

Description

This process relates to a novel vapor state process for the preparation of diesters of oxalic acid from a nitrogen oxide, an alcohol and carbon monoxide. (The terms "vapor state" and "vapor phase" are used interchangeably to refer to a process carried out in the gaseous phase).

Background of the invention

The preparation of diesters of oxalic acids (oxalates) is of particular interest to the chemical industry owing to the varied uses of these compounds. Not only may these diesters serve to act as the starting materials for such important compounds as oxalic acid, oxamide or ethylene glycol, but they may also find extensive use as intermediates for dyes, pharmaceuticals and the like.

Prior to the instant invention there have been proposed conventional liquid phase processes for the formation of these diesters which employ various catalyst systems, co-catalysts, reaction accelerators and the like. However, these conventional processes have suffered from the serious effects arising from conventional liquid phase processes.

A particularly interesting process for preparing diesters of oxalic acid in the liquid phase is disclosed in U.S. Patent No. 4,138,587. U.S. Patent No. 4,138,587 employs nitric acid or a nitrogen oxide as the accelerator in the presence of a solid platinum group metal or salt thereof, alcohol, molecular oxygen and carbon monoxide. The process is a liquid phase process and suffers from significant practical defects related to liquid phase processes, such as catalyst losses large by-product formation, low efficiencies to product, to name a few.

U.S. Patent No. 4,229,591 discloses, in part, a vapor phase process. The process disclosed therein involves contacting an ester of nitrous acid with carbon monoxide in the gaseous phase under ordinary pressure in the presence of a solid catalyst containing metallic palladium or a salt thereof at a temperature of 50 to 200°C, in which the ester of nitrous acid is an ester of nitrous acid with an alcohol having 1 to 8 carbon atoms such as saturated monohydric aliphatic alcohols and alicyclic alcohols. Although this process provides advantages over the corresponding liquid phase process, the vapor phase process does not provide a completely vapor phase process in which the alkyl nitrite is also prepared in the vapor state in a separate step. An exception described in this patent involves nitrite formation *in situ* in the oxalate reactor concurrent with oxalate formation. Such *in situ* formation adds a potential hazardous procedure and introduces water into the reactor in amounts which affect the production of significant quantities of undesirable by-products.

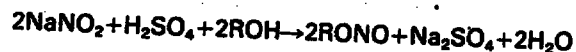
Japanese Application No. 53-8268/78 describes the preparation of nitrite esters by conventional liquid phase processes as part of the continuous production of oxalic acid diester using nitrite ester

as a starting material by the vapor phase oxalate process of U.S. Patent No. 4,229,591. The nitrous acid ester is formed by employing a gas-liquid contacting apparatus to contact a gaseous nitrogen oxide mixture with liquid alcohol at a temperature lower than the boiling point of the alcohol.

There is foreseen herein an advantage of having a multi-step wholly vapor phase process where the presence of undesirable amounts of water in the oxalate reaction can be avoided. For example, effecting the process in two vapor phase reaction zones both greatly improves the conversion of reactants to desired product (the diester of oxalic acid) and minimizes by-product formation. Other advantages are achieved, such as enhancement of catalyst life, due to minimization of deleterious by-products which can attack the catalyst either to dissolve a portion of it or to form stable and unreactive species.

In order to have a "true" vapor state process the entire process must be effected in the vapor state and, further, if the process is to be optimized, the nitrite formation should be in a reaction zone apart from the oxalate forming reaction zone. In the present process, because the ester of nitrous acid is prepared in the vapor state in a nitrous ester forming reaction zone the overall process minimizes by-product formation, enhances catalyst life, provides higher conversions to and yields of the diester of oxalic acid, and the like. By correlating the process steps so as to have an integrated vapor state process, i.e., have the formation of both the ester of nitrous acid and the diester of oxalic acid in the vapor state, in nitrous acid ester forming and oxalate forming reaction zones, respectively, an optimized process is obtained.

The classical method for preparing nitrite esters involves the liquid phase reaction of sodium nitrite and sulfuric acid with a desired alcohol. The reaction is normally carried out at ice temperatures, due to the extremely exothermic nature of the reaction, to form nitrite ester as follows:



The nitrite ester formed is essentially insoluble in water (less than about 1 percent in water or water in the nitrite ester) so that the nitrite ester is separated from the reaction products by liquid separation.

The production of nitrite esters in the liquid phase is disclosed in U.S. Patent No. 2,166,698 wherein nitrite esters are produced by reacting an appreciably water soluble saturated open-chain aliphatic compound containing a plurality of esterifiable carbinol groups with nitrous acid in an aqueous medium and removing a nitrite ester from the reaction system substantially as soon as it is formed therein. The nitrite esters formed therein react rapidly with alcohols, e.g., ethyl alcohol, to form alkyl nitrites, e.g., ethyl nitrite.

In U.S. Patent No. 2,739,166 alkyl nitrites are produced in a liquid phase process by bubbling

nitrogen dioxide gas into a cooled liquid monohydric aliphatic alcohol.

In British Patent Specification No. 586,022 a liquid phase process is disclosed for the preparation of nitric acid esters which comprises reacting an alcohol with dinitrogen tetroxide in the liquid phase.

In German Patentschrift 1,156,775 a liquid phase process is disclosed for preparing esters of nitrous acid by employing alcohol in molar excess over dinitrogen trioxide at temperatures below the boiling point of the alcohol and simultaneously distilling off the ester formed. In addition, the reference acknowledges that the vapor phase decomposition of alcohols with nitrogen dioxide-nitrogen monoxide mixtures at temperatures between 100 and 420°C is known.

The aforementioned processes are to be distinguished from a vapor phase process that may be employed in the process of this invention in that in the liquid phase processes the separation of the nitrite ester product is difficult and oxidation of alcohol in the liquid phase during the manufacture or separation can occur to form unwanted by-products. In addition, the separation of the highly flammable and toxic nitrite ester from the liquid phase can prove to be a major safety and health problem. The resulting ester of nitrous acid can be obtained only after separation and purification.

A vapor phase process for the preparation of ester of nitrous acid is disclosed in U.S. Patent No. 2,831,882. The patent's process comprises reacting a vaporized alcohol with from 0.4 to 0.6 mole of nitrogen dioxide and 0.4 to 2.0 moles of nitric oxide per mole of alcohol in the presence of from 2 to 25 moles of diluent selected from the group consisting of water, nitrogen, and carbon dioxide at a temperature between 100°C and 420°C with a contact time of 1-10 seconds.

Summary of the invention

The process of this invention involves the preparation of diesters of oxalic acid from a nitrogen oxide, a saturated monohydric aliphatic alcohol containing 1 to 8 carbon atoms, and carbon monoxide, comprising forming an ester of nitrous acid from the nitrogen oxide and alcohol, and contacting said ester of nitrous acid with carbon monoxide in the vapor state at a temperature of between 50°C and 200°C over a supported palladium containing catalyst in which the palladium is metallic palladium or a salt thereof to produce the diester of oxalic acid and recovering the diester of oxalic acid, characterized in that the contacting of the nitrogen oxide and the alcohol to form an ester of nitrous acid is in the vapor state in a nitrite-forming reaction zone (24, 74); the ester of nitrous acid is maintained in the vapor state and contacted with carbon monoxide in an oxalate-forming reaction zone (42, 92) and deleterious amounts of water formed in the nitrite-forming reaction zone (24, 74) are removed prior to introduction to the oxalate-forming reaction zone (42, 92).

Preferably, the process is operated continuously and as a cyclic process wherein there exists at least one cycle (recycle) gas stream.

Detailed description

The present process relates to a wholly vapor state process for the preparation of diesters of oxalic acid. The process is carried out in the vapor state in two correlated steps: the first step comprises the vapor state formation in a nitrous ester forming reaction zone of an ester of nitrous acid; and the second step comprises the reaction of an ester of nitrous acid and carbon monoxide in the vapor state in an oxalate forming reaction zone over a supported palladium catalyst. In addition, the process provides for the removal of deleterious amounts of water formed in the first step prior to introducing the ester of nitrous acid to the aforementioned second step.

The esters of nitrous acid may be formed by most any vapor state synthetic scheme from a nitrogen oxide gas and vaporous alcohol which provides an ester of nitrous acid in the vapor state in the reaction system. Exemplary of such nitrogen oxides are nitrogen monoxide (nitric oxide), nitrogen dioxide, dinitrogen trioxide, dinitrogen tetroxide, and hydrates of the aforementioned. In the case where nitrogen monoxide (nitric oxide) is employed it is necessary to employ molecular oxygen therewith. Nitric oxide is the preferred nitrogen oxide.

The preferred esters of nitrous acid are those esters formed from a saturated monohydric aliphatic alcohol having 1 to 8 carbon atoms, such as a saturated monohydric open-chain aliphatic alcohol or an alicyclic alcohol having 1 to 8 carbon atoms. The most preferred esters of nitrous acid are those prepared from methanol and ethanol. As the alcohol component may be mentioned an aliphatic alcohol such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, n-amyl alcohol, isoamyl alcohol, hexanol, octanol, and an alicyclic alcohol such as cyclohexanol, methylcyclohexanol. These alcohols may contain therein a substituent such as an alkoxy group which does not inhibit the reaction.

The process by which the ester of nitrous acid is prepared is not narrowly critical so long as the ester of nitrous acid is prepared in the vapor state from gaseous nitrogen oxide and alcohol vapors, and the presence of components deleterious to the oxalate reaction is minimized. Such a component is nitric acid which may adversely affect the supported palladium catalyst employed in the formation of the diester of oxalic acid.

A particularly advantageous process, and preferred in the present invention when the methyl or ethyl esters of nitrous acid are employed, is disclosed in copending application U.S. Serial No. 227,798 to Arthur R. Doumaux et. al., filed January 23, 1981 and copending application U.S. Serial No. 239,761 filed March 12, 1981, filed concurrently herewith both commonly assigned and both are incorporated herein by reference for

their teachings of making methyl and/or ethyl nitrites.

In these applications a novel process is disclosed for the preparation of esters of nitrous acid wherein the process relates particularly to the manufacture of methyl or ethyl nitrite. The process disclosed therein may, in part, be understood more fully by reference to the following equations:

- (1) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
- (2) $\text{NO}_2 + \text{NO} \rightleftharpoons \text{N}_2\text{O}_3$
- (3) $2\text{ROH} + \text{N}_2\text{O}_3 \rightarrow 2\text{RONO} + \text{H}_2\text{O}$
- (4) $\text{ROH} + \text{N}_2\text{O}_3 \rightarrow \text{RONO} + \text{HONO}$
- (5) $\text{ROH} + \text{HONO} \rightarrow \text{RONO} + \text{H}_2\text{O}$
- (6) $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$
- (7) $\text{ROH} + \text{N}_2\text{O}_4 \rightarrow \text{RONO} + \text{HNO}_3$

wherein R is methyl or ethyl.

A goal of the vapor state process disclosed therein is to maximize the production of methyl or ethyl nitrite in the vapor state while minimizing or preferably, essentially eliminating the formation of nitric acid and other unwanted by-products. Thus, it is believed that the product formed in the reaction characterized by equation (2) is employed in equations (3) and (4). Reaction (4) supplies the nitrous acid for reaction (5). That reaction sequence, i.e. (1) through (5), is preferred while the reactions characterized by equations (6) and (7) are to be avoided because of the formation of nitric acid.

In addition, this process discloses, surprisingly, that by providing NO, NO₂ and ROH in specific molar ratios that the alkyl nitrite will be formed in high yield with minimal to no formation of nitric acid. To achieve these results the molar ratio of nitric oxide to nitrogen dioxide is provided such that it is greater than one and the molar ratio of alcohol to the combined molar amount of nitric oxide and nitrogen dioxide is greater than one. By thus correlating these two molar ratios the novel process disclosed therein is achieved.

In carrying out the process of U.S. Serial Nos. 227,798 and 239,761, the source of the reactants is not critical. (This is equally true for other vapor state processes as well). Nitric oxide may be provided by the decomposition of nitric acid and/or nitrogen dioxide, or may be introduced from an ammonia oxidation unit. The process is generally carried out by introducing nitric oxide and oxygen to form the required amounts of nitrogen dioxide (see equation (1) above). The molar ratio of nitric oxide to nitrogen dioxide is maintained above one in this case by providing nitric oxide and oxygen at a molar ratio of greater than 4 to 1 such that the molar ratio of nitric oxide to the nitrogen dioxide that is formed is greater than 1 (see equation (2) above). In other words, the amount of oxygen converts less than fifty percent (50%) of the nitric oxide to nitrogen dioxide. Also a gaseous medium having the desired ratio of nitric oxide to nitrogen dioxide may be obtained by use of higher oxides of nitrogen (N₂O₃, N₂O₄, N₂O₅, etc.) and to the extent that such higher oxide may be employed to provide a gaseous medium, with or without the

additions of molecular oxygen, having a molar ratio of NO to NO₂ greater than 1, said higher oxides may be employed herein. In addition, compounds, such as nitrous acid, which can be decomposed or reacted to provide a gaseous medium having a molar ratio of NO to NO₂ greater than one may be employed.

As noted above, the process of U.S. Serial No. 227,798 and 239,761 is preferably carried out by forming the desired molar ratio of NO to NO₂ by reacting NO and molecular oxygen at a molar ratio of 4 to 1 or greater. Though the process may be carried out by mixing nitric oxide, molecular oxygen and alcohol (methanol or ethanol) together at the desired molar ratios, such mixing is undesirable because oxygen will oxidize the alcohol to a variety of undesirable reaction by-products with the consequential loss of valuable starting material. Moreover, many of such byproducts, if carried into the oxalate reaction zone would adversely affect the catalyst and contaminate the oxalate ester formed. Therefore, the process is preferably staged such that nitric oxide and molecular oxygen are mixed first and are provided sufficient time for the reaction to consume the oxygen prior to mixing the resulting nitrogen oxide mixture (a mixture having a molar ratio of NO to NO₂ greater than 1) with the alcohol. Further this staged addition may reduce the safety problems associated with mixtures of oxygen and alcohols.

As stated in U.S. Serial Nos. 227,798 and 239,761 the molar ratio of nitric oxide to nitrogen dioxide is greater than 1. Typically the molar ratio (NO to NO₂) is from greater than 1 to about 10, most preferably from greater than 1 to about 1.5. The molar ratio of alcohol (methanol or ethanol) to the combined molar amount of nitric oxide and nitrogen dioxide is greater than one. The term "combined molar amount" means the numerical sum of the molar amounts of NO and NO₂ that react according to equation (2) above. Typically, the molar ratio of ROH to (NO+NO₂) is from greater than 1 to 10, preferably from greater than 1 to 2 and most preferably from greater than 1 to 1.5. The aforementioned molar ratios are thus correlated to optimize the process.

A vapor state alkyl nitrite process is generally carried out in the presence of an inert gaseous diluent to moderate the reaction to preclude the formation of explosive mixtures and prevent the formation of excessive amounts of undesirable by-products. As the inert gaseous diluent, it is preferred to employ nitrogen, carbon dioxide or other inert gaseous compounds. The use of carbon dioxide provides higher heat capacity relative to nitrogen. The inert gaseous diluent is employed in sufficient amounts to provide the aforementioned objectives. The inert gaseous diluent is generally employed in the process such that between 1 and 99 mole percent, preferably between 30 and 90 mole percent, and most preferably between 30 and 70 mole percent comprises inert gaseous diluent.

Further, the alkyl nitrite process is carried out at a temperature sufficient to maintain the nitrogen oxide, alcohol and alkyl nitrite in the vapor state and is typically between 10°C and 300°C, preferably between 20°C and 130°C, and most preferably between 50°C and less than 110°C. The lowest temperature at which the process is conducted is generally determined by the dew point of the alcohol employed and the concentration of the reactants.

The pressure at which the vapor state alkyl nitrite process is carried out is not narrowly critical. It is preferred to employ atmospheric (0.103 MPa absolute) or superatmospheric conditions between 0.103 MPa absolute and 0.7 MPa absolute and most preferably at between 0.14 MPa absolute and 0.42 MPa absolute. Pressures less than 0.103 MPa absolute may be employed, if desired.

The vapor state alkyl nitrite process is preferably carried out under conditions wherein the concentration of water in the feed to the nitrite forming reaction zone is minimized.

The vapor state alkyl nitrite process may be practiced in almost any commercial reactor (i.e., nitrous ester forming reaction zone) and is generally carried out on a continuous basis by employment of a tubular reactor. The contact time (or residence time) during which the gaseous materials react to form methyl or ethyl nitrite is generally between 0.1 and 30 seconds, preferably between 0.1 and 2 seconds. Shorter or longer times may be employed depending on the temperature, pressure, molar ratios, gaseous diluent and feed rate employed so long as sufficient time for reaction is provided. In addition, the selection of the reactor geometry of the nitrite forming reaction zone will affect the actual residence time employed.

Because the vapor state alkyl nitrite process is carried out in a continuous manner the feed rate is not narrowly critical, and is selected to satisfy the particular design of the continuous system.

After the ester of nitrous acid (e.g., alkyl nitrite) is formed in the vapor state, the ester in the vapor state is contacted with carbon monoxide in the vapor state in an oxalate forming reaction zone over a palladium supported catalyst containing metallic palladium or salts thereof. The vapor state reaction for the formation of the diesters of oxalic acid is carried out by providing an oxalate forming reaction zone which is without deleterious amounts of water. While some amount of water may be tolerated the amount of water formed in the nitrous ester forming reaction zone is deleterious and a sufficient amount of said water is removed prior to introduction to the oxalate forming reaction zone. This may be accomplished by use of a water condenser (in conjunction with a vapor-liquid separator) after alkyl nitrite formation or by the use of any other suitable dehydration process. The amount of water which is deleterious to the vapor state reaction for the formation of diesters of oxalic acid is determined, in part, by the selection of

ester of nitrous acid, temperature, pressure, etc. In general, a deleterious amount of water is that amount of water which causes a significant change in the rate and selectivity to oxalate as compared to the rate and selectivity when a non-deleterious amount is present. The amount of water in the oxalate forming reaction zone is preferably less than 5.0 mole percent, more preferably less than 2.0 mole percent and most preferably less than 1.0 mole percent.

Carbon monoxide to be used in oxalate formation by the process of this invention may be obtained from any conventional source. It may be pure or be contaminated with small amounts of hydrogen and/or inert hydrocarbons, or it may be diluted with an inert gas, such as nitrogen, carbon dioxide and the like. The concentration of carbon monoxide in the reaction zone is not narrowly critical and may vary over a wide range between 1 and 99 mole percent. Typically, the concentration of carbon monoxide is in the range of between 10 percent and 95 mole percent, wherein the actual concentration of carbon monoxide in the reaction mixture will depend on the alkyl nitrite employed and its concentration, the catalyst employed in the process, concentration of inert gaseous diluent and the selected process conditions. The molar concentration of carbon monoxide is preferably selected to provide an excess of carbon monoxide over the ester of nitrous acid so that the molar ratio of carbon monoxide is between 2 and 20.

The reaction for the formation of the diester of oxalic acid is carried out in the presence of an inert gaseous diluent to moderate the reaction, and in part, to preclude the formation of explosive mixtures and prevent the formation of excessive amounts of undesirable byproducts. When carrying out the continuous process of the present invention some amount of inert gaseous diluent is present in the gaseous stream containing alkyl nitrite. Additional inert gaseous diluent may be added concurrently with the carbon monoxide or at some time before or after the addition of carbon monoxide. As the inert gaseous diluent, it is preferred to employ nitrogen, carbon dioxide or other gaseous compounds inert in the reaction. The use of carbon dioxide provides high molar heat capacity relative to nitrogen. The total amount of inert gaseous diluent present in the oxalate forming reaction zone is that amount sufficient to provide the aforementioned objectives, and is such that the concentration of inert gaseous diluent is between 1 and 99 mole percent. Typically, the concentration of inert gaseous diluent is between 0 (zero) percent and 90 mole percent, wherein the actual concentration employed is chosen as before discussed with respect to the concentration of carbon monoxide.

The vapor state process for forming the diester of oxalic acid is generally carried out at a temperature of between 50°C and 200°C and preferably between 75°C and 150°C.

The formation of diester of oxalic acid is generally carried out under atmospheric or super-atmospheric pressure, preferably such that the pressure is between atmospheric (0.103 MPa absolute) and 0.7 MPa absolute and more preferably between 0.105 MPa absolute and 0.42 MPa absolute. Pressures less than 0.103 MPa absolute may be employed, if desired.

The formation of the diester of oxalic acid is preferably carried out in a reactor with a fixed bed or dynamic bed, such as a fluidized bed, of the catalyst. The particulate catalyst may be diluted by particles of inert carrier or other inert materials, to enhance control over the reaction temperature.

The contact or residence time during which the diester of oxalic acid is formed is not narrowly critical and generally less than 30 seconds and preferably between 0.05 and 10 seconds such that the time is sufficient for reaction.

The supported palladium catalyst employed in the process is preferably formed with a non-acidic carrier with a surface area less than 10 square meters per gram.

However, the catalysts may be formed with carriers such as activated charcoal, alpha or gamma alumina, silica, diatomaceous earth, pumice, and molecular sieves.

U.S. Patent No. 4,038,175 discloses a hydrogenation process which employs palladium or platinum metal dispersed on the surface of an alpha-alumina support. The description beginning at column 3, line 42 to column 4, line 24, and the description at column 5, line 2 to column 8, line 22, relating to the description of palladium supported on the carrier alpha-alumina and the process for preparing the catalyst disclosed therein are incorporated herein by reference.

A preferred catalyst carrier for use in the preparation of diesters of oxalic acid is disclosed in commonly assigned U.S. applications, Serial Nos. 227,640, filed January 23, 1981, and 239,762 filed March 12, 1981, both to Lou Kapicak, et al., the latter application filed concurrently herewith, and both incorporated herein by reference. Exemplary of such a catalyst carrier is alpha-alumina.

The catalyst carrier employed in U.S. Serial Nos. 227,640 and 239,762 in practicing the invention thereof, may be selected from conventional, porous, refractory materials which are essentially inert to the reactants and products at reaction conditions. These materials are generally labelled as "macroporous" and consist of porous materials having low surface area of less than 10 m²/g (square meters per gm) and preferably less than 5 m²/g and greater than 0.001 m²/g. The surface area is measured by the conventional B.E.T. method described by Brunauer, S., Emmet, P., and Teller, E., in J. Am. Chem. Soc., Vol. 60, pp. 309-16, (1938). The carrier may be shaped in the form of pellets, spheres, rings, cylindrical rings; desirably a shape which provides the optimum gas flow for the selected reactor.

The amount of palladium deposited on the carrier is not narrowly critical and is in the range of 0.001 to 10% by weight, preferably between 0.01 and 5% by weight and most preferably between 0.05 and 2% by weight, calculated as metallic palladium.

The particle size of palladium metal or salt thereof deposited upon the carrier and the dispersion of the palladium are a function of the catalyst preparation procedure employed. Thus, the particular choice of solvent and/or complexing agent, palladium salt, heat treatment conditions and catalyst carrier may affect, to varying degrees, the size of the resulting palladium particle. For catalysts of general interest for the production of diesters of oxalic acid, a distribution of palladium particle sizes below about 10,000 Angstroms is preferred. However, the role of particle size of the palladium catalyst upon the effectiveness of the catalyst in making the diesters of oxalic acid is not clearly understood. In view of the fact that the palladium particles may migrate on the surface of the catalyst when used in the catalytic reaction resulting in a marked change in their size and shape, palladium particle size may or may not be a significant factor in affecting catalytic performance. Further, the dispersion of the palladium catalyst may be determinant in optimizing the production of oxalic acid diester, and even though such dispersion is not clearly understood at present a high dispersion of palladium particles is considered to be preferred.

The process of the invention is an "integrated" process wherein the term "integrated" is meant to refer to a process wherein the vapor state formation of alkyl nitrite and the vapor state formation of dialkyl oxalate ester are coupled and correlated so as to provide an overall vapor state process that may be continuous or cyclic in operation. The use of a continuous vapor state process comprising the coupling of the formation of alkyl nitrite and the formation of dialkyl oxalate is advantageous because the process minimizes the formation of by-products, achieves enhanced ease of operation and enhances production efficiencies.

Description of the figures

In carrying out the process of this invention it is important to maintain both the formation of alkyl nitrite and the formation of diester of oxalic acid in the vapor state. Such an integrated vapor state process is shown in Figures 1 and 2 wherein the input and output of the nitrite reactor and the input and output of oxalate reactor are correlated to provide an integrated and optimized process in the vapor state.

Figure 1 depicts schematically an integrated vapor state process suitable for use in practicing the invention. Referring to Figure 1, inert diluent (designated herein as nitrogen) is introduced at 10 of line 12, and admixes with a nitrogen oxide (in this case nitric oxide) at 14. The order of introduction is not critical. The N₂/nitrogen oxide

mixture at 14 is provided to the process as make-up to replace, as required, routine losses of nitrogen and nitrogen oxide, which may occur in carrying out the process. Molecular oxygen is added at 18 when its addition is required to form nitrogen dioxide for the process. Alternatively, molecular oxygen may be added to the recycle gas in line 54 (not shown). The addition of molecular oxygen to the process is provided so that oxygen is added to the nitrogen oxide prior to the introduction of alcohol to prevent oxidation of alcohol and thus prevent the formation of deleterious by-products and to avoid the formation of flammable mixtures. Alcohol is vaporized in heat exchanger (vaporizer) 22 and is added to the mixture of line 12 at 20. The recycled gas in line 54 is introduced into line 12 at point 16.

The mixture in line 12 is maintained in the vapor state and is introduced into nitrite reactor 24 (nitrous ester forming reaction zone) at a specified temperature and pressure, as discussed above, wherein the ester of nitrous acid is formed. The ester of nitrous acid exits nitrite reactor 24, passes to heat exchanger 26 wherein it is sufficiently cooled for condensation of water and unreacted alcohol as necessary, and passes via line 28 to vapor-liquid separator 30 from which water and unreacted alcohol are removed through line 32.

The gaseous mixture containing the ester of nitrous acid passes from vapor-liquid separator 30 by way of line 34 through a purification process 36, if necessary, for removal of residual water and trace impurities, so that the concentration of undesired materials is controlled at a predetermined level. The ester of nitrous acid then is contacted with carbon monoxide introduced at 38 prior to heat exchanger (heater) 40. The mixture of carbon monoxide and ester of nitrous acid are heated in heat exchanger 40 to about the desired inlet temperature of oxalate reactor 42. The mixture is introduced to oxalate reactor 42 (oxalate forming reaction zone) wherein is contained the supported palladium catalyst at a specified temperature and pressure, as previously discussed. The stream exiting oxalate reactor 42 through line 44 contains the formed diester of oxalic acid, gaseous components, such as N_2 , CO, NO, CO_2 , N_2O , and the like, and a minor amount of by-products.

The stream in line 44 passes through heat exchanger 46 wherein the stream is cooled for condensation of the oxalate product prior to introduction to vapor-liquid separator 50 wherein the liquid oxalate product is collected and removed as product through line 52.

The effluent gases from vapor liquid separator 50 exit the separator through line 54 and are recycled to incoming line 12 through compressor 56 to point 16. Compressor 56 is provided to adjust the pressures between the exit of oxalate reactor 42 and the inlet pressure of nitrite reactor 24. A gas purge is provided at point 58 of line 54 to allow for control of the components in the recycle gas (effluent gas from vapor-liquid

separator 50) provided to nitrite reactor 24 and to provide a control on the amount of inert gas in the process, particularly to prevent build up of inerts such as carbon dioxide. It has been found that correlation of the composition of the recycling gas for nitrite reactor 24 is significant in providing an optimized integrated process.

As will be obvious to one skilled in the art, when a continuous process is carried out as set forth in Figure 1, the inert gaseous diluent introduced through line 10 and the nitrogen oxide introduced through line 12 are provided as required to make up losses occurring in the process, due to routine losses and to losses resulting from the use of the gas purge at 58.

For examples 1 to 7, hereinafter, reference will be made to Figure 2 which schematically depicts an apparatus for carrying out the process of the present invention. The process is preferably carried out in a continuous manner in a series of elongated tubular zones, although alternative zone geometries may be employed. The material of construction should be such that it is inert during the reaction and the fabrication of the equipment should be able to withstand the reaction temperatures and pressures. The reaction zones may be fitted with internal or external heat exchanger(s) to thus control temperature, and to prevent any possible "run-away" reaction temperatures due to the exothermic nature of any of the reactions. In Figure 2, no mixing apparatus is shown for the various gaseous components at their various points of introduction since mixing is generally achieved through the turbulent condition present at the point of introduction of the process reactant. Mixing induced by vibration, shaker, stirrer, rotation, oscillation, ultrasonic, are all illustrative of the types of agitation means which may be employed to mix the gaseous component in the several lines and the nitrite reactor and oxalate reactor. Such means are available and well-known to the art. The supported palladium catalyst employed in the oxalate forming reaction zone is generally introduced into the oxalate reactor prior to the start of the process but may be provided continuously to the process as in the case of a dynamic reactor bed, particularly a fluidized bed, wherein new catalyst is introduced into the oxalate reactor during the course of the process. Means to introduce and/or adjust the reactants (i.e., gaseous process components), either intermittently or continuously, in the reaction zone during the course of the reaction can be conveniently utilized in the process especially to maintain the desired molar ratios of the reactants in the nitrous acid ester forming zone and the oxalate forming zone.

The operative conditions, e.g., temperature, pressure, relative molar ratios of reactants, may be adjusted to optimize the conversion to the desired product and/or the economics of the process. In the following description of Figure 2 the described conditions are for the preparation of the ethyl ester of nitrous acid and for diethyl

oxalate and are not intended to limit but serve only to illustrate the conditions which may be used for the ethyl ester of nitrous acid in forming diethyl oxalate.

With respect to Figure 2, inert gaseous diluent (designated in Figure 2 as nitrogen) is introduced at 60 of line 62 and admixes with a nitrogen oxide (nitric oxide in the instant case) at 64 of line 62. (Mixing here and in subsequent process steps may be by means as above-described). The order of introduction is not critical. In the continuous process the N_2 /nitrogen oxide mixture at point 64 is provided as required to makeup any losses, e.g., by purging of nitrogen or nitrogen oxide from the cycle gas. This "make-up" gas is combined with recycle stream 104 at 68. Molecular oxygen is added via line 106 to nitrogen oxide generator 70 as required. The addition of molecular oxygen to nitrogen oxide generator 70 is provided so that the addition of oxygen is prior to the introduction of ethanol and is essentially consumed by reaction with nitric oxide so as to prevent the possible oxidation of the ethanol by oxygen, the resultant formation of deleterious by-products and to avoid the formation of flammable mixtures. Ethanol is added to nitrite reactor 74 after having been heated to the vapor state by heat exchanger 72. Additional heat exchangers (not shown) may be provided to adjust the stream temperatures to the desired inlet temperature of nitrite reactor 74.

The stream in line 62 is also introduced to nitrite reactor 74 (nitrous acid ester forming reaction zone), shown as a tubular reactor, at a specified temperature and pressure (between 50°C and 110°C and between 0.1 and 0.3 MPa for ethyl nitrite formation) wherein ethyl nitrite is formed. Alternatively the nitrite reactor may be as described in U.S. Serial No. 227,798, filed January 23, 1981 or U.S. Serial No. 239,761 filed March 12, 1981, both pending applications being discussed above. The effluent (containing ethyl nitrite) from nitrite reactor 74 passes via line 78 to heat exchanger 76 where it is sufficiently cooled for condensation of water and unreacted alcohol, as necessary, prior to introduction to vapor-liquid separator 80 from which condensed water and unreacted alcohol are removed through line 82. Vapor-liquid separator 80 generally comprises a wide tubular body with a width greater than line 78 to reduce gas flow rate. Alternatively, the vapor-liquid separator may comprise a tubular zone with internal mesh or struts or a pot having a tangential entrance for incoming gases causing swirling of gases.

The effluent (containing ethyl nitrite) is removed by way of line 84 and passes through a purification process tank 86, if necessary, for removal of residual water and trace impurities, so that the concentration of undesired materials is controlled at a predetermined level. The ethyl nitrite in line 87 is then admixed with carbon monoxide at 88 prior to heat exchanger (heater) 90 wherein the mixture is heated to about the desired inlet temperature of oxalate reactor 92.

The formation of diethyl oxalate takes place in oxalate reactor 92 (oxalate forming reaction zone) at a specified temperature and pressure (e.g., at a temperature of between 110°C and 130°C and between 0.1 and 0.2 MPa for the formation of diethyl oxalate). The stream exiting oxalate reactor 92 via line 94 contains diethyl oxalate, minor amounts of by-products, unreacted CO, inert diluent (e.g., nitrogen), and other gaseous components, such as NO, CO_2 , N_2O .

The stream in line 94 passes through heat exchanger 96 wherein it is cooled for condensation of the oxalate product prior to introduction to vapor-liquid separator 100 wherein the liquid oxalate product is collected and removed through line 102 for subsequent treatment processes, if any, as desired.

The effluent gases from vapor-liquid separator 100 exit the separator through line 104 and are recycled to incoming line 62 through compressor 106. Compressor 106 is provided to increase the pressure in line 104 to the desired pressure in nitrogen oxide generator 70 and may comprise a blower-type compressor or a pump-type compressor. The selection of the compressor is dependent on the pressure differential between the operating pressures of nitrogen oxide generator 70 and oxalate reactor 92, such selection being within the skill of the practitioner once the pressure differential is known. A gas purge is provided at 108 in line 104 to allow for control of components in the recycle stream, provide for control of the amount of inert gaseous diluent present in the process and provide a means for controlling the pressure in the process. Particularly, the gas purge is provided to prevent the build up inerts and/or by-products beyond a predetermined level. By carefully correlating the recycled effluent gases in line 104, the reactions in nitrogen oxide generator 70, and nitrite reactor 74 may be optimized.

Examples 1—7

The several examples set forth hereinafter are understood by reference to Fig. 2 and by reference to the mole percent of the dialkyl oxalate (diethyl oxalate is the dialkyl oxalate in each example), alkyl nitrite (ethyl nitrite is alkyl nitrite in each example), carbon monoxide, nitrogen oxide (nitric oxide is the nitrogen oxide in each example), inert diluent (nitrogen is the inert diluent in each example), oxygen, alcohol (ethanol is the alcohol in each example) and water; and such mole values (given as the mole percent) are set forth by reference to the composition of streams 94, 84, 62, 78 and 87 as designated in Figure 2, wherein these streams are also designated by the letters A, B, C, D and E, respectively. It is noted that the composition of stream 104 at A' of Figure 2 is simply the composition at A less the condensed liquid in line 102.

In each example the following is the molar ratio of carbon monoxide to ethyl nitrite in the diethyl oxalate forming reaction zone:

TABLE I
Carbon monoxide to
ethyl nitrite ratio

Example	Carbon monoxide to ethyl nitrite ratio
1	4:1
2	8:1
3	4:1
4	2:1
5	1.87:1
6	1.75:1
7	4:1

In Examples 1 to 7 the catalyst is a 2.0 percent palladium catalyst on an alpha-alumina carrier having the following chemical composition and physical properties:

Chemical composition	Wt. percent
Alpha-alumina	98.5
Silicon dioxide	0.74
Calcium oxide	0.22
Sodium oxide	0.16
Ferric oxide	0.14
Potassium oxide	0.04
Magnesium oxide	0.03
Physical properties	
Surface area ⁽¹⁾	~0.03 m ² /g
Pore volume ⁽²⁾ (or water adsorption)	~0.50×10 ⁻⁶ m ³ /g
Packing density ⁽³⁾	0.70×10 ⁶ g/m ³
Median pore diameter ⁽⁴⁾	21 microns

Pore size distribution, percent total pore volume⁽⁴⁾
Pore size, microns TPV (percent)

0.1—1.0	1.5
1.0—10.0	38.5
10.0—30.0	20.0
30—100	21.0
>100	8.0

⁽¹⁾ Method of measurement described in "Adsorption, Surface Area and Porosity", S. J. Gregg and K. S. W. Sing, Academic Press (1967), pages 316—321.

⁽²⁾ Method of measurement as described in ASTM C20-46.

⁽³⁾ Calculated value based on conventional measurement of the weight of the carrier in a known volume container.

⁽⁴⁾ Method of measurement described in "Application of Mercury Penetration to Materials Analysis", C. Orr Jr., Powder Technology, Vol. 3, pp. 117—123 (1970).

In Examples 1—7, referring to Figure 2, the temperature of nitrite reactor 74, is between 50°C and 110°C and the pressure is between 0.1 and 0.3 MPa. The temperature of oxalate reactor 92 is between 110°C and 130°C with a pressure of between 0.1 and 0.2 MPa. Nitrite reactor 74 is as shown in Figure 1 of U.S. Serial No. 227,798 and oxalate reactor 92 is a 1.22 meter long No. 304 stainless steel tube having an inside diameter of 1.27 cm with seven sheathed thermocouples placed every 15.2 cm in a gravity packed catalyst bed. Vapor-liquid separators 80 and 100 and heat exchangers 72 and 90 are of standard design. The various lines are of 6.35 mm outside diameter (4.70 mm inside diameter) stainless steel tubing. Compressor 106 is a pump-type compressor.

Examples 1 to 7 are set forth in Tables II to VIII, respectively, as follows:

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65

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TABLE II^{1,2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	2	—	—	—	—
Carbon monoxide	12	15.69	11.54	11.88	12.24
Nitric oxide	5	0.98	4.51	0.99	1.02
Nitrogen	81	79.41	77.88	80.20	82.66
Oxygen ⁴	—	—	0.96	—	—
Ethyl nitrite	—	3.92	—	3.96	4.8
Ethanol ³	—	—	4.81	0.97	—
Water	—	—	—	1.98	—

¹ Example 1.² Mole percent based on total moles in stream over a one hour period.³ Alcohol recycled to oxalate reactor.⁴ Oxygen feed to line 106.TABLE III^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	2	—	—	—	—
Carbon monoxide	28	31.37	26.92	27.72	28.5
Nitric oxide	5	0.98	4.81	0.99	1.0
Nitrogen ³	65	63.73	62.50	64.36	66.3
Oxygen ⁴	—	—	0.96	—	—
Ethyl nitrite	—	3.92	—	3.96	4
Ethanol	—	—	4.81	0.97	—
Water	—	—	—	1.98	—

¹ Example 2.² Mole percent based on total moles in said stream over a one hour period.³ Nitrogen as the inert.⁴ Oxygen feed to line 106.

TABLE IV^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	8	—	—	—	—
Carbon monoxide	48	59.26	41.38	46.15	52.17
Nitric oxide	20	3.70	17.24	3.85	4.35
Nitrogen ^{3, 4}	24	22.22	20.69	23.08	26.09
Oxygen ⁵	—	—	3.45	—	—
Ethyl nitrite	—	14.82	—	15.38	17.39
Ethyl alcohol	—	—	17.24	3.85	—
Water	—	—	—	7.69	—

¹ Example 3.² Mole percent based on total moles in stream over a one hour period.³ Inert is nitrogen.⁴ Use of only 24 mole percent inert is close to presenting a safety hazard.⁵ Oxygen feed to line 106.TABLE V^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	8	—	—	—	—
Carbon monoxide	16	29.63	13.79	15.38	17.39
Nitric oxide	20	3.70	17.24	3.85	4.35
Nitrogen ³	56	51.85	48.28	53.85	60.87
Oxygen ⁴	—	—	3.45	—	—
Ethyl nitrite	—	14.82	—	15.38	17.39
Ethanol	—	—	17.24	3.85	—
Water	—	—	—	7.69	—

¹ Example 4.² Mole percent based on total moles in stream over a one hour period.³ Nitrogen is the inert gas.⁴ Oxygen feed to line 106.

TABLE VI^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	8	—	—	—	—
Carbon monoxide	14	27.78	12.04	13.46	15.22
Nitric oxide	20	3.70	17.24	3.85	4.35
Inert ³	58	53.7	50.0	55.77	63.04
Oxygen ⁴	—	—	3.45	—	—
Ethyl nitrite	—	14.82	—	15.38	17.39
Ethanol	—	—	17.24	3.85	—
Water	—	—	—	7.69	—

¹ Example 5.² Mole percent based on total moles in stream over a one hour period.³ Nitrogen is the inert gas.⁴ Oxygen feed to line 106.TABLE VII^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	8	—	—	—	—
Carbon monoxide	12	25.93	10.71	12	13.04
Nitric oxide	20	3.70	17.86	4	4.35
Nitrogen ³	56	51.85	50	56	60.87
Oxygen ⁵	—	—	3.57	—	—
Ethyl nitrite	—	14.82	—	16	17.39
Ethanol ⁴	4	3.7	17.86	4	4.35
Water	—	—	—	—	—

¹ Example 6.² Mole percent based on total moles in stream over a one hour period.³ Inert is nitrogen.⁴ Ethanol recycled to oxalate reactor.⁵ Oxygen feed to line 106.

TABLE VIII^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	4.76	—	—	—	—
Carbon monoxide	28.57	36.36	26.09	27.91	30.0
Nitric oxide	11.90	2.27	10.87	2.32	2.5
Nitrogen ³	54.76	52.27	50	53.49	57.5
Oxygen ⁵	—	—	2.17	9.30	—
Ethyl nitrite	—	9.09	—	2.32	10.0
Ethanol ⁴	—	—	10.87	4.65	—
Water	—	—	—	—	—

¹ Example 7.² Mole percent based on total moles in stream over a one hour period.³ Inert is nitrogen.⁴ Alcohol recycled to oxalate reactor.⁵ Oxygen feed to line 106.**Claims**

1. A process for the preparation of diesters of oxalic acid from a nitrogen oxide, a saturated monohydric aliphatic alcohol containing 1 to 8 carbon atoms, and carbon monoxide comprising forming an ester of nitrous acid from the nitrogen oxide and alcohol, and contacting said ester of nitrous acid with carbon monoxide in the vapor state at a temperature of between 50°C and 200°C over a supported palladium containing catalyst in which the palladium is metallic palladium or a salt thereof to produce the diester of oxalic acid and recovering the diester of oxalic acid, characterized in that the contacting of the nitrogen oxide and the alcohol to form an ester of nitrous acid is in the vapor state in a nitrite-forming reaction zone (24, 74); the ester of nitrous acid is maintained in the vapor state and contacted with carbon monoxide in an oxalate-forming reaction zone (42, 92), and deleterious amounts of water formed in the nitrite-forming reaction zone (24, 74) are removed prior to introduction to the oxalate-forming reaction zone (42, 92).

2. The process of claim 1 characterized in that the alcohol is methanol or ethanol.

3. The process of claim 1 characterized in that the supported palladium containing catalyst is supported on a non-acidic carrier having a surface area no greater than 10 square meters per gram of carrier.

4. The process of claim 3 characterized in that the carrier is an alpha alumina.

5. The process of any of the preceding claims characterized in that at least a portion (54, 104) of the nitrogen oxide-containing effluent of the

oxalate-forming reaction zone (42, 92) is recycled to the nitrite forming reaction zone (24, 74) and the process is continuous.

6. The continuous process of claim 5 characterized in that in the nitrite-forming reaction zone (24, 74) a molar amount of a nitrogen oxide composition containing a nitric oxide to nitrogen dioxide molar ratio of greater than 1 is reacted with a molar amount of vaporized alcohol wherein the molar ratio of alcohol to the combined molar ratio of nitric oxide and nitrogen dioxide is greater than 1.

7. The continuous process of claim 5 characterized in that in the nitrite-forming reaction zone (24, 74) a nitrogen oxide, oxygen and the alcohol are reacted and at least a portion (54, 104) of the nitrogen oxide containing effluent from the recovery of the dialkyl oxalate is recycled to the nitrite-forming reaction zone (24, 74).

8. The process of any of the preceding claims characterized in that the process is carried out at atmospheric pressure or superatmospheric pressure.

9. The process of any of the preceding claims characterized in that an inert gaseous diluent is present in both reaction zones.

10. The process of any of the preceding claims characterized in that the amount of water in the oxalate forming zone is less than 5.0 percent by weight.

11. The process of claim 10 characterized in that the amount of water in the oxalate-forming reaction zone is less than 1.0 percent by weight.

12. The process of any of the preceding claims characterized in that nitrogen dioxide is present in both reaction zones.

TABLE VIII^{1, 2}

	Stream A	Stream B	Stream C	Stream D	Stream E
	Mole (%)	Mole (%)	Mole (%)	Mole (%)	Mole (%)
Diethyl oxalate	4.76	—	—	—	—
Carbon monoxide	28.57	36.36	26.09	27.91	30.0
Nitric oxide	11.90	2.27	10.87	2.32	2.5
Nitrogen ³	54.76	52.27	50	53.49	57.5
Oxygen ⁵	—	—	2.17	9.30	—
Ethyl nitrite	—	9.09	—	2.32	10.0
Ethanol ⁴	—	—	10.87	4.65	—
Water	—	—	—	—	—

¹ Example 7.² Mole percent based on total moles in stream over a one hour period.³ Inert is nitrogen.⁴ Alcohol recycled to oxalate reactor.⁵ Oxygen feed to line 106.**Claims**

1. A process for the preparation of diesters of oxalic acid from a nitrogen oxide, a saturated monohydric aliphatic alcohol containing 1 to 8 carbon atoms, and carbon monoxide comprising forming an ester of nitrous acid from the nitrogen oxide and alcohol, and contacting said ester of nitrous acid with carbon monoxide in the vapor state at a temperature of between 50°C and 200°C over a supported palladium containing catalyst in which the palladium is metallic palladium or a salt thereof to produce the diester of oxalic acid and recovering the diester of oxalic acid, characterized in that the contacting of the nitrogen oxide and the alcohol to form an ester of nitrous acid is in the vapor state in a nitrite-forming reaction zone (24, 74); the ester of nitrous acid is maintained in the vapor state and contacted with carbon monoxide in an oxalate-forming reaction zone (42, 92), and deleterious amounts of water formed in the nitrite-forming reaction zone (24, 74) are removed prior to introduction to the oxalate-forming reaction zone (42, 92).

2. The process of claim 1 characterized in that the alcohol is methanol or ethanol.

3. The process of claim 1 characterized in that the supported palladium containing catalyst is supported on a non-acidic carrier having a surface area no greater than 10 square meters per gram of carrier.

4. The process of claim 3 characterized in that the carrier is an alpha alumina.

5. The process of any of the preceding claims characterized in that at least a portion (54, 104) of the nitrogen oxide-containing effluent of the

oxalate-forming reaction zone (42, 92) is recycled to the nitrite forming reaction zone (24, 74) and the process is continuous.

6. The continuous process of claim 5 characterized in that in the nitrite-forming reaction zone (24, 74) a molar amount of a nitrogen oxide composition containing a nitric oxide to nitrogen dioxide molar ratio of greater than 1 is reacted with a molar amount of vaporized alcohol wherein the molar ratio of alcohol to the combined molar ratio of nitric oxide and nitrogen dioxide is greater than 1.

7. The continuous process of claim 5 characterized in that in the nitrite-forming reaction zone (24, 74) a nitrogen oxide, oxygen and the alcohol are reacted and at least a portion (54, 104) of the nitrogen oxide containing effluent from the recovery of the dialkyl oxalate is recycled to the nitrite-forming reaction zone (24, 74).

8. The process of any of the preceding claims characterized in that the process is carried out at atmospheric pressure or superatmospheric pressure.

9. The process of any of the preceding claims characterized in that an inert gaseous diluent is present in both reaction zones.

10. The process of any of the preceding claims characterized in that the amount of water in the oxalate forming zone is less than 5.0 percent by weight.

11. The process of claim 10 characterized in that the amount of water in the oxalate-forming reaction zone is less than 1.0 percent by weight.

12. The process of any of the preceding claims characterized in that nitrogen dioxide is present in both reaction zones.



Patentansprüche

1. Verfahren zur Herstellung von Diestern der Oxalsäure aus einem Stickstoffoxid, einem gesättigten einwertigen aliphatischen Alkohol mit 1 bis 8 Kohlenstoffatomen und Kohlenmonoxid, bei welchem man aus dem Stickstoffoxid und dem Alkohol einen Ester der salpetrigen Säure bildet und diesen Ester der salpetrigen Säure mit Kohlenmonoxid im Dampfzustand bei einer Temperatur von 50 bis 200°C über einem Palladium enthaltenden Trägerkatalysator, in welchem das Palladium metallisches Palladium oder ein Salz desselben ist, zur Bildung des Diesters der Oxalsäure in Berührung bringt und den Diester der Oxalsäure gewinnt, dadurch gekennzeichnet, daß das In-Berührung-bringen des Stickstoffoxids und des Alkohols zur Bildung eines Esters der salpetrigen Säure im Dampfzustand in einer nitritbildenden Reaktionszone (24, 74) erfolgt; der Ester der salpetrigen Säure im Dampfzustand gehalten und mit Kohlenmonoxid in einer oxalatbildenden Reaktionszone (42, 92) in Berührung gebracht wird, und schädliche, in der nitritbildenden Reaktionszone (24, 74) gebildete Wassermengen vor der Einführung in die oxalatbildende Reaktionszone (42, 92) entfernt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Alkohol Methanol oder Ethanol ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der palladiumhaltige Trägerkatalysator auf einem nichtsauren Träger mit einer Oberfläche nicht über 10 m²/g Träger abgetrennt ist.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Träger eine α -Tonerde ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß mindestens ein Teil (54, 104) des stickstoffoxidhaltigen Ausflusses aus der oxalatbildenden Reaktionszone (42, 92) zur nitritbildenden Reaktionszone (24, 74) zurückgeführt wird und das Verfahren kontinuierlich ist.

6. Kontinuierliches Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß in der nitritbildenden Reaktionszone (24, 74) eine molare Menge einer Stickstoffoxidzusammensetzung, die ein molares Verhältnis von Stickstoffmonoxid zu Stickstoffdioxid über 1 enthält, mit einer molaren Menge des verdampften Alkohols umgesetzt wird, wobei das molare Verhältnis von Alkohol zum kombinierten Verhältnis aus Stickstoffmonoxid zu Stickstoffdioxid größer als 1 ist.

7. Kontinuierliches Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß in der nitritbildenden Reaktionszone (24, 74) ein Stickstoffoxid, Sauerstoff und der Alkohol umgesetzt werden und mindestens ein Teil (54, 104) des stickstoffoxidhaltigen Ausflusses aus der Gewinnung des Dialkyloxalates zur nitritbildenden Reaktionszone (24, 74) zurückgeführt wird.

8. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß es bei

atmosphärischem oder überatmosphärischem Druck durchgeführt wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß in beiden Reaktionszonen ein inertes gasförmiges Verdünnungsmittel anwesend ist.

10. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Wassermenge in der oxalatbildenden Zone weniger als 5,0 Gew.-% beträgt.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß die Wassermenge in der oxalatbildenden Reaktionszone weniger als 1,0 Gew.-% beträgt.

12. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß in beiden Reaktionszonen Stickstoffoxid anwesend ist.

Revendications

1. Procédé de préparation de diesters d'acide oxalique à partir d'un oxyde d'azote, d'un alcool aliphatique monohydroxylique saturé contenant 1 à 8 atomes de carbone et d'oxyde carbone, comprenant la formation d'un ester d'acide nitreux à partir de l'oxyde d'azote et de l'alcool et la mise en contact dudit ester d'acide nitreux avec de l'oxyde de carbone à l'état de vapeur à une température comprise entre 50 et 200°C sur un catalyseur contenant du palladium fixé sur un support, dans lequel le palladium est du palladium métallique ou un sel de palladium pour produire le diester d'acide oxalique, et isolement du diester d'acide oxalique, caractérisé en ce que la mise en contact de l'oxyde d'azote et de l'alcool pour former un ester d'acide nitreux est effectué à l'état de vapeur dans une zone de réaction (24, 74) formant un nitrite; l'ester d'acide nitreux est maintenu à l'état de vapeur et mis en contact avec de l'oxyde de carbone dans une zone de réaction (42, 92) formant un oxalate, et des quantités nuisibles d'eau formées dans la zone de réaction (24, 74) formant un nitrite sont éliminées avant l'introduction dans la zone de réaction (42, 92) formant un oxalate.

2. Procédé suivant la revendication 1, caractérisé en ce que l'alcool est le méthanol ou l'éthanol.

3. Procédé suivant la revendication 1, caractérisé en ce que le catalyseur contenant du palladium supporté est fixé sur un support non acide dont la surface spécifique ne dépasse pas 10 m² par gramme de support.

4. Procédé suivant la revendication 3, caractérisé en ce que le support est une alpha-alumine.

5. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'au moins une portion (54, 104) de l'effluent contenant de l'oxyde d'azote de la zone de réaction (42, 92) formant un oxalate est recyclée à la zone de réaction (24, 74) formant un nitrite et le procédé est continu.

6. Procédé continu suivant la revendication 5, caractérisé en ce que dans la zone de réaction (24,



74) de formation d'un nitrite, une quantité molaire d'une composition d'oxydes d'azote contenant du bioxyde d'azote et du peroxyde d'azote dans un rapport molaire ne dépassant pas 1 est amenée à réagir avec une quantité molaire d'alcool vaporisé, le rapport molaire de l'alcool à la proportion molaire total de bioxyde d'azote et de peroxyde d'azote étant supérieur à 1.

7. Procédé continu suivant la revendication 5, caractérisé en ce que, dans la zone (24, 74) de réaction de formation de nitrite, un oxyde d'azote, de l'oxygène et l'alcool sont amenés à réagir et au moins une portion (54, 104) de l'effluent contenant l'oxyde d'azote venant de la séparation de l'oxalate de dialkyle est recyclée dans la zone (24, 74) de réaction de formation du nitrite.

8. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'il est mis en oeuvre à la pression

atmosphérique ou à une pression supérieure à la pression atmosphérique.

9. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'un diluant gazeux inerte est présent dans les deux zones de réaction.

10. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que la quantité d'eau dans la zone de formation de l'oxalate est inférieure à 5,0% en poids.

11. Procédé suivant la revendication 10, caractérisé en ce que la quantité d'eau dans la zone de réaction de formation de l'oxalate est inférieure à 1,0% en poids.

12. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que du peroxyde d'azote est présent dans les deux zones de réaction.



* C L N S *