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CHLORINATION OF ETHYLENE IN DILUTE MIXTURES

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The present invention relates to processes for the production of olefin dihalides from gaseous mixtures normally containing small quantities of olefin in the presence of substantial amounts of gaseous hydrocarbons other than olefin. The invention has particular reference to the halogenation of olefins found in small quantities in commercial gases or other gaseous mixtures, under superatmospheric pressure.

This application is a continuation in part of application Serial No. 30,794, filed June 3, 1948.

At the present time, olefinic dihalides are manufactured commercially by the reaction of a desired halogen with an olefin prepared in a relatively purified, concentrated form. Even with carefully controlled conditions of reaction, undesirable contamination of the olefin dihalide end products through the occurrence of side and substitution reactions of the halogen with gaseous components other than olefins occurs, yielding polyhalogens of little value compared with the desired olefin dihalide end product.

Attempts have been made heretofore to utilize olefins occurring in very small amounts in commercial gases, as a source material for the manufacture of olefin dihalides. These commercial gases comprise for the most part hydrogen, methane and carbon dioxide, all of which are known to react with a halogen such as chlorine. A coke oven gas of characteristic composition may contain as much as 2.3% of ethylene, which indicates in some degree the large amounts of ethylene which are burned yearly, without any attempt at recovery. Processes for the recovery of such dilute concentrations of olefins from commercial gases as dihalides have not been successful commercially, for the gases other than olefins present dissipate the halogen constituent available for reaction with the olefins, undesirable contaminants formed being of little commercial value. The use of superatmospheric pressures in carrying out the halogenation of olefins considerably aggravates the problem of contaminant formation, and accordingly has not been accepted as a practical expedient.

A process for the halogenation of olefins found in relatively dilute concentration in commercial gases, has been disclosed and claimed in application Serial No. 30,794. The present invention has specific reference to the reaction of olefins with halogens under conditions of pressure greater than atmospheric, in combination with procedural techniques disclosed in the above application Serial No. 30,794, as well as procedural steps advantageously employed in connection

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with olefin halogenation operations carried out under superatmospheric pressures.

It is an object of the present invention to provide a new and economical process for the preparation of olefin dihalides by the reaction of gaseous olefins and halogen under superatmospheric pressure, whereby a more complete and economical halogenation of olefins is accomplished.

It is a further object of the present invention to provide a new process for the manufacture of ethylene dichloride by the reaction of gaseous ethylene with chlorine, under superatmospheric pressure.

It is a further object to provide a new process for the manufacture of olefin dihalides by the reaction of gaseous olefins found in relatively small constituent percentage in tail gases purged from an ethylene oxide converter system with a halogen, under conditions of pressure greater than atmospheric.

Yet a further object is to provide a new process for the manufacture of olefin dihalides employing as source materials olefins found in admixture with relatively substantial amounts of gaseous hydrocarbons other than olefins, and other ingredients capable of halogenation, the reaction being carried out under superatmospheric pressure without incurring such substantial side or substitution reactions with the gaseous hydrocarbons other than olefins as to render the process commercially unacceptable.

A further object is to provide a method for the manufacture of olefin dihalides under conditions of superatmospheric pressure, the reaction being catalyzed by the presence of iron.

A further object is to provide a method for the manufacture of olefin dihalides employing superatmospheric pressures and an excess of halogen in terms of molal concentration of halogen to olefin in carrying out the reaction.

A further object of the invention is to provide a method for the halogenation of olefins, whereby the amount and size of equipment required for the halogenation operation is substantially reduced, without sacrificing in terms of rate of production or quality of the halogenated olefin product.

Yet a further object is to provide a method for the halogenation of olefins, wherein the recovery of olefin dihalide end product from the reaction mixture, is facilitated.

Other objects and advantages of the present invention will be apparent from the following detailed description.

In accordance with the present invention, there is provided a method for the halogenation of olefins found in relatively dilute concentration in commercial gases comprising essentially hydrocarbons other than olefins and inert gases, by reacting the olefin present with halogen under conditions of superatmospheric pressure, whereby substantially complete and accelerated conversion of olefin present in the gaseous reaction mixture to the corresponding dihalide is accomplished, with minimum formation of undesirable substitution products and incurrence of side reactions of hydrocarbons other than olefin, with the halogen.

The process of the invention permits of a substantial reduction in the amount of equipment necessary to carry out the halogenation of the olefin, as well as equipment required for the recovery and purification of the olefin dihalide end product. The process also has the advantage of providing olefin dihalides substantially free of undesirable side products of little comparative commercial value, without incurring the expense incident to the incorporation of relatively complex predrying and precompression procedures which are required otherwise in the process.

The invention will now be described in detail in connection with one of its preferred applications to the production of ethylene dichloride, it being understood that the principles of the invention are equally applicable to the chlorination of olefins other than ethylene, as well as the use of halogens other than chlorine for reaction with the selected olefin.

The source of the ethylene to be employed in carrying out the process comprises gaseous mixtures characterized by the presence of a small percentage of olefin hydrocarbons such as ethylene as part of the gaseous mixture, constituted in the main of other hydrocarbons, inert gases and similar non-reactants. For example, the source of ethylene may comprise a commercial gas such as refinery waste gas or producer gas, wherein ethylene occurs in such dilute quantities as to render recovery economically unfeasible under presently available processes. A tail gas from a hydrocarbon catalytic cracking operation may contain up to 5% ethylene and may be employed advantageously.

The preferred source of ethylene resides in the residual ethylene component found in the tail gases purged from ethylene oxidation systems, which may have the following typical composition:

Tail gas

Ethylene	2.0
Ethane	0.5
Carbon dioxide	10.0
Oxygen	3.0
Nitrogen	Balance
Water	Saturated

The tail gases from ethylene oxide units result from the catalytic oxidation of relatively pure ethylene, in the presence of relatively large amounts of inert gases such as nitrogen. The reaction is carried out under superatmospheric pressures of 150 to 200 pounds gauge. The conversion ratio seldom exceeds 50% per pass through the system, necessitating recycling of unoxidized ethylene. However, some of the gaseous reaction mixture must be purged from the system, to permit of introduction of necessary gaseous reactants such as oxygen, to bring the recycled reactants into proper ratio. This purge gas contains a small proportion of unreacted ethylene, as well as a major proportion of inert gases, oxygen, and hydrocarbons other than ethylene.

Due to the very small amounts of hydrocarbons other than olefins and hydrogen present in the tail gases, the incidence of undesirable side reactions and substitution reactions during chlorination of the ethylene component, is a negligible factor. Also, as the initial oxidation of ethylene is carried out under superatmospheric pressure, the tail gases purged from the system are available for ethylene halogenation purposes, under superatmospheric pressure, thereby eliminating the necessity for impressing superatmospheric pressure on the halogenation system, as in the case of other commercial gases used as source materials. It will be thus observed that substantial economies in equipment and in the process may be effected by using ethylene oxide tail gases as the source of ethylene.

The ethylene component found in very dilute concentration in gaseous mixtures of this type, is reacted with chlorine under conditions of superatmospheric pressure, avoiding any substantial amount of reaction of the chlorine with other hydrocarbon components. The conditions under which the reaction is carried out, render the presence of a moisture factor in the gaseous mixture of no material consequence. This is of considerable importance from the standpoint of process cost reduction, for ethylene oxide tail gas and other readily available sources of ethylene normally containing substantial amounts of moisture, may be employed, without incorporating expensive predrying procedures in the process.

The superatmospheric pressure employed in carrying out the process may fall within a wide range, the specific pressures employed in a particular instance depending upon the factors of: (1) the type of olefinic source material employed; (2) the possible incidence of an explosion hazard due to the presence of chlorine and ethylene under pressure; and (3) the proportion of halogen to olefinic material, employed in the gaseous reaction mixture. The lower and upper pressure limits are also dictated by practical considerations of procedural economies and equipment cost, balanced against the increased production of end product obtained by use of the superatmospheric pressure in the reaction zone. With these determinative factors in mind, pressures ranging between 15 and 500 pounds gauge, may be employed advantageously.

In connection with ethylene oxide tail gases, as the oxidation of the ethylene is carried out in a system under 150 to 200 pounds gauge, the same pressures may be employed advantageously in the halogenation of the ethylene component of the tail gases.

The process is operative in connection with gaseous mixtures containing ethylene in concentrations ranging from as low as 0.1% to as high as 20% by volume of the gaseous mixture. However, use of gaseous feed mixtures containing less than 0.5% of ethylene has proven uneconomical in actual practice, and for this reason initial concentrations of above 0.5% are desirable. The use of gaseous mixtures containing over 20% of ethylene raises a serious problem of temperature control, discussed in more detail hereinafter, which renders it more profitable to use gaseous mixtures containing such high concentrations for purposes other than direct chlorination of ethylene. Accordingly, it is preferred to employ gas-

eous mixtures containing ethylene in concentration ranging between about 0.5% and 5% by volume.

Where the gaseous reaction mixture comprising the ethylene source contains relatively large amounts of hydrocarbons other than olefins, the chlorine constituent should be added to the gaseous reaction mixture in such amount as to avoid the presence of excess chlorine in the reaction zone. This is preferred for reasons of economy to assist in the inhibition of side and substitution reactions, and to reduce the explosion hazard attendant upon hydrocarbon and chlorine mixtures. Thus, it is preferred to add chlorine or other halogen to the gaseous reaction mixture in an amount sufficient to provide 0.7 to 0.95 moles of halogen for each mole of olefinic compound present. Excellent results are obtained by employing from 0.8 to 0.95 moles of chlorine to ethylene. Unwanted substitution and side reactions in the gaseous reaction mixture, may be further avoided by carefully avoiding the concentration of excesses of chlorine or other halogen at any point in the reaction stream. This may be accomplished by the introduction of chlorine into the reaction zone at a plurality of points, so spaced that the chlorine is absorbed by addition reaction with the ethylene component present, at substantially the rate of introduction into the reaction zone. Also, the chlorine may be introduced through a single inlet, exercising a careful control of the rate of chlorine injection in accordance with other reaction conditions present so as to accomplish the complete reaction thereof with the ethylene. The reaction may also be accomplished advantageously by introducing the chlorine into the reaction zone at a plurality of points, properly spaced to achieve a desired overall rate of chlorine injection.

It has further been found that the reaction is markedly improved by varying the proportions of chlorine added to the reaction stream at the above mentioned plurality of points of introduction, so that a substantial proportion of the total amount of halogen reactant to be added, is injected in the reaction zone adjacent the point of entry of the ethylene, accomplishing a major proportion of the chlorination reaction before the temperature of the reaction mixture rises beyond permissible limits. Addition of progressively smaller amounts of chlorine to the partially chlorinated reaction mixture, at subsequent points along the reaction zone, permits maintenance of such control of the temperature and rate of reaction as will permit of substantially complete chlorination of the ethylene component, minimizing the chlorination of other hydrocarbon components present.

The chlorine may be added in the gaseous phase. However, in certain applications of the invention, it is advantageous to add the chlorine in the liquid phase, as described in detail in application Serial No. 30,794.

It is preferred to carry out the reaction in the absence of light, in order to eliminate the effects of light as a promoter of substitution or side reactions.

When the gaseous reaction mixture comprising the ethylene source contains relatively small amounts of hydrogen and hydrocarbons other than olefins, the problems of explosion hazard and incidence of substitution and side reactions, are minimized to an extent permitting the use of excesses of chlorine in carrying out the reaction. This is particularly so in the case where ethylene oxide tail gases are employed as the ethylene source material, for the tail gases contain large amounts of inert gases. The amount of excess chlorine employed in terms of molal concentration of chlorine to ethylene, is determined by weighing the increase in end product obtained against the additional cost factor of the excess chlorine. In practice, it has been found that best results are obtained employing about 1.05 mols of chlorine per mol of ethylene present in the tail gases.

In cases where less than molal equivalents of chlorine to ethylene are employed, the gaseous reaction mixture emerges from the reaction zone with minute or substantially no traces of unreacted chlorine present, eliminating the introduction of costly purification procedures in the process. This is especially important when the gases comprising the sources of ethylene are to be employed subsequently for such purposes as heating and illuminating. The presence of chlorine in the residual gaseous mixture subsequent to completion of the olefin-halogen phase of the reaction, provides serious problems of equipment corrosion, and produces offensive, corrosive fumes when the residual gaseous mixture is burned.

The reaction temperatures employed are important from the standpoint of inhibiting side and substitution reactions of hydrocarbons with halogen in the reaction zone, as well as elimination of the explosion hazard. It is known that the addition of a halogen to an olefinic double bond, liberates considerable heat, for example 930 B. t. u. for each pound of ethylene dichloride formed. In accordance with the present invention, reaction temperatures are selected with the object in view that liberated heat will be absorbed and dissipated by the diluent gases present in the reaction stream along with the ethylene dichloride. This procedure is particularly advantageous, employing gaseous mixtures containing less than about 5% of ethylene by volume. In this instance, the presence of an excess of gases other than ethylene assists in maintaining the reaction temperature at permissible and preferred levels, minimizing side reactions and rendering the use of artificial cooling means unnecessary.

Under the conditions of superatmospheric pressure indicated, the olefin-halogen reaction will occur at temperatures ranging from −10° C. to 200° C. and above. However, with the above expressed factors of process economy and hazard elimination in mind, it is preferred to use initial reaction temperatures ranging between 15° C. to 150° C. Temperatures above this range render the use of special reaction and temperature control procedures and equipment necessary.

The rate of reaction may vary within wide limits determined by factors of pressures employed, temperature control, chlorine concentration and rate of addition of chlorine to the reaction mixture. However, following the procedures expressed above, the time of contact of chlorine and ethylene in the reaction zone may be as short as one tenth of a second to thirty seconds, producing excellent results in terms of completeness of reaction. This reaction time is determined in accordance with the length of the reaction zone, and the rate of flow of the reaction components. For example, when the reaction zone is six feet long and the rate of flow one foot per second, the reactant contact time can be adjusted with practicality to six seconds. In special applications of the process, it may be

desirable to appreciably extend the time of contact of the reactants.

The process of the invention proceeds substantially to completion of the olefin-halogen reaction in the absence of conventional chlorinating catalysts. Several advantages stem from this, a major consideration being the elimination of this substantial cost factor and the substantial reduction in amount of substitution products formed such as polyhalogens and hydrochloric acid. While catalytic agents accelerate the rate of reaction of olefins and halogens, the resulting waste of chlorine in the formation of substitution byproducts and the resultant necessity for costly and tedious product purification, render the elimination of the use of conventional catalysts desirable, providing a commercially acceptable rate of reaction can be maintained. This is accomplished by the present invention. It will be understood, however, that the usual chlorinating catalysts may be employed in carrying out the invention, if desired, but that an outstanding feature of the process of the invention resides in obtaining a maximum of uncontaminated end product in the absence of catalysts.

It has been discovered that the rate of reaction of the olefin-halogen mixture may be appreciably accelerated if the reaction is carried out in the presence of iron, preferably in the form of iron reaction vessels or containers such as a tubular member, defining the reaction zone. The explanation of this acceleration of the rate of reaction is not known, but the process is accomplished with little or no increase in the amount of substitution and side products formed.

The presence of small amounts of oxygen in the reaction zones, within the limits of 0.5% and 5.0%, materially assists in reducing the amount of substitution reaction taking place. As tail gas from ethylene oxide converters usually contains several percent of oxygen, this gas is particularly suited for use in the process.

Under some unfavorable reaction conditions, it may be found that the formation of substitution and side products other than ethylene dichlorides will go as high as 50% of the chlorinated product, forming, for example, 1,1,2 trichlorethane, which is valueless commercially, as compared with ethylene dichloride. Under the preferred reaction conditions of the invention, this ratio of unwanted substitution products is reduced sharply to as low as, for example, 10% and lower, particularly where tail gases from ethylene oxide converters are used as the source material. It has been found that the undesired yield of trichlorethane may be further diminished by adding initially a small amount of trichlorethane to the reaction mixture, which acts in the nature of a depressant. The depressant is recovered in the subsequent refining treatment of the end product, for recycling through the system.

In some instances, it is preferred to remove a portion of the ethylene dichloride end product from the reaction zone at a point or points intermediate the length thereof. It has been found that when the reaction mixture becomes saturated with ethylene dichloride, at temperatures over 60° C. and approaching 100° C., conditions are more favorable for the incidence of undesirable substitution reactions, than when the reaction mixture is unsaturated. The intermediate withdrawal of ethylene dichloride may be effected with an activated carbon adsorption bed, or by solvent extraction. The preferred method of intermediate withdrawal embodies the introduction of liquid ethylene dichloride into the reaction zone, to effect condensation of a portion of the gaseous end product, thereby maintaining the concentration of product in the reaction mixture below the saturation point. The condensant ethylene dichloride preferably may be chilled, whereby the temperature in the reaction zone may be reduced and maintained at a desired level. The chilled material may be introduced into the reaction vessel in any convenient way. For example, chilled ethylene dichloride may be sprayed into the reaction mixture stream in the reaction vessel and condensed product and spray collected in a suitable sump for delivery to the processing stage to be described. A portion of the product thus obtained may be recycled in the condensing step, the remainder being passed along for further purification.

Also, advantageous results in terms of accelerated rate of reaction are achieved by using a vertically disposed reaction tube or tower, the reaction stream being introduced at the bottom of the tower. Ethylene dichloride recycled from the end product is introduced at a controlled temperature of from —10° C. to 80° C. This embodiment of the invention is found to increase the rate of reaction, and reduces the contact time necessary. This modified method further minimizes conditions leading to occurrence of undesired side and substitution reactions, particularly as to the formation of local zones of elevated temperatures in the reaction zone.

The step of recycling ethylene dichloride through the reaction zone may be advantageously employed in connection with the introduction of chlorine reactant into the reaction stream. The ethylene dichloride may be used as a vehicle for the introduction of chlorine into the system, the chlorine being dissolved in the ethylene dichloride, in the liquid phase.

Where intermediate condensation of product is effected by means of chilled ethylene dichloride, it is permissible and may be desirable to heat the initial reaction mixture, with or without a small proportion of chlorine added, in order to accelerate the rate of reaction upon introduction of the reaction mixture into the reaction zone. If this is done, the chilled liquid ethylene dichloride added, additionally serves to regulate the temperature of chlorination of the bulk of the reaction mixture in the reaction zone, avoiding the incidence of undesirable excessive temperatures therein.

Upon completion of the olefin-halogen reaction phase in the reaction zone, the gases may be cleansed to remove any trace of unreacted chlorine, hydrochloric acid and other acidic impurities. This is important where the residual gases are to be used subsequently as a fuel, for example. This may be accomplished by treating the reaction mixture with a slurry of lime, using a packed or spray column of suitable design for this purpose. It has been found that the lime slurry also effectively lowers the temperatures of the reaction mixture, eliminating the necessity for employing special cooling equipment for this purpose.

The reaction mixture, thus purged of acidic impurities and cooled, preferably is passed over activated carbon for the selective extraction of ethylene dichloride. The residual gases may be passed to waste or as in the case where coke oven

gas is employed as the source of ethylene, passed directly into the gas mains for consumption.

Upon saturation, the activated carbon may be treated for the recovery of adsorbed ethylene dichloride, as for example by steaming or other application of heat, with or without the application of vacuum. The ethylene dichloride product may be further purified by conventional distillation methods, if desired.

Ethylene dichloride may be absorbed direct from the reaction mixture by passing the gases through a solvent absorption system, containing as a solvent an organic compound of higher vapor pressure than ethylene dichloride. Preferably, a halogenated organic solvent is employed. However, other conventional hydrocarbon solvents may be employed satisfactorily. The ethylene dichloride product may be removed from the solvent by conventional distillation methods. Under superatmospheric pressures of operation, the recovery of the ethylene dichloride by solvent absorption, or even by condensation, is rendered easier.

If desired, the lime slurry scrubbing step may be eliminated and the gaseous reaction mixture passed directly to a bed of activated carbon for selective adsorption of ethylene dichloride. In this instance, if it is intended to use the residual gases for heat and light purposes, it may prove to be desirable to scrub the residual gases with water to remove acidic residues, before introduction into the gas mains. This procedure is feasible in view of the very small amounts of chlorinated substitution products formed in the reaction zone.

EXAMPLE

Tail gas similar in composition to the gaseous mixture hereinbefore described was passed through an iron reaction tube at room temperature under a pressure of 150 pounds gauge. The tube approximated six feet in length, and the gas velocity was approximately 0.4 foot per second. Chlorine as a gas was passed into the iron reaction tube through a series of nozzles evenly spaced along the length of the chlorinator tube. The total chlorine added for one mole of olefinic compound present in the tail gas, in this case primarily ethylene, was about 1.05 mols. The heat of the reaction sufficed to raise the temperature about 100° C. No cooling step was employed. The gaseous mixture leaving the chlorinator contained ethylene dichloride in an amount comprising a substantially complete conversion of the ethylene component to the dichloride, along with residual unreacted gases.

This gaseous mixture was treated with a 2% lime slurry in a small packed column to scrub and cool the gases, which were passed through the slurry in a countercurrent manner. The scrubbed gases were then passed through an activated carbon bed which adsorbed the ethylene dichloride component as well as any traces of polychlor compounds present. The gases leaving this tower contained substantially no chlorinated organic compounds and no chlorine.

Using the alternative direct adsorption procedure described above, the gases from the reactor were passed directly through the carbon bed, and the residual gases were scrubbed with water in a packed column to remove traces of acidic gases. The gases contained substantially no chlorinated organic compounds and no chlorine.

The adsorptive carbon eventually became saturated with ethylene dichloride and contained a small amount of polychlor compounds. By steaming the carbon, the ethylene dichloride and other compounds were driven off and condensed to obtain the organic liquids. The ethylene dichloride was separated from the water layer and distilled to obtain high grade commercial ethylene dichloride.

The procedural requirements hereinabove set forth in connection with the chlorination of ethylene, are equally applicable to the halogenation of ethylene or other olefins, and the invention is not to be limited in this respect, except as defined in the appended claims.

The advantageous procedures of the invention permit of the recovery of halogenated olefins as a valuable byproduct of industrial gases, without impairing the values of the industrial gases for their intended purposes. The process is of particular advantage when used in connection with the treatment of olefins found in tail gases purged from ethylene oxide systems.

The process provides for substantially complete halogenation of the available olefins without the use of catalysts and in the absence of expensive procedures for preconditioning the gases prior to reaction. The use of iron reaction chambers has the surprising effect of catalyzing the rate and extent of reaction, without adding to the cost of the process or promoting side reactions.

Due to the small proportions of contaminants present in the gaseous mixture subsequent to reaction, the olefin dihalide constituent may be separated from the reaction stream and condensed with a minimum of expense and time consuming operations, obtaining a product meeting all but the more rigid commercial standards of purity.

The process permits of the reaction of olefins and halogens under conditions of superatmospheric pressure which would normally be expected to result in the occurrence of undesirable substitution reactions, to a prohibitive degree.

We claim:

1. A process for the manufacture of ethylene dichloride from gaseous mixtures containing from 0.5 to 5% by volume of ethylene and a major portion of inert gases, said ethylene being the major reactive component thereof, which process comprises contacting said gaseous mixture with chlorine at an elevated pressure in the range of 15 to 500 pounds per square inch gauge in a reaction zone maintained in a gaseous phase at a temperature in the range of 60 to 100° C., the amount of chlorine being about 1.05 mols per mol of ethylene and being introduced at spaced intervals along the reaction zone with the first introduction containing the major portion thereof, maintaining the concentration of ethylene dichloride in the reaction zone below the saturation point by condensation and withdrawal thereof at intervals along the reaction zone, said condensation being effected by introducing cooled ethylene dichloride into the reaction zone at appropriate intervals therealong, whereby a high yield of ethylene dichloride end product is obtained, and recovering said end product.

2. A process of claim 1 wherein the gaseous mixture is the tail gas from the oxidation of ethylene.

3. A process of claim 1, wherein the chlorine is introduced with the cooled liquid ethylene dichloride.

4. A process of claim 1, wherein trichlorethane

is introduced into the reaction zone to depress the substitution reaction between chlorine and ethylene dichloride.

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