or further chlorinated.

While, in the specific examples, I have described the chlorination of butadiene, the present process also comprehends the chlorination of other dienes with conveniently available chlorinating agents such as 2-methyl butadiene-1,3, 2,3-dimethyl butadiene-1,3, etc., and their homologs and analogs.

The present process also contemplates the further chlorination of such compounds as monochlor butadienes and the like.

It can be seen that the present process provides a continuous method of forming the dichlorobutene; the gases being continuously passed through the reaction tube and the accumulated dichlorobutenes being drawn off from time to time.

If desired, the unreacted gases from the vent 25 can be re-cycled through the process.

While water is preferred for effecting the separation of the dichlorobutenes from the reaction mixture, any other inert liquid, with which the dichlorobutenes are immiscible and in which the unreacted gases are insoluble, may be used instead.

While the examples given herein relate to chlorination, the present invention comprehends the use of the halogens, bromine, to effect the low-temperature vapor-phase formation of the corresponding dihalogeno butenes and their homologs and analogs.

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof, and it is therefore desired that the present embodiments be considered in all respects as illustrative and not restrictive, reference being had to the appended claims rather than to the foregoing description to indicate the scope of the invention.

Having thus described my invention, what I claim as new and desire to protect by Letters Patent is:

1. A process for producing dichlorobutenes which comprises passing gaseous butadiene through a reaction zone, introducing undiluted gaseous chlorine thereinto in amount insufficient for complete saturation of the butadiene, maintaining the temperature of the reaction zone between about 25° C. and about 100° C., and quickly passing the reaction mixture into water to separate the dichlorobutenes from the unreacted gaseous butadiene and chlorine in the form of relatively dense water-immiscible oily globules and thereby substantially to inhibit interaction between the chlorine and the dichlorobutenes.

2. A process for converting butadiene into a mixture of chlorinated hydrocarbons predomi- nating in 1,2-dichloro butene-3 and 1,4-dichloro butene-2, the latter being in excess, comprising passing gaseous butadiene through a reaction zone, introducing undiluted gaseous chlorine thereinto in amount insufficient for complete saturation of the butadiene, cooling to maintain the temperature in the reaction zone between about 25° C. and about 100° C., and immediately passing the effluent from the reaction zone into water whereby to separate the dichlorobutenes formed in the reaction zone from the unreacted gases in the form of relatively dense water-immiscible oily globules.

3. A process for converting butadiene into a mixture of chlorinated hydrocarbons predomi- nating in 1,2-dichloro butene-3 and 1,4-dichloro butene-2, the latter being in excess, comprising passing gaseous butadiene through a reaction zone, introducing undiluted gaseous chlorine thereinto in amount insufficient for complete saturation of the butadiene, cooling to maintain the temperature in the reaction zone between about 25° C. and about 100° C., and immediately passing the effluent from the reaction zone into water whereby to separate the chlorinated hydrocarbons from the unreacted gases in the form of relatively dense water-immiscible oily globules, and fractionally distilling the chlorinated hydrocarbons to recover 1,2-dichloro butene-3 and 1,4-dichloro butene-2 from the distillate as separate fractions.

4. A process for effecting the halogenation of an aliphatic conjugated diene to a correspond- ing dihalo monodien or which comprises reacting the diene in the vapor phase with an undiluted halogen of the group consisting of chlorine and bromine in an amount insufficient to effect complete saturation of the diene, maintaining the temperature of the reaction between about 25° C. and about 100° C., and quickly passing the reaction mixture into water to separate the dihal mono-dien from the unreacted halogen in the form of relatively dense water-immiscible oily globules, thereby substantially to inhibit interaction between the halogen and the dihal mono- olefin and substantially to minimize the formation of saturated polyhalogen compounds.

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