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PROCESS FOR THE CHLORINATION OF SATURATED HYDROCARBONS.

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By recent publications it is known that hydrochloric acid acts upon non-saturated aliphatic hydrocarbons with formation of additive products. All experiments intending to bring to reaction saturated hydrocarbons with hydrochloric acid have however failed up to the present.

We have found that, in the presence of oxygen, hydrochloric acid can be brought to reaction with hydrocarbons of the methane group at higher temperatures chlorine substitution products such as CH_3Cl, CH_2Cl_2, $CHCl_3$ being formed.

According to the well known facts, it was to be expected that the oxygen would oxidize or burn the hydrocarbon at the high temperatures necessary for carrying through the process. Our experiments however have shown, that it is possible to carry out substitution reactions, for instance the reaction,

$$2CH_4+2HCl+O_2=2CH_3Cl+2H_2O$$

at elevated temperatures without oxidizing the hydrocarbon. Convenient reaction temperatures are for instance those between approximately 300° C. and approximately 650° C. but preferably those between approximately 450°C. and 550° C. Temperatures which essentially exceed 650° C. must generally be avoided as they lead to undesired oxidation of the hydrocarbon.

The process can be carried out in absence of catalysts. It has however been found advantageous to provide for the presence of such catalysts which favor the oxidation of the hydrochloric acid and, if possible, at the same time the chlorination of the hydrocarbon. We have found that both conditions are satisfied by such substances, which are known as promoting chlorination, for instance carbon, cupric chloride, ferric chloride, thallic chloride, the chlorides of the alkaline earths and of the rare earths. The presence of such catalysts allows the desired oxidation of the hydrochloric acid to take place at comparatively low temperatures, while on the other hand it favors the desired chlorination but not the undesired oxidation of the hydrocarbons.

As to the ratio of the reaction components it depends on the working method and on the desired reaction products. The oxygen for instance may be applied in the theoretically required quantity. Frequently however it will be advisable to use a suitable excess of oxygen preferably not too large.

The chlorination according to the invention may also be carried through in presence of diluting means, e. g. in presence of steam. Consequently it is possible to use aqueous hydrochloric acid instead of hydrogen chloride. Oxygen-containing gases, for instance air, may replace oxygen.

Examples:

1. At about 500° C. a mixture of 25 liters of methane, 12 liters of oxygen, 12 liters of hydrochloric acid and 55 liters of steam (corresponding to 60 grams of aqueous hydrochloric acid of 30%) per hour is conducted through a tube of 30 mm. inner diameter heated over a length of 600 mm., the tube being filled with grains of fire brick prepared with cupric chloride. 63½% of the hydrochloric acid introduced is converted to chlorination products of the methane, only 3½% of the methane used is burnt to carbonic acid.

2. If in the same tube the gases are introduced with half the velocity as stated under 1, the utilization of the hydrochloric acid may be considerably increased, notwithstanding lower temperature, by which burning of the methane on a larger scale is avoided. For instance at temperatures between 450° C. and 500° C. 12 liters of methane, 6 liters of oxygen, 6 liters of hydrochloric acid and 27 liters of steam (corresponding to 30 grams of 30% aqueous hydrochloric acid) are conducted through per hour. 81½% of the hydrochloric acid is converted to chlorination products of methane, the burning of methane to carbon dioxide not exceeding 5%.

3. The charge of methane and hydrochloric acid being reduced by one half according to Example No. 2, the use of air instead of oxygen does not essentially impair the conversion of the hydrochloric acid, the formation of carbonic acid however being slightly reduced. If for instance per hour 12 liters of methane, 30 liters of air, 6 liters of hydrochloric acid and 27 liters of steam at 450° C. to 500° C. are conducted through the same tube, 66½% of the hydrochloric acid is con-

verted to chlorination products, and 4 to 4½ parts of carbon dioxide are formed from 100 parts of methane.

4. Working with hydrochloric acid gas instead of aqueous hydrochloric acid larger charges easily may be treated. At the same time burning of methane to carbon dioxide may be reduced to a minimum by avoiding the excess of oxygen which in the Examples Nos. 1–3 amounted to 100%. At 450° C.–500° C. 12 liters of marsh gas, or natural gas, 12 liters of hydrochloric acid and 6 liters of oxygen per hour being conducted through, 60% of the hydrochloric acid is converted to chlorination products and 2% of the methane to carbon dioxide.

As numerous experiments have shown the losses resulting from the undesired oxidation processes generally never exceed 5% of the introduced hydrocarbon, thus being so low that they are practically of no account. The hydrochloric acid which is not converted and the unchanged portion of the hydrocarbon may be used for new charges.

As has been described and shown by the examples above it is possible to control the chlorination process in such a manner that the oxygen oxidizes only the hydrochloric acid, but practically does not attack the hydrocarbon to be chlorinated. The invention thus permits the production of partially chlorinated products that is those containing hydrogen which are generally most valuable, this result being mainly obtained by avoiding injurious superheating. The use of suitable catalysts allowing the temperature to be lowered, has proved to be very advantageous, as has already been stated above.

Starting from this knowledge experiments make it easily possible to find out in every case the most favorable conditions as to ratio of reacting gases, height of temperature, catalysts, velocity of flow of the reacting gases, dilution means and so on, in order to obtain a good yield of the desired chlorination products.

The method is extraordinarily successful for the chlorination of methane and its homologues. Methane may be used pure or mixed with other gases, for instance, as marsh gas or natural gas which contains sometimes also considerable quantities of homologues of methane, as gas from distillations, as gas from coke ovens or the like.

We claim:

1. Process for the chlorination of saturated hydrocarbons consisting in causing the said hydrocarbons to react with hydrochloric acid and oxygen at temperatures of 300° C. to 650° C., the quantity of oxygen employed and the velocity of the gases being such that the oxidation of the hydrocarbon is avoided.

2. Process for the chlorination of saturated hydrocarbons consisting in causing the said hydrocarbons to react with hydrochloric acid and oxygen at temperatures of 300 ° C. to 650° C. in the presence of a catalyst capable of promoting chlorination, the quantity of oxygen employed and the velocity of the gases being such that the oxidation of the hydrocarbon is avoided.

3. Process for the chlorination of saturated hydrocarbons consisting in causing the said hydrocarbons to react with hydrochloric acid and oxygen at temperatures of 300° C. to 650° C. in the presence of metallic chlorides as catalysts, the quantity of oxygen employed and the velocity of the gases being such that the oxidation of the hydrocarbon is avoided.

4. Process for the chlorination of methane consisting in causing the same to react with hydrochloric acid and oxygen at temperatures of 300° C. to 650° C., the quantity of oxygen employed and the velocity of the gases being such that the oxidation of the methane is avoided.

5. Process as claimed in claim 4 in which the reaction is effected in the presence of a catalyst capable of promoting chlorination.

In testimony whereof we affix our signatures.

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