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PRODUCTION OF CYCLOALKYL NITRITES

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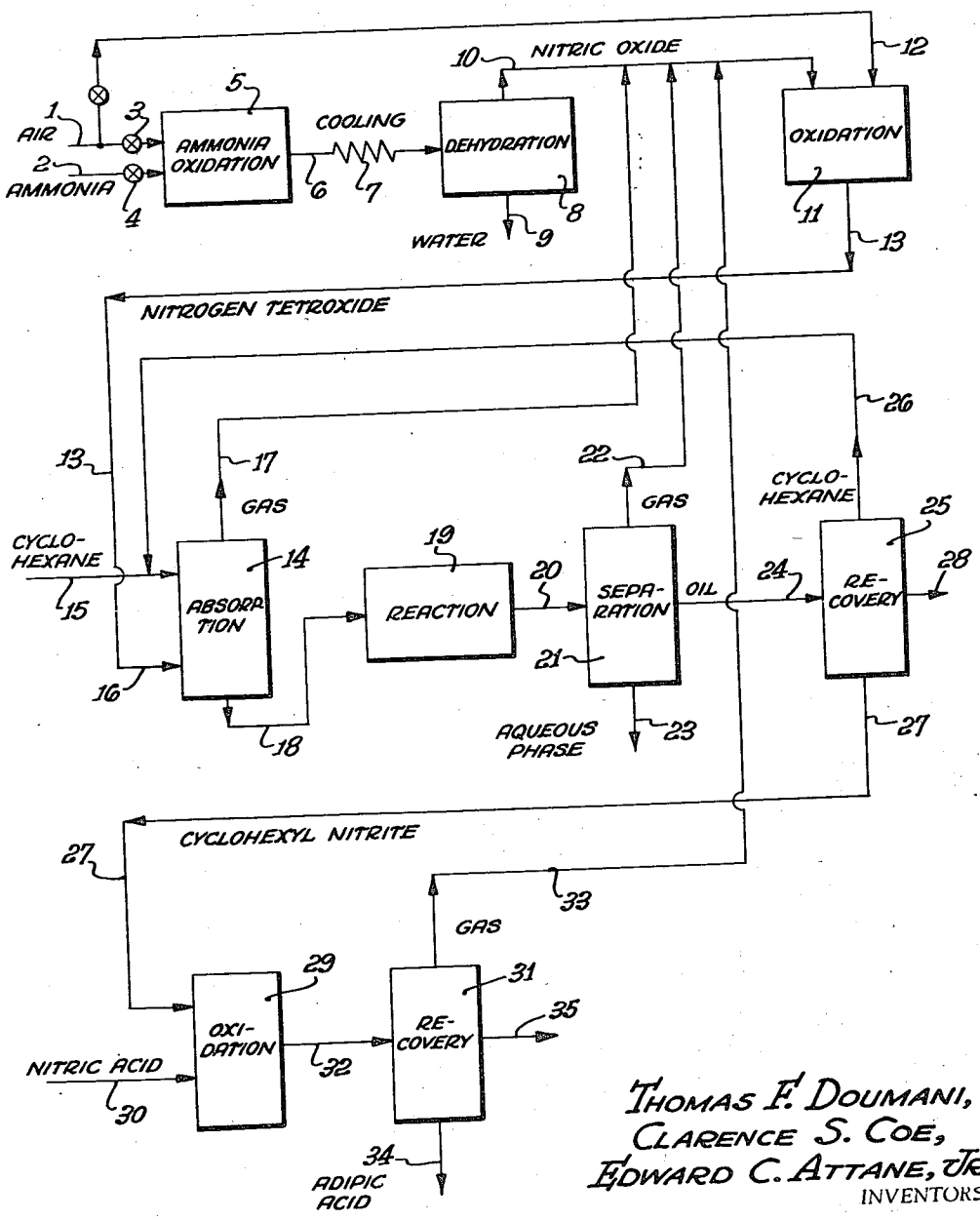

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PRODUCTION OF CYCLOALKYL NITRITES

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14 Claims. (Cl. 260—466)

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This invention relates to a method for the production of esters of nitrous acid and reaction products thereof and relates particularly to the esterification of saturated hydrocarbons, especially of cycloalkyl hydrocarbons.

Esters of nitrous acid have been prepared in the past by the usual esterification reaction between an alcohol and an acid to form the ester and water. In the case of nitrous acid esters however, the esterification process is complicated by the instability of nitrous acid as well as the reactivity of the esters formed. Possibly this explains the fact that there is comparatively little information available on this esterification. The few processes described in the prior art generally involve the reaction of an alcohol with nascent nitrous acid formed in situ by acidification of a nitrite salt. Thus the method described on page 108 of "Organic Syntheses," Coll., vol. 2, published by John Wiley and Sons Inc. of New York city, for the preparation of n-butyl nitrite involves the gradual addition of sulfuric acid and n-butyl alcohol to a sodium nitrite solution in the cold. As far as applicants are aware the preparation of esters of nitrous acid by direct esterification of hydrocarbons has never been carried out.

Applicants have discovered that esters of nitrous acid, or organic nitrites, as they may also be termed, may be prepared by reacting alcohols, especially cycloalkyl alcohols, with nitrogen tetroxide in the liquid phase, at atmospheric temperatures or below, in the absence of catalysts.

Applicants have also discovered another entirely unexpected reaction, i. e., that the same esters of nitrous acid may also be prepared by reacting the same reagent, nitrogen tetroxide, with a different material, namely the hydrocarbon rather than the alcohol. It is most unusual that the same reagent will react with two different materials to form the same product.

It has been discovered that if saturated hydrocarbons are maintained at an elevated temperature in the liquid phase, and contacted for a relatively short contact time with a minor proportion of nitrogen tetroxide, good yields of the organic nitrites may be obtained. In this process it is preferable that the nitrogen tetroxide be dissolved in the hydrocarbon, and that the addition of water or nitric acid be avoided, since the presence of any substantial amount of water or nitric acid in the reaction zone tends to reduce the production of the nitrite and results in the formation of nitro compounds and oxi-

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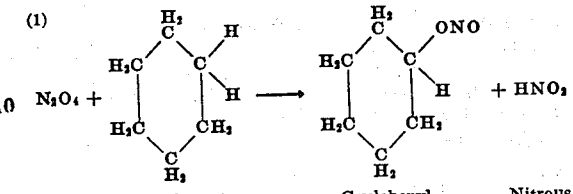
dation products. Continuous concurrent flow of the hydrocarbon and the nitrogen tetroxide is also preferred.

The main reaction involved in the process of this invention is believed to be as follows:

(1) 

Nitrogen tetroxide — Cyclohexane — Cyclohexyl-nitrite — Nitrous acid

Since nitrous acid is very unstable, the principal products other than the nitrite are nitric oxide and water rather than nitrous acid; thus the overall reaction is believed to be:

(2) $3N_2O_4 + 4C_6H_{12} \longrightarrow 4C_6H_{11}ONO + 2NO + 2H_2O$

Nitrogen tetroxide — Cyclohexane — Cyclohexyl nitrite — Nitric oxide — Water

The nitric oxide of Equation 2 may be readily oxidized to nitrogen tetroxide by the following reaction:

(3) $2NO + O_2 \longrightarrow N_2O_4$

Nitric oxide — Oxygen (air) — Nitrogen tetroxide

Thus the by-product nitric oxide may be very readily reconverted to the nitrogen tetroxide reactant, and substantially all of the nitrogen of nitrogen tetroxide is utilized for the esterification.

It has also been discovered that the organic nitrites may be readily converted to additional valuable products. For example, the cycloalkyl nitrites have been found to be very readily oxidized to dibasic acids of unusually high purity. This provides an improved process for the production of such dibasic acids, namely, converting the cycloalkanes to the cycloalkyl nitrites, and oxidizing the latter to the dibasic acids. In the case of cyclohexane for example, the cyclohexyl nitrite prepared by equations 1 or 2 above may be oxidized to adipic acid. The overall oxidation reaction apparently is as follows, where nitric acid is used as the oxidizing agent:

(4) $3C_6H_{11}ONO + 7HNO_3 \longrightarrow 3COOH(CH_2)_4COOH + 5H_2O + 10NO$

Cyclohexyl nitrite — Nitric acid — Adipic acid — Water — Nitric oxide

The nitric oxide by-product may be reconverted

to the nitrogen tetroxide reactant employed in Equation 1 or 2 by oxidation according to Equation 3 above. It may also be converted to the nitric acid reactant employed in Equation 4 by the following oxidation:

(5) $4NO + 3O_2 + 2H_2O \longrightarrow 4HNO_3$
Nitric oxide; Oxygen; Water; Nitric acid

Thus the overall reaction for production of adipic acid by Reactions 2, 3, 4 and 5 is simply:

(6) $2C_6H_{12} + 5O_2 \longrightarrow 2C_6H_{10}O_4 + 2H_2O$
Cyclohexane; Oxygen; Adipic acid; Water

It has also been discovered that nitrogen tetroxide is much more soluble in hydrocarbons than are the other nitrogen oxides such as nitrous oxide or nitric oxide or other gases such as nitrogen itself. This makes possible a further improvement in the above process for preparing organic nitrites, namely preparing the desired solution of nitrogen tetroxide in the feed hydrocarbon by selectively extracting the nitrogen tetroxide from a gaseous mixture containing the tetroxide in admixture with less soluble gases such as other nitrogen oxides, nitrogen, ammonia, air and water vapor. Such gaseous mixtures are economically prepared by the oxidation of ammonia. This oxidation is preferably carried out in two steps, the main reaction in the first step being as follows:

(7) $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
Ammonia; Oxygen; Nitric oxide; Water

The second step is the oxidation of the nitric oxide, after separating it from the water, to obtain the tetroxide, according to Equation 3. The resulting gaseous mixture, containing nitrogen tetroxide in admixture with impurities such as other nitrogen oxides, nitrogen, air and the like, is then contacted with the hydrocarbon feed, which selectively dissolves the nitrogen tetroxide to form the reaction mixture.

Thus the primary process of this invention is the esterification of hydrocarbons with nitrogen tetroxide to form the organic nitrites, and this process may be elaborated by the use of the feed preparation process involving the selective extraction of the nitrogen tetroxide by the hydrocarbon feed, and by the subsequent conversion of the cycloalkyl nitrites to the dibasic acids by oxidation.

The invention will become more clear by reference to the attached drawing, in which cyclohexane is indicated as the hydrocarbon feed, although other hydrocarbons may also be employed, as described below. Referring to the drawing, air or oxygen, and ammonia are introduced through lines 1 and 2 and valves 3 and 4 into ammonia oxidation zone 5 in which they are contacted with a catalyst such as platinum gauze heated to red heat, and thus converted to a mixture of water and nitric oxide as indicated in Equation 6. The resulting product is passed through line 6 and cooling means 7 into dehydration zone 8 in which the water is removed by condensation and/or other dehydration and withdrawn through line 9, while the remaining gas, largely nitrogen and nitric oxide, is removed through line 10 and passed to oxidation zone 11. In this zone it is contacted with air introduced through line 12, whereby the nitric oxide is converted to nitrogen tetroxide in accordance with Equation 3. The resulting gas, principally nitrogen and nitrogen tetroxide is removed through line 13, and the

nitrogen tetroxide is selectively dissolved in cyclohexane in absorption system 14. This system may be in the form of a countercurrent absorber in which liquid hydrocarbon feed is introduced in the upper part of the absorber, and the nitrogen tetroxide containing gas is introduced into the lower part of the absorber. The non-absorbed gas is withdrawn through line 17 and discarded, or if sufficiently rich in nitric oxide, may be returned to oxidation zone 11. The solution of nitrogen tetroxide in cyclohexane is withdrawn through line 18 and sent to reaction zone 19, in which the cyclohexane is converted to cyclohexyl nitrite in accordance with Equation 1 or 2. The resulting product is withdrawn through line 20 and separated in separation zone 21 to obtain a gas fraction largely nitric oxide, which may be withdrawn through line 22 and returned to oxidation zone 11, a small amount of an aqueous phase which may be withdrawn through line 23, and an oil phase which may be withdrawn through line 24 and sent to recovery system 25. In the recovery system 25, which may be merely a fractional distillation zone or any other type of separation system, the unreacted cyclohexane may be separated, withdrawn through line 26 and returned to absorption system 14; the cyclohexyl nitrite may be recovered and withdrawn through line 27, and by-products including nitrocyclohexane may be withdrawn through line 28. The cyclohexyl nitrite may then be converted to adipic acid by introducing it into oxidation zone 29 where it is contacted with nitric acid introduced through line 30 and converted to adipic acid in accordance with Equation 4. The resulting product may be transferred to recovery zone 31 through line 32. A gas fraction, which is primarily nitric oxide may be withdrawn through line 33 and returned to oxidation zone 11, and the remaining material may be treated for recovery of the adipic acid which is withdrawn through line 34, and by-products such as small amounts of other dibasic acids, withdrawn through line 35.

It must be emphasized that the process as shown in the drawing is merely illustrative of the invention, and the invention is not limited thereto, since other cycloalkanes, oxidizers, etc., may be used, as described below. A more complete description of the conditions of operation of each stage of the process will first be presented however.

The oxidation of the ammonia in zone 5 is known, being described for example, in an article by Guy B. Taylor, entitled "Oxidation of ammonia," found in the Journal of Industrial and Engineering Chemistry, vol. 19 (1927), page 1250. It is there shown that various catalytic agents may be employed and that the reaction is substantially complete. Temperatures above 700° C. are used. An excess of oxygen is desirable, the relative amounts of air and ammonia being generally about 90% air to 10% ammonia. This is about 50% more oxygen than required by Equation 7.

In the process described in the Taylor article and the other prior art, the mixture of nitric oxide and water resulting from the above ammonia oxidation is converted to nitric acid rather than to nitrogen tetroxide, i. e., the reaction of Equation 5 rather than that of Equation 3 is carried out. Both reactions occur very readily at atmospheric temperatures or slightly elevated temperatures, but for the production of nitric acid, water is essential, whereas for production

of nitrogen tetroxide it is most desirable that the presence of any appreciable quantity of water be avoided. Accordingly, the water is removed. The dehydration in zone 8 may be merely a cooling or combination of cooling and compressing sufficient to reduce the water content of the gas to a concentration lower than that of the nitric oxide and preferably less than 10% of the concentration of the nitric oxide. Driers such as calcium chloride, silica gel or the like may also be employed if desired.

The oxidation of the nitric oxide in zone 11 may be carried out at atmospheric pressure but is preferably carried out under moderate pressures such as about 50 to 500 pounds per sq. in. Temperatures between about 0° C. and about 100° C. may be used, preferably about 25° to 50° C. An excess of air up to 2 or 3 times theoretical should be used. Contact times need not be over about ten minutes and may be as short as one-half second or less.

As an example of the conversion of ammonia to nitrogen tetroxide by the 2-stage process described above air and ammonia in the proportions of about 90% air to 10% ammonia are preheated to a temperature of about 700° C. and the mixture is passed at substantially atmospheric pressure through a platinum gauze heated to red heat. The resulting mixture contains about 9% of nitric oxide together with about 7% of excess oxygen, 13% water, and less than 1% unconverted ammonia, the remainder being oxygen. This mixture is cooled and compressed to a temperature in the neighborhood of 100° F. and a pressure of about 100 pounds per sq. inch gage, under which conditions the bulk of the water settles out as an aqueous nitric-acid containing condensate, which is withdrawn. The resulting partially dehydrated gas is substantially completely dehydrated by passing it through a silica gel drier bed. The nitric oxide in the dehydrated mixture is then converted to nitrogen tetroxide by adding air to the mixture in such a proportion that there is about a 50% excess of oxygen over that required by Equation 3. At 100° F. and 100 pounds per sq. in. gage the conversion of the nitric oxide to nitrogen tetroxide is complete in about 10 to 15 seconds, giving as a product a gas containing about 6% of nitrogen tetroxide (including dioxide), about 4% of oxygen, and less than 1% of nitric oxide, ammonia, and water, the remainder being nitrogen.

The separation of the nitrogen tetroxide from the above gaseous mixture is preferably carried out by selective absorption in the hydrocarbon feed in zone 14 as indicated in the drawing, since this method of separation automatically accomplishes the also desired effect of dissolving the nitrogen tetroxide in the hydrocarbon feed stock.

The absorption in zone 14 is preferably carried out at temperatures below about 40° C. down to about −10° C., or below, and superatmospheric pressures such as about 50 pounds to 500 pounds per sq. in. gage. A sufficient proportion of hydrocarbon to nitrogen tetroxide-containing gas is employed to remove the bulk of the nitrogen tetroxide from the mixture. A small amount of the other gases may also be tolerated. The equipment employed may be a conventional absorber such as employed for natural gasoline production or the like, i. e., a packed or bubble cap type tower. The gas stream is injected in the lower part of the tower and travels upward countercurrently to a down flowing stream of the hydrocarbon, which is introduced near the top of the tower. The unabsorbed gas is removed from the top of the tower, and may be discarded or further treated for recovery of desired constituents. If there is sufficient nitric oxide in this unabsorbed gas it may be returned to dehydration zone 8 or oxidation zone 11; or if there is sufficient ammonia in this stream, it may be recycled to oxidation zone 5. Conventional methods of separation and concentration of ammonia or nitric oxide may also be employed prior to the recycling as indicated. The solution of nitrogen tetroxide in the hydrocarbon feed is withdrawn from the bottom of the tower in the above operation.

As an example of the above absorption process for separation of the nitrogen tetroxide, the mixture previously described, containing about 6% of nitrogen tetroxide, is cooled to a temperature of about 10° C. without substantially reducing the pressure, and is passed countercurrently to a stream of cyclohexane in a packed tower. The unabsorbed gas withdrawn from the top of the tower contains about 1% of nitrogen tetroxide or less, and the bulk of the nitric oxide, ammonia, oxygen, and nitrogen, while the cyclohexane solution withdrawn from the bottom of the tower contains about 10% by weight of nitrogen tetroxide. Similar absorption processes are carried out with the other hydrocarbon feed stocks of this invention under the same conditions or other conditions within the above ranges, to obtain suitable separations of nitrogen tetroxide and to prepare suitable solutions for carrying out the esterification process of this invention whereby the hydrocarbon feed stocks are reacted to form the nitrites.

The conditions which we have found favorable for the formation of the nitrites from the corresponding cycloalkanes in reaction zone 19 are superatmospheric temperatures below the critical temperature of the feed stock, i. e., temperatures between about 25° C. and 400° C., preferably between about 100° C. and 250° C. superatmospheric pressures up to about 2000 pounds per sq. in. or higher may be used, preferably pressures between about 75 pounds and about 300 pounds per sq. in. gage. The pressure should be sufficiently high to insure a substantially liquid phase reaction. By this term it is meant that the hydrocarbon is substantially completely in the liquid phase, and some nitrogen tetroxide is dissolved therein. All of the nitrogen tetroxide need not be dissolved in the hydrocarbon, although it is desirable that great intimacy of contact between the hydrocarbon and any gaseous nitrogen tetroxide be obtained. It has been found desirable to dissolve the nitrogen tetroxide in an excess of the hydrocarbon at a relatively low temperature, such as about 40° C. or below and introduce this solution at this low temperature continuously into the reactor. By this mode of operation continuous concurrent flow is obtained, and the nitrogen tetroxide is liberated as the solution is warmed to reaction temperature, but is liberated in extremely small bubbles, which provide the desired intimacy of contact. This type of operation is believed to be of value in any situation in which great intimacy of contact is desired between a liquid and a gas, namely dissolving the gas in the liquid at a lower temperature, and allowing the gas to be liberated in the reactor as the solution is warmed to the reaction temperature.

It has also been found desirable to employ a very short contact time, i. e., preferably less than

about 15 minutes, and no longer than is necessary to form the desired nitrite, so as to minimize decomposition and isomerization of the nitrite to the nitro-hydrocarbon. In the continuous process any accumulation of an aqueous phase in the reactor should also be avoided. As observed from Equation 1, nitrous acid may be formed in the reaction, and nitric acid is formed by its decomposition. Water and nitric oxide are also formed, as indicated in Equation 2, the water in relatively small amounts. If allowed to accumulate in the reactor, this water or aqueous phase may accelerate side reactions such as hydrolysis, nitration, and oxidation resulting in the production of nitro compounds and dibasic acids. Therefore the conditions in the reactor should be such as to prevent accumulation of aqueous phase there, e. g., the flow through the reactor should be sufficiently rapid to prevent retention of the aqueous phase. Obviously, the desired control of reaction time and velocity of flow may be obtained by appropriate reactor design as to length and diameter. Downflow may also advantageously be employed. The proportion of nitrogen tetroxide to cycloalkane should be relatively low, such as between about 1% and 25%, and preferably in the region of about 5% to 15% by weight. This permits substantially complete utilization of the nitrogen tetroxide in each pass through the reactor. Conditions of temperature and contact time should also be adjusted to reduce the nitrogen tetroxide only to nitric oxide, rather than to nitrogen or nitrous oxide, since the latter two are rather difficult to reoxidize to nitrogen tetroxide, whereas the reoxidation of the nitric oxide to nitrogen tetroxide occurs spontaneously at atmospheric temperature in contact with air.

The entire reaction product withdrawn from zone 19 may be transferred directly to oxidation zone 29 as described below, or may be first separated in zone 21, merely by stratification, with or without cooling, to obtain a gas phase and a liquid phase. The gaseous fraction obtained from separator 21, which is largely nitric oxide, may be merely recycled to zone 11, where it is contacted with air and reused in the reaction. It may also be purified of the bulk of the contaminating water vapor by recycling it to cooler 7 or dehydration zone 8. It may also be recycled to absorption zone 14 if it contains an appreciable quantity of nitrogen tetroxide, thereby purifying it of water, nitrogen, nitric and nitrous oxides and the like.

The liquid reaction product may be transferred directly to oxidation zone 29 as described below, or may be first separated into an oil phase and an aqueous phase. The aqueous phase may be discarded or treated by known methods to recover nitrogen oxides or nitric acid therefrom. The oil phase may be transferred directly to oxidation zone 29, or may be first treated to obtain an unreacted hydrocarbon fraction which is recycled entirely or in part to the absorption or reaction step. The remaining material, after part or all of the unreacted hydrocarbon has been removed, may be transferred directly to oxidation zone 29, or may first be treated to separate the desired nitrite and other products of side reaction such as the nitro-hydrocarbons. Fractional distillation is a convenient method of accomplishing both separations since the boiling points of the hydrocarbon, the nitrite, and the nitro compound are very different. Solvent extraction, azeotropic distillation, or other methods of separation may also be used. Prior to distillation it is desirable to remove residual traces of nitrogen oxides and water from the oil phase. This may be done by passing air over the vigorously stirred oil phase to remove the gases, and by dehydrating with anhydrous sodium sulfate. Other conventional methods of purification may also be employed.

As a specific example of the esterification process of this invention a solution containing 9.1% by weight of nitrogen tetroxide in cyclohexane is prepared as above by two-stage oxidation of ammonia to nitrogen tetroxide, followed by absorption of the latter in cyclohexane. This solution is fed at an average rate of 100 ml. per minute through a spray nozzle at the bottom of a 6 ft. vertical reactor of $1\frac{1}{16}$ inch I. D. stainless tubing, packed with 4 mm. glass Raschig rings. The reactor is equipped with heating elements, so that the feed, though introduced at a temperature of about 20° C. is heated to a temperature of about 100° C. within approximately the lower one foot of reactor, and is further heated in the remainder of the reactor to a maximum temperature of about 152° C., the average temperature through the upper ⅝ of the reactor, which is referred to herein as the reaction temperature, being about 135° C. The pressure on the reactor is approximately 100 pounds per sq. in. gage, so that the cyclohexane is maintained substantially in the liquid phase. Under these conditions the average contact time at the reaction temperature of 135° C. is about 3 minutes, and the nitrogen tetroxide is substantially completely consumed forming a gas which is largely nitric oxide. A very small amount of aqueous phase, largely nitric acid, is formed in the reactor, and is carried through the reactor with the oil phase.

The reaction products are withdrawn from the top of the reactor, and cooled to about room temperature. The oil phase is separated from the gas and aqueous phases, and subjected to distillation to recover unreacted cyclohexane and cyclohexyl nitrite therefrom. The remainder is further distilled to recover cyclohexanol and nitrocyclohexane as successive overhead distillate fractions, leaving a residual bottoms fraction believed to contain polymers and poly-substituted cyclohexanes such as nitrocyclohexanols, dinitrocyclohexanes, nitroso-nitrocyclohexanes, nitritonitrocyclohexanes, and the like.

Under the above conditions, about 8% of the cyclohexane reacts, this being nearly the theoretical amount according to Equation 1, and the remainder of the cyclohexane is suitable for recycling. Of the cyclohexane-free reaction products, about 27% is cyclohexyl nitrite. The remainder consists of about 6% cyclohexanol, 49% nitrocyclohexane and 18% bottoms. Little or no adipic acid is formed in the reaction. The cyclohexane, cyclohexyl nitrite, cyclohexanol, and nitrocyclohexane may be identified by their boiling points, which are approximately 81° C. at 760 mm., 41° C. at 20 mm., 71° C. at 20 mm., and 80° C. at 10 mm., respectively; and by their refractive indices at 20° C. which are about 1.4261, 1.4349, 1.4658 and 1.4612 respectively. The cyclohexyl nitrite may be further identified by a characteristic nitrite reaction with a solution of phenol and copper sulfate in acetic acid. This test is described in the Industrial and Engineering Chemistry, Analytical edition, vol. 13 (1941), page 555.

Under other conditions within the ranges of

temperature, contact time, etc., defined above, cyclohexane is also esterified to obtain substantial yields of the nitrite, as well as other reaction products described above. Similarly, under these conditions other cycloalkane hydrocarbons are esterified, such as cyclopentane, methylcyclopentane, dimethylcyclopentane, ethylcyclopentane, methylcyclohexane, and the like, and the corresponding cycloalkyl nitrites are obtained. Upon oxidation of these nitrites in zone 29 however, as indicated in the drawing, it is clear that adipic acid will not be the only dibasic acid obtained. In the case of cyclopentyl nitrite substantially pure glutaric acid is produced, and in the case of the nitrites of the alkylated cycloalkanes, mixtures of adipic, glutaric, succinic and other acids are formed.

The above cycloalkanes need not be pure, since the esterification will also take place with mixtures of different cycloalkanes, and with mixtures of cycloalkanes with other hydrocarbons such as minor proportions of paraffins or aromatic hydrocarbons of similar boiling point. A mixture containing about 80% of cyclohexane and about 20% of isoparaffins of similar boiling point, for example, may be readily obtained by fractionation of petroleum, and is an excellent stock.

Although the above description has been confined largely to the cycloalkanes, which are the preferred stocks of this invention, it has been found that other saturated hydrocarbons, such as the normal paraffins, pentane, hexane and the like or isoparaffins such as isopentane, isooctane and the like will also form nitrites under the above conditions, and such processes are also within the scope of this invention. As pointed out above pure hydrocarbon feed stocks need not be used, although they are preferred; and pure nitrogen tetroxide also is not necessary although it is preferred. Minor proportions of relatively inert gases such as nitric oxide, nitrogen, or nitrous oxide and ammonia may also be present.

As a specific example of the esterification of acyclic alkanes, 20 g. of nitrogen tetroxide is dissolved in 180 g. of isooctane and the solution is charged to a bomb, pressured with nitrogen to 100 lb. gage, and heated at about 70° C. for about 26 hours. The nitrogen tetroxide is substantially entirely reduced to nitric oxide, and on topping off the unreacted isooctane and vacuum distilling the residue, a distillate fraction of about 2 ml., having a boiling point of about 59.6° C. at 4.4 mm. and a refractive index at 20° C. of about 1.4281, and giving a very positive characteristic test for nitrite, is obtained.

Normal paraffins may also be esterified as above, and valuable products may be prepared. For example, by esterification of C_{14} to C_{18} normal paraffins, the corresponding nitrites are obtained, and these are readily hydrolyzed to form the corresponding alcohols, which in turn are sulfated with sulfuric acid to obtain excellent detergents.

Returning now to the cycloalkyl nitrites prepared as above, these are very susceptible to oxidation to dibasic acids. For example, liquid cyclohexyl nitrite retained in a glass container on the laboratory shelf exposed to diffused light apparently undergoes auto-oxidation and reduction, and over a period of about a week, a substantial formation of crystals occur, which crystals are found to be adipic acid. In general, the cycloalkyl nitrites are readily oxidized to dibasic acids at superatmospheric temperatures, using any conventional oxidizing agent. For this oxidation nitric acid and nitrogen tetroxide are preferred, but other oxidizing agents such as air, oxygen, hydrogen peroxide, organic peroxides, ozone, inorganic persalts such as sodium perchlorate, potassium permanganate, sodium dichromite and the like may also be used. An excess of oxidizing agent should generally be employed. Reaction temperatures should be between about 25° C. and and 250° C.; pressures may be between about 0 pounds and 1000 pounds per sq. in. gage; and contact times just long enough to obtain the desired conversion may be used. The reaction is preferably carried out in the liquid phase. Means should be provided for maintaining good contact between the cycloalkyl nitrite and the oxidizing agent.

When nitric acid is employed as the oxidizing agent, temperatures above about 50° C. are preferred since these higher temperatures favor the oxidation reaction over the competing nitration reaction. Excessively long reaction times should be avoided, since these tend to degrade the purity of the dibasic acid product. Nitric acid of the strength greater than about 60% by weight is preferred, although lower concentrations may be employed at the higher temperatures within the above range and at higher contact times. Atmospheric pressure is suitable although superatmospheric pressures may also be employed. It is desirable to expel the nitrogen oxides from the reaction mixture as rapidly as possible, and for this purpose an inert gas such as nitrogen may be used as a stripping gas if desired. Because of the high reactivity of the cycloalkyl nitrites, the presence of an inert diluent in the reaction mixture is desirable.

As a specific example of the above oxidation, using nitric acid, to 50 ml. of boiling nitric acid (70%) at atmospheric pressure over a reflux condenser is added during 15 minutes, 50 ml. of a 10% solution by volume of cyclohexyl nitrite in cyclohexane. Oxides of nitrogen are rapidly evolved. The mixture is refluxed for five minutes after the addition of all the cyclohexyl nitrite-cyclohexane solution, and is then cooled, causing the separation of crystals of adipic acid from the aqueous phase. The cyclohexane phase is separated from the aqueous phase, and the latter is evaporated to dryness to give a solid white product consisting of adipic acid of over 98% purity. This is a surprising degree of purity, since adipic acid produced by the oxidation of cyclohexanol, cyclohexanone, or cyclohexane with nitric acid, by the methods of the prior art, does not exceed about 60 to 70% purity. The cyclohexane phase in the above specific example is found to be entirely free of cyclohexyl nitrite.

The above example shows that the cyclohexyl nitrite is oxidized selectively to substantially pure adipic acid, without appreciable reaction of the cyclohexane. Other cycloalkyl nitrites are similarly selectively oxidized in the presence of cycloalkanes, and are also selectively oxidized in the presence of nitrocycloalkanes. This permits a very efficient combination of the esterification reaction with the oxidation reaction, since the entire reaction product from the esterification may be reacted with an oxidizing agent and the nitrite thereby selectively oxidized to the dibasic acid. As an example of this type of oxidation, the above oxidation with boiling 70% nitric acid is carried out in the same manner, employing in place of the above cyclohexane-cyclohexyl ni-

trite solution, the separated oil phase from the esterification reaction as described above, containing about 92% unreacted cyclohexane and about 8% of reaction products comprising about 27% cyclohexyl nitrite, together with nitrocyclohexane, and other reaction products. It is found that under these conditions, the cyclohexane and nitrocyclohexane are substantially unaffected, and substantially all of the cyclohexyl nitrite, as well as a portion of the other esterification reaction products, are converted to adipic acid. Similar results are obtained by employing the entire esterification reaction product, without separation of gas or aqueous phases; or by employing an oil phase which has been freed from part or all of its unreacted cyclohexane content.

Thus a high quality adipic acid may be produced by subjecting the product of the esterification reaction as described above directly to the oxidation reaction as described above; or between the esterification and the oxidation there may be a separation of the gas phase or of the liquid phase or of a portion of the unreacted hydrocarbon feed stock, or of any or all of these. Also if desired other products such as nitrocycloalkanes or cycloalkyl alcohols or the like may be separated before the oxidation.

Nitrogen tetroxide is also an excellent oxidizing agent for the conversion of the cycloalkyl nitrites to disbasic acids as above. For example, a solution of about 10% of nitrogen tetroxide and 10% of cyclohexyl nitrite in cyclohexane is decolorized at room temperature in a matter of a few hours, i. e., all of the nitrogen tetroxide is reduced to nitric oxide, with the production of adipic acid, which settles as a crystalline solid from the solution. Nitrogen tetroxide may also be employed under other conditions within the above limits, to oxidize cyclohexyl nitrite or other cycloalkyl nitrites to dibasic acids. The use of nitrogen tetroxide furthermore, permits the simultaneous esterification of cyclohexane and oxidation of the nitrite ester to adipic acid. The latter reaction proceeds at a much faster rate, so that when a solution of about 10% of nitrogen tetroxide in an excess of cyclohexane is allowed to react at room temperature in a clear glass container in the laboratory, crystals of adipic acid appear within about two days, and within about two weeks, the solution is completely decolorized. Substantially no cyclohexyl nitrite or nitrocyclohexane is observed in the product, which is substantially pure adipic acid and unreacted cyclohexane, the nitrogen tetroxide being reduced to nitric oxide. This is explainable on the basis that the cyclohexyl nitrite is the primary reaction product, and this is oxidized to adipic acid at a faster rate than its rate of formation, so that the concentration of the nitrite at any given time is almost negligible. If greater yields of the nitrite are desired, without further oxidation to adipic acid, a continuous system should be employed wherein an excess of liquid cyclohexane containing dissolved nitrogen tetroxide is passed continuously and concurrently through a tube at the desired temperature. Temperatures between about 50° C. and 200° C. are preferred. If it is desired to oxidize the nitrite to dibasic acid directly as produced, either a batch system should be employed as described above, or a concurrent system should be used, wherein the cyclohexane is allowed to flow countercurrently to a stream of nitrogen tetroxide.

In the oxidation of the nitrite with either nitric acid or nitrogen tetroxide, nitric oxide is produced as a by-product. Since this is readily reoxidized to nitrogen tetroxide by air or oxygen, it is advantageous to introduce oxygen or air into the reaction mixture, either together with the feed in a batch or concurrent system, or at an intermediate stage of the reaction in a countercurrent system, or at a subsequent stage of the reaction in a concurrent system. It has also been discovered that nitric oxide has a catalytic effect on the oxidation, so it is advantageous to introduce nitric oxide with the reactants. This is true not only for the oxidation reaction but also for esterification reaction. Furthermore, other products of the esterification reaction, such as the nitrite, and the other products mentioned above, also exert a catalytic effect on the esterification reaction. Thus the recycling of the unreacted hydrocarbon, and also recycling of a portion of the reaction products, is desirable. Large areas of surface contact also appear to be advantageous in both the esterification and oxidation reactions.

By employing peroxides as oxidizing agents, the cycloalkyl nitrites may not only be converted to dibasic acids, but may also be converted to nitrates. As far as applicants are aware, cycloalkyl nitrates have not previously been prepared. It is also within the scope of this invention to prepare cycloalkyl nitrates by the reaction of the cycloalkyl nitrites of this invention with peroxides, whether hydrogen peroxide or organic hydroperoxides such as tertiary butyl hydroperoxide, dimethyl cyclopentyl hydroperoxide, methyl cyclohexyl hydroperoxide and the like, or other organic peroxides such as benzoyl peroxide and the like. In this reaction the hydrogen peroxide is reduced to water; the organic hydroperoxides are reduced to the corresponding alcohols; and the benzoyl peroxide is reduced to benzoic acid anhydride.

In this reaction an excess of the nitrite should be employed. Atmospheric temperature and higher temperatures up to about 100° C. are satisfactory. The reactants are preferably employed in solution in a common solvent so as to obtain a homogeneous reaction. Organic solvents are preferred over aqueous solvents. Thus the nitrites and the organic peroxides and hydroperoxides may be dissolved in hydrocarbons such as the hydrocarbon feed stocks of this invention or other petroleum fractions or the like. Hydrogen peroxide is preferably employed in alcohol or ether solution although it may be used in water solution. In the event that a water solution is employed, the reaction mixture will not be homogeneous, and means should be provided to assure sufficient intimacy of contact between the peroxide and the nitrite. If desired, the hydrogen peroxide may also be obtained by the action of water or mineral acids on inorganic hydroperoxides such as barium peroxide, sodium peroxide and the like. Other oxidizing agents of the types described above may also be employed to oxidize the nitrites to the nitrates.

As an example of the preparation of cycloalkyl nitrates, a solution containing about 25% by weight of dimethylcyclopentyl hydroperoxide in cyclohexane is added gradually to a solution containing about 25% of cyclohexyl nitrite in cyclohexane, the molal proportion of hydroperoxide to nitrite being about 1 to 2. Upon gentle warming, the reaction goes substantially to completion, and cyclohexane, dimethylcyclopentyl alcohol and

unreacted nitrite are separated from the solution by distillation, leaving a residue which is substantially pure cyclohexyl nitrate. This material is an excellent additive for Diesel fuels, to improve their ignition characteristics. For this purpose they are employed in the Diesel fuel in concentrations between about 0.1% and about 5% by weight. If desired, the preparation may be carried out by employing the Diesel fuel itself as the diluent. Thus Diesel fuel may be substituted for cyclohexane in the above preparation, and the resulting product diluted with additional Diesel fuel to the desired concentration. In another mode of operation, about 1% of cyclohexyl nitrite may be dissolved in the Diesel fuel, and an equimolal amount of the hydroperoxide dissolved in Diesel fuel may be added thereto. On slightly warming, the above reaction will take place. Although the reaction goes substantially to completion, this is not vital, and an excess of unreacted nitrite or hydroperoxide, or both, may be present in the reaction product, since all of these are effective in improving the ignition characteristics of the Diesel fuel.

The other cycloalkyl nitrites and the other peroxides and other oxidizing agents described above may also be reacted as above to obtain the corresponding cycloalkyl nitrates, which may be utilized as above.

Many modifications of the processes of this invention may be employed. For example, the nitrogen tetroxide need not be prepared by the oxidation of ammonia as described above, but may also be prepared by direct oxidation of nitrogen of the atmosphere by the Birkeland-Eyde process, or a modification thereof recently disclosed in the literature, whereby a fuel such as methane is burned in an excess of air at a temperature in the neighborhood of 4,000° F. or above to form nitric oxide, which is oxidized to the tetroxide as described above. In this mode of preparation, the concentration of the nitric oxide or nitrogen tetroxide is quite low, and consequently it may be desirable to employ other modes of purification in addition to or in place of those described above, such as for example, low temperature fractional distillation, charcoal adsorption, silica gel adsorption, and the like.

It is also apparent that in the course of the above esterification and oxidation reactions nitric oxide may be liberated, and this is readily oxidized to form the desired nitrogen tetroxide. Furthermore, nitric acid itself may be decomposed to form nitrogen tetroxide, which may be extracted or separated from the product by the methods above. Nitric oxide formed by the decomposition of nitric acid may also be oxidized to supply the necessary nitrogen tetroxide.

As mentioned previously, catalysts may be desirable in the esterification reaction as well as the oxidation reaction. It is also desirable to employ a dehydrating agent in the esterification reaction zone itself, so that the water liberated in the reaction is not allowed to hydrolyze the nitrite esters. Silica gel and diatomaceous earth are suitable dehydrating agents, which also act as catalysts. These are introduced in suspension in the feed, or are placed in the reactor as a bed. Light, especially ultraviolet light, is a catalyst for the above esterification also, and appears to inhibit the production of nitro hydrocarbons as well as catalyze the production of the nitrite and the oxidation products thereof. Also, as previously pointed out, recycling of the esterification reaction products is desirable because of catalytic effects of nitric oxide and other reaction products. Recycling of nitro hydrocarbons has the additional desirable effect of inhibiting the formation of these nitro hydrocarbons.

The nitrite esters of this invention are extremely useful products. As described above they may be oxidized to dibasic acids or to organic nitrates. They are also readily hydrolyzed by water or aqueous solutions of mineral acids to obtain the corresponding alcohols. They also react with mercaptans to form thionitrites. For example, ethyl mercaptan reacts with cyclohexyl nitrite to form cyclohexyl alcohol and ethyl thionitrite. The thionitrites are also excellent additives for improving the ignition quality Diesel fuels. This reaction also takes place at atmospheric or slightly elevated temperatures, and is preferably carried out in oil solutions as with the preparation of the nitrates above described.

As indicated above the nitrite esters of this invention are of great value because of their great reactivity to form other chemicals. However, they are also valuable in themselves as ignition promoters for Diesel fuels or jet propulsion fuels, as effective components of insecticides or fungicides, and for other uses.

Although the term "nitrogen tetroxide" is used exclusively herein it is to be understood that this term includes other forms which may be in equilibrium with the tetroxide such as nitrogen dioxide. As shown by Riebsomer in "The reactions of nitrogen tetroxide with organic compounds," in Chemical Reviews, vol. 36, No. 2, April 1945, page 159, the structure of nitrogen tetroxide is not definitely known and undoubtedly changes with changes in temperature or other conditions. We have found however that nitrogen tetroxide is very different in its reactions with hydrocarbons than is nitric acid. In the presence of appreciable amounts of water or nitric acid the organic nitrites are apparently not formed, or possibly are immediately destroyed with the production of oxidation or isomerization products.

Other modifications of this invention which would be apparent to one skilled in the art are to be included within the scope of the invention as defined in the following claims.

We claim:

1. A process for the production of cycloalkyl nitrites which comprises dissolving a minor proportion of nitrogen tetroxide in a cycloalkane, heating the resulting solution in the liquid phase so as to form the corresponding cycloalkyl nitrite and separating from the liquid product a fraction rich in said nitrite.

2. A process for the production of a cycloalkyl nitrite which comprises dissolving a minor proportion of nitrogen tetroxide in a cycloalkane, maintaining the resulting solution at an elevated temperature so as to form a liquid product containing the corresponding cycloalkyl nitrite and a gaseous product containing nitric oxide, separating said nitrite and unreacted cycloalkane from said liquid product, recycling said unreacted cycloalkane, oxidizing said gaseous product containing nitric oxide to obtain additional nitrogen tetroxide, and recycling said nitrogen tetroxide.

3. A process for the production of cycloalkyl nitrites which comprises oxidizing ammonia so as to obtain an ammonia oxidation product containing water and nitric oxide, dehydrating the said ammonia oxidation product to remove said water therefrom, oxidizing the dehydrated ammonia oxidation product to obtain a gaseous mixture containing nitrogen tetroxide, contacting

said gaseous mixture with a liquid cycloalkane thereby absorbing said nitrogen tetroxide in said cycloalkane to form a solution containing a minor proportion of nitrogen tetroxide, maintaining the resulting solution at an elevated temperature so as to form a liquid product containing the corresponding cycloalkyl nitrite and a gaseous product containing nitric oxide, separating said nitrite and unreacted cycloalkane from said liquid product, recycling said unreacted cycloalkane, and recycling said gaseous product containing nitric oxide to the stage in which the dehydrated ammonia oxidation product is oxidized to form nitrogen tetroxide.

4. A process for the production of cycloalkyl nitrites which comprises dissolving a minor proportion of nitrogen tetroxide in a cycloalkane, introducing the resulting solution having a temperature lower than about 40° C. into the reaction zone, heating the solution in said reaction zone, to a reaction temperature greater than about 100° C., maintaining the solution in the liquid phase for a sufficient contact time to form the cycloalkyl nitrite, removing the reaction mixture from the reaction zone, and recovering said cycloalkyl nitrite therefrom.

5. A process for the production of cycloalkyl nitrites which comprises dissolving a minor proportion of nitrogen tetroxide in a cycloalkane, introducing said solution having a temperature below about 40° C. into a reaction zone, maintaining said solution as it passes through said reaction zone substantially in the liquid phase while heating it to a reaction temperature above about 100° C., maintaining it at said temperature while reacting said nitrogen tetroxide with part of said cycloalkane so as to form a liquid product containing unreacted cycloalkane and cycloalkyl nitrite, separating said unreacted cycloalkane from said product and recycling it, and recovering said cycloalkyl nitrite from the remainder of said product.

6. A process for the production of cycloalkyl nitrites which comprises dissolving a minor proportion of nitrogen tetroxide in a cycloalkane, introducing said solution having a temperature below about 40° C. into a reaction zone, maintaining said solution as it passes through said reaction zone substantially in the liquid phase while heating it to a reaction temperature above about 100° C. and maintaining it at said temperature while reacting said nitrogen tetroxide with part of said cycloalkane so as to form a liquid product containing unreacted cycloalkane and cycloalkyl nitrite and a gaseous product comprising nitric oxide, separating said gaseous product from said liquid product, oxidizing the nitric oxide therein to nitrogen tetroxide and recycling said nitrogen tetroxide, separating said unreacted cycloalkane from said liquid product and recycling it, and recovering said cycloalkyl nitrite from the remainder of said product.

7. A process for the production of cycloalkyl nitrites which comprises oxidizing ammonia so as to obtain an ammonia oxidation product containing water and nitric oxide, dehydrating the said ammonia oxidation product to remove said water therefrom, oxidizing the dehydrated ammonia oxidation product to obtain a gaseous mixture containing nitrogen tetroxide, contacting said gaseous mixture with a liquid cycloalkane thereby absorbing said nitrogen tetroxide in said cycloalkane to form a solution containing a minor proportion of nitrogen tetroxide, introducing said solution having a temperature below about 40° C. into a reaction zone, maintaining said solution as it passes through said reaction zone substantially in the liquid phase while heating it to a reaction temperature above about 100° C. and maintaining it at said temperature while reacting said nitrogen tetroxide with part of said cycloalkane so as to form a liquid product containing unreacted cycloalkane and cycloalkyl nitrite and a gaseous product comprising nitric oxide, separating said gaseous product from said liquid product, recycling said gaseous product to the stage in which the dehydrated ammonia oxidation product is oxidized to form nitrogen tetroxide, separating said unreacted cycloalkane from said liquid product and recycling it, and recovering said cycloalkyl nitrite from the remainder of said product.

8. A process according to claim 7 in which an aqueous phase is formed in the reaction zone, and is not permitted to separate from the liquid reaction product until the latter is removed from the reaction zone.

9. A continuous process for the production of cyclohexyl nitrite which comprises oxidizing ammonia with air so as to obtain an ammonia oxidation product containing water and nitric oxide, dehydrating the said ammonia oxidation product to remove said water therefrom, oxidizing the dehydrated ammonia oxidation product to form a gaseous mixture containing nitrogen tetroxide, absorbing said nitrogen oxide in cyclohexane to form a solution containing about 5% to 15% of nitrogen tetroxide, introducing said solution at a temperature below about 40° C. into a reaction zone, maintaining said solution as it passes through said reaction zone substantially in the liquid phase while heating it to a reaction temperature between about 100° C. and 250° C. and maintaining it at said reaction temperature for a contact time sufficient to react said nitrogen tetroxide with a part of said cyclohexane so as to form a gaseous product comprising nitric oxide and a liquid product containing cyclohexyl nitrite and unreacted cyclohexane, recycling said gaseous product to the stage in which the dehydrated ammonia oxidation product is oxidized to form nitrogen tetroxide, separating said unreacted cyclohexane from said liquid product, recycling said unreacted cyclohexane to the absorption step, and recovering said cyclohexyl nitrite from the remainder of said liquid product.

10. A process for the production of nitrous acid esters of cycloalkanes which comprises dissolving a minor proportion of dry nitrogen tetroxide in said liquid cycloalkane and continuously passing the resulting solution through an elongated reaction zone at an elevated temperature between about 100° C. and 250° C. and a pressure sufficient to maintain the hydrocarbon substantially in the liquid phase, at a rate sufficient to consume substantially all of the nitrogen tetroxide prior to leaving the reactor.

11. A process according to claim 1 in which the cycloalkane is cyclohexane.

12. A process according to claim 1 in which the cycloalkane is cyclopentane.

13. A process according to claim 4 in which the cycloalkane is cyclohexane.

14. A process according to claim 4 in which the cycloalkane is cyclopentane.

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