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VAPOR PHASE NITRATION OF THE LOWER ALKANES

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My invention relates to the production of nitroparaffins by the vapor phase nitration of paraffin hydrocarbons by means of nitric acid. More specifically, my invention relates to an improved method for vaporizing nitric acid in such a process.

The nitration of paraffin hydrocarbons, such as ethane, propane, butane, and the like, by means of nitric acid is most advantageously carried out in a continuous vapor phase process as described in U. S. Patents 1,967,667 and 2,071,122 of H. B. Hass et al. For his reaction it is necessary to provide nitric acid in the vapor form, and up to the present time all of the procedures suggested for this step of the process have had serious disadvantages. The simple method of boiling liquid nitric acid is disadvantageous from the standpoint of lack of control of the ratio of nitric acid vapor and hydrocarbon for the reaction. This and other similar methods involving the use of directly heated vessels have the disadvantage that serious corrosion is encountered, particularly when operating under superatmospheric pressure, in which case liquid nitric acid is in contact with the apparatus at high temperatures. In the patents referred to above, it is suggested that the hydrocarbon to be nitrated may be passed through hot liquid nitric acid to effect the vaporization. However, this procedure is disadvantageous from the standpoint of safety of operation. In such a process the hydrocarbon is contacted with a large excess of nitric acid with the result that highly explosive mixtures may be produced. The possibility of vaporizing the nitric acid by preheating the hydrocarbon to a high temperature and contacting the hot gas with liquid nitric acid has not appeared to be feasible in view of the probability of nitration taking place in the vaporizer, or even oxidation of the hydrocarbon taking place due to its extremely high temperature when contacted with the nitric acid.

I have now discovered, however, that nitric acid may be successfully vaporized by preheating the hydrocarbon to be nitrated in the process and contacting the hot gas with liquid nitric acid, and that in such a procedure none of the expected difficulties are encountered. Substantially no oxidation of the hydrocarbon takes place, and any nitration occurring in the vaporizer is insufficient to adversely affect the reaction yield. Although it had seemed probable that the formation of mononitro compounds in the vaporizer would result in oxidation or other further reaction of these products in the reaction vessel, I have found that such reactions take place only to a negligible degree, if at all, and that it is possible to secure high yields of substantially pure mononitro compounds when utilizing my process.

In accordance with my invention the hydrocarbon to be nitrated is simply preheated to a heat content sufficient to vaporize the desired quantity of nitric acid, and is then contacted with such quantity of liquid nitric acid to form a reaction mixture of hydrocarbon and nitric acid vapors. The hydrocarbon may be heated in any suitable manner as, for example, in a direct fired heating coil, and the heated gas may then be contacted with liquid nitric acid in the desired ratio for the nitration reaction. The hydrocarbon may be heated to any desired temperature preferably substantially above the boiling point of nitric acid at the pressure employed, and below the cracking or decomposition temperature of the hydrocarbon at such a pressure.

The preheated hydrocarbon and liquid nitric acid may be contacted in any suitable manner as, for example, by spraying liquid nitric acid into a chamber through which the heated hydrocarbon is passed. Various equivalent procedures will be evident to those skilled in the art, such as flowing liquid nitric acid down a packed column through which the heated hydrocarbon is passed, or flowing a thin stream of liquid nitric acid through a relatively long pipe through which the heated hydrocarbon is passed to the reaction vessel. My invention is not limited to any particular type of apparatus for this purpose, and any suitable corrosion resistant vessel designed for contacting gases and liquids may satisfactorily be employed.

My invention may be illustrated by the following specific example:

Example

Nitric acid of 40° Bé. concentration is allowed to flow downward in a packed column through which propane is passed concurrently at a pressure of 30 lbs. per square inch, and at a temperature of 500° C. By maintaining the molar ratio of propane to nitric acid slightly above 3.8 to 1, the nitric acid is completely vaporized and a suitable reaction mixture for the nitration of propane is continuously produced.

It will, of course, be evident that the procedure of the above example is subject to numerous modifications. Thus, by increasing the ratio of propane to nitric acid the propane could be pre-

heated to a lower temperature, in some cases even below the boiling point of nitric acid, and still secure complete vaporization of all of the nitric acid. Similarly by operating at a pressure below 30 lbs. per square inch less heat would be required for vaporizing the nitric acid, and the propane could thus be preheated to a lower temperature or the ratio of propane to nitric acid could be reduced. If it is desired to operate at a higher pressure, or to utilize a lower ratio of propane to nitric acid at a pressure of 30 lbs. per square inch, it will be necessary to preheat the propane to a somewhat higher temperature. However, in view of the danger of cracking or decomposition it is desirable to heat propane only to temperatures below 600° C., and for this reason it may be found to be preferable to decrease the water content of the nitric acid to be vaporized, thus reducing the amount of heat required. It will, of course, be evident in this connection that other hydrocarbons may be heated to higher or lower temperatures than propane before cracking is encountered, and that processes employing these hydrocarbons may be modified accordingly. Thus in the case of butane it is preferred to preheat only to temperatures below 500° C.

It will, of course, also be evident that some of the heat may be supplied directly to the nitric acid as well as by means of the heated hydrocarbon. In accordance with this modification the nitric acid may be preheated to any temperature below its boiling point at the pressure employed, prior to contacting it with the heated hydrocarbon. In this manner the hydrocarbon may be preheated to a lower temperature than would otherwise be necessary, or a lower ratio of hydrocarbon to nitric acid may be employed. Such a procedure is particularly desirable in the case of the higher hydrocarbons which tend to crack or decompose at substantially lower temperatures than propane. Various other modifications of procedure will, of course, naturally occur to those skilled in the art, and it is to be understood that my invention incudes within its scope the use of any such modifications or equivalents.

My invention now having been described, what I claim is:

1. In a process in which nitric acid is vaporized and reacted with a lower alkane in the vapor phase to form lower nitroalkanes, the steps which comprise preheating said lower alkane to a temperature at which any cracking which takes place occurs only to such an extent that the resulting heated gas comprises primarily lower alkanes and continuously introducing liquid nitric acid and said heated gas into a vaporizing zone, the said heated gas having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of lower alkane and nitric acid vapors is continuously produced.

2. In a process in which nitric acid is vaporized and reacted with a lower alkane in the vapor phase to form lower nitroalkanes, the steps which comprise preheating said lower alkane to a temperature above the boiling point of nitric acid and such that any cracking which takes place occurs only to such an extent that the resulting heated gas comprises primarily lower alkanes and continuously introducing liquid nitric acid and said heated gas into a vaporizing zone, the said heated gas having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of lower alkane and nitric acid vapors is continuously produced.

3. In a process in which nitric acid is vaporized and reacted with a lower alkane in the vapor phase to form lower nitroalkanes, the steps which comprise preheating the nitric acid to a temperature below its boiling point, preheating said lower alkane to a temperature above the boiling point of nitric acid and such that any cracking which takes place occurs only to such an extent that the resulting heated gas comprises primarily lower alkanes and continuously introducing liquid nitric acid and said heated gas into a vaporizing zone, the said heated gas having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of lower alkane and nitric acid vapors is continuously produced.

4. In a process in which nitric acid is vaporized and reacted with a lower alkane in the vapor phase to form lower nitroalkanes, the steps which comprise preheating said lower alkane to a temperature above the boiling point of nitric acid and below a temperature which gives rise to substantial cracking of said lower alkane and continuously introducing liquid nitric acid and the heated alkane into a vaporizing zone, the said heated alkane having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of lower alkane and nitric acid vapors is continuously produced.

5. In a process in which nitric acid is vaporized and reacted with ethane in the vapor phase to form nitroethane, the steps which comprise preheating said ethane to a temperature above the boiling point of nitric acid and below 600° C. and continuously introducing liquid nitric acid and the heated ethane into a vaporizing zone, the heated ethane having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of ethane and nitric acid vapors is continuously produced.

6. In a process in which nitric acid is vaporized and reacted with propane in the vapor phase to form nitropropane, the steps which comprise preheating said propane to a temperature above the boiling point of nitric acid and below 600° C. and continuously introducing liquid nitric acid and the heated propane into a vaporizing zone, the heated propane having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of propane and nitric acid vapors is continuously produced.

7. In a process in which nitric acid is vaporized and reacted with butane in the vapor phase to form nitrobutane, the steps which comprise preheating said butane to a temperature above the boiling point of nitric acid and below 500° C. and continuously introducing liquid nitric acid and

the heated butane into a vaporizing zone, the heated butane having a heat content sufficient to supply substantially all of the heat of vaporization necessary to vaporize the said nitric acid at the same rate at which said nitric acid is introduced into the vaporizing zone, whereby a reaction mixture of butane and nitric acid vapors is continuously produced.

8. In a process in which nitric acid is vaporized and reacted with propane in the vapor phase to form nitropropane, the steps which comprise preheating said propane to a temperature of approximately 500° C. and continuously introducing the heated propane and liquid nitric acid of approximately 40° Bé. concentration into a vaporizing zone in a ratio of approximately 4 mols of propane per mol of nitric acid, whereby a reaction mixture of propane and nitric acid vapors is continuously produced.

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