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MANUFACTURE OF ALKYL HALIDES

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This invention relates more particularly to the manufacture of halogen compounds corresponding to the replacement of the hydrogen atoms of paraffin hydrocarbons with chlorine, bromine or iodine.

In a more specific aspect the invention is concerned with a process for the manufacture of these alkyl halides by the interaction of mono olefins and halogen acids while under specific and selective catalytic influences.

Unsaturated straight chain hydrocarbons comprising mono, di and tri olefins and the acetylene series of hydrocarbons are commonly employed as starting materials for the ultimate production of a great many types of organic derivatives on account of their ready reactivity with various treating reagents due to their unsaturated character. Their behavior contrasts strongly with that of their saturated counterparts, the paraffins, which have substantially no reactivity with ordinary reagents at moderate temperatures.

It is characteristic of olefins and particularly the mono olefins with which the present invention is principally concerned that they can be made to react directly and additively with all mineral acids such as sulphuric, phosphoric and the halogen acids, with the halogens themselves, with oxygen and oxidizing compounds and with hydrogen under suitable catalytic influence. However, owing to their general reactivity which involves also their tendency to polymerize under catalytic or chemical influences, it is frequently difficult to confine the reaction between a given olefin and a reagent in one precise direction so that high yields of a desired compound are obtained with a minimum of undesirable by-products. It is a feature of the present invention which will be presently developed that, by using a particular catalyst and certain limited conditions of operation, a certain type of additive reaction between mono olefins and halogen acids is held more closely along a given line than has been heretofore possible.

In one specific embodiment the present invention comprises the production of alkyl halides particularly secondary alkyl halides, by interacting mono olefins and halogen acids including hydrochloric, hydrobromic and hydriodic acids with mono olefins in the presence of phosphoric acids or composite solid catalysts comprising such acids as their active ingredient.

The invention is more particularly directed to the production of alkyl halides from mono olefins which are normally gaseous, though it is not limited thereto and may be applied to the treatment of liquid olefins as well with proper modifications in treating conditions in respect to temperature and the type and phase of the catalyst.

Olefins which are readily reacted with halogen acids according to the present invention are those containing from 2 to 5 carbon atoms in a molecule and to indicate the character of these compounds the following table is introduced which is a partial list of the low molecular weight olefins.

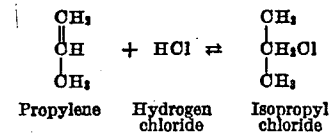
Compounds	Formula	Boiling point
		°C.
Ethylene	$CH_2=CH_2$	−105
Propylene	$CH_3CH=CH_2$	−48
Ethyl ethylene	$CH_3CH_2CH=CH_2$	−5
Plane-sym. dimethyl ethylene	$CH_3\cdot CH=CH\cdot CH_3$	+1
Axial-sym. dimethyl ethylene	$CH_3\cdot CH=CH\cdot CH_3$	+2.5
Unsym. dimethyl ethylene	$(CH_3)_2C=CH_2$	−6
n-Propyl ethylene. α-Amylene.	$CH_3CH_2CH_2CH=CH_2$	+39
Isopropyl ethylene. α-Isoamylene.	$(CH_3)_2CH\cdot CH=CH_2$	+21
Sym. methyl ethyl ethylene. β-Amylene.	$CH_3\cdot CH_2\cdot CH=CH\cdot CH_3$	+36
Unsym. methyl ethyl ethylene. γ-Amylene.	$CH_3\cdot CH_2$ $\diagdown$ $C=CH_2$ $\diagup$ CH_3	+31
Trimethyl ethylene. β-Isoamylene.	$(CH_3)_2C=CH\cdot CH_3$	+36
Tetramethyl ethylene	$(CH_3)_2C=C(CH_3)_2$	+73

As the molecular weight of hydrocarbons of any given series increases the number of isomers increases very rapidly and their separation is difficult so that the preceding table has not been extended to include higher molecular weight homologs.

The process may be employed to produce alkyl halides from individual olefins or from mixtures of the same with each other or with their corresponding paraffinic compounds as in the mixtures of hydrocarbons which are normally produced when cracking petroleum oils for the primary purpose of producing maximum yields of motor fuel fractions in most commercial oil cracking plants. Obvoiusly the reactions may be most closely controlled when individual compounds are being dealt with although when using the preferred catalysts there is at all times a minimum of undesirable side reactions even with mixtures.

In the direct addition of halogen acids to mono olefins the production of secondary compounds is the invariable rule. Thus the reaction between propylene and hydrochloric acid is expressed by

the following equation in which the compounds involved are represented structurally:



Similarly sulphuric and other acids add to form the isopropyl sulphates, etc.

The catalysts which have been found to accelerate the specific additive reactions between mono olefins and halogen acids are the acids of phosphorus in which phosphorus has a valence of 5 including the ortho, pyro and meto phosphoric acids. For purposes of reference the names, formulas and common properties of the acids are given below:

Acids of Phosphorus

Acid	Formulas		M. P.	Dec.
			°C.	°C.
Orthophosphoric	H_3PO_4	$P_2O_5.3H_2O$	38.5	Loses $\frac{1}{2}H_2O$ at 213
Pyrophosphoric	$H_4P_2O_7$	$P_2O_5.2H_2O$	61	
Metaphosphoric	HPO_3	$P_2O_5.H_2O$	Sublimes	

These acids may be employed alone in liquid phase or as the active ingredient in solid composite contact materials, the details of operation of the process being modified accordingly.

When using ordinary orthophosphoric acid, for example, to catalyze the reaction expressed by the foregoing equation an equimolecular mixture of hydrogen chloride and propylene may be bubbled through a stationary pool of the phosphoric acid or the stream of gases may be passed upwardly countercurrent to descending streams or rivulets of the liquid acid as it passes downwardly over filling or baffling material in vertical cylindrical treating towers. The first method of operation is essentially of a batch character and the second is continuous and generally to be preferred in commercial practice. The temperature and pressure conditions may be modified to suit the boiling point of the compound produced in greatest quantity so that it passes out of the reaction zone as a vapor and does not leave any liquid in contact with the catalytic material. The temperature ranges employed will vary with the individual olefin or mixture of olefins treated from approximately 200 to 500° F. A series of experiments which will be described in more detail in a subsequent example indicates that for propylene a temperature of approximately 300° F., gives a maximum yield of isopropyl chloride.

As a general rule best results are obtained at atmospheric or slightly superatmospheric pressures, since the effect of increased pressures is to speed up polymerization reactions so that higher boiling polymers of the olefins tend to be formed instead of the desired halogen derivatives.

In lieu of the liquid acids a convenient method of operation for producing the present type of reaction consists in employing stationary beds of solid contact materials consisting of adsorbent particles containing high percentages of the acids. Thus composites may be obtained by adding any of the phosphoric acids to such relatively inert spacing or supporting materials as activated charcoal, fuller's earth, ground pumice, clays such as Bentonite and Montmorillonite, diatomaceous earth or kielseguhr. Metal oxides and chlorides in minor amounts may be incorporated in the original mixes to exert a favorable promoting action if desired.

In making such solid phosphoric acid catalysts the general procedure is to intimately mix regulated amounts of a selected adsorbent material and a liquid acid, followed by heating for a protracted period until a certain amount of water is driven off and a solid cake of desired chemical composition and physical properties is obtained and finally grinding and sizing the cake out of contact with moist air to produce particles of desired size. Any loss in fines in a single operation of this character may be returned to another primary mix so that ultimately no loss is suffered from this source.

When using orthophosphoric acid of ordinary commercial concentration and purity, say from 75 to 90% by weight of acid in water, the acid and absorbent may be mixed at ordinary temperatures by efficient mechanical stirring and grinding devices after which the mass is heated for from about 24 to 60 hours at temperatures varying between 220 and 300° C. depending upon the concentration of the acid employed. The cake produced at this point is found by analysis to contain a ratio of phosphorus pentoxide to water corresponding to a mixture of the meta and pyro acids.

Greater efficiency in the manufacture of this type of solid catalyst may be obtained by starting with pyrophosphoric acid particularly when such finely divided siliceous adsorbents as kieselguhr are employed. In this case the mixing may be done at a temperature somewhere within the range of 160 to 200° C., and it is found that under these conditions a solid cake is produced in a much shorter time and that the time of heating at a more elevated temperature to produce the solid cake is lessened and sometimes is reduced below 24 hours.

When using kieselguhr and pyrophosphoric acid the final catalyst particles which are used for promoting the present type of reaction may contain as high as 60% or over of pyrophosphoric acid without exhibiting any tendency to flux or disintegrate under the conditions of use.

When using the solid type of catalyst operations are considerably simplified and consist essentially in passing proportioned mixtures of the vapors of an olefin and a halogen acid through solid contact materials consisting in particles of graded size, usually somewhere within the range of from 4 to 30 mesh. As a rule best results are obtained with downflow treatments on account of the formation of small amounts of liquid products which are thus automatically washed from the catalyst particles by the gas stream so that the effective surface is not reduced to any appreciable extent. It is usually preferable to preheat the gaseous mixture to the desired operating temperature prior to contact with the solid catalyst rather than to attempt to heat the catalyst chamber exteriorly on account of the difficulties in heat distribution through the cross section of units of commercial size. After passing through the

catalyst the gas-vapor mixture is cooled and the halogenated products are liquefied and recovered. Selected solvent adsorption may be employed.

The following is given as an example of results obtainable by the process although it is not to be considered in a strict sense as limiting the invention correspondingly.

A mixture of 4½ volumes of propylene and 3½ volumes of hydrogen chloride was passed at atmospheric pressure and an entering temperature of 305° F. through a bed of 10 to 20 mesh solid catalyst particles previously made by incorporating 80% by weight of 89% orthophosphoric acid with 20% by weight of kieselguhr followed by heating, grinding and sizing as described in a previous paragraph.

The liquid obtained after the cooling of the reaction products boiled over a range of from 30 to 207° C., although 75% boiled within the range of from 30 to 52° C. (boiling point of isopropyl chloride 35.5° C.) After a fractionation to recover isopropyl chloride and a determination of the weight yields it was found that 70% of the theoretical yield of isopropyl chloride had been produced.

In proportioning halogen acid and olefins best results are usually obtained when using approximately equimolecular proportions which avoids necessity for disposing of excess of either reactant. It has been found that the reactions are sufficiently unidirectional so that this particular method of proportioning can be used in practically all cases.

The foregoing specification and example have described and exemplified the present invention but neither is to be construed in a limiting sense as imposing undue restrictions upon its generally broad scope.

I claim as my invention:

1. A process for the production of alkyl halides which comprises additively reacting a halogen acid with a mono-olefin at temperatures of from 200 to 500° F. in the presence of an acid of phosphorous in sufficient amount to catalyze the reaction.

2. A process for the production of alkyl halides which comprises, additively reacting a halogen acid with a mono-olefin at elevated temperatures of from 200 to 500° F., and in the presence of a phosphoric acid in sufficient amount to catalyze the reaction.

3. A process for the production of alkyl chlorides which comprises, additively reacting a mono olefin with hydrochloric acid at elevated temperatures of from 200 to 500° F. and in the presence of phosphoric acid in sufficient amount to catalyze the reaction.

4. A process for the production of alkyl bromides which comprises, additively reacting a mono olefin with hydrobromic acid at elevated temperature of from 200 to 500° F. and in the presence of a phosphoric acid in sufficient amount to catalyze the reaction.

5. A process for the production of alkyl iodides which comprises, additively reacting a mono olefin with hydriodic acid at elevated temperature of from 200 to 500° F. and in the presence of a phosphoric acid in sufficient amount to catalyze the reaction.

6. A process for the production of alkyl halides which comprises additively reacting a halogen acid with a mono-olefin at temperatures of from 200 to 500° F. in the presence of a solid mixture of an acid of phosphorus in sufficient amount to catalyze the reaction and a siliceous adsorbent material.

7. A process for producing alkyl halides which comprises additively reacting a halogen acid with a mono-olefin in vapor phase at a temperature of from 200 to 500° F. under a pressure not substantially in excess of atmospheric and in the presence of an acid of phosphorus in sufficient amount to catalyze the reaction.

8. A process for producing alkyl halides which comprises additively reacting a gaseous halogen acid with a gaseous mono-olefin at a temperature of from 200 to 500° F. under a pressure not substantially in excess of atmospheric and in the presence of a phosphoric acid in sufficient amount to catalyze the reaction.

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