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CATALYTIC REDUCTION OF AROMATIC POLYNITRO COMPOUNDS

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This invention relates to an improved method of catalytic hydrogenation of aromatic dinitro compounds, to reduce them to the corresponding amino compounds; and is particularly concerned with an improved process whereby this reduction is carried out in liquid phase, and in the presence of an inert liquid solvent.

The process of the present invention is of particular advantage for the production of aromatic diamines by the catalytic hydrogenation of the corresponding aromatic dinitro compounds. However, it has been found that, in practicing the process of the present invention, the reduction of the nitro groups of the aromatic dinitro starting material, proceeds in a step-wise manner, so that, when reducing an aromatic dinitro compound to the amine, there is obtained, during the course of the reaction, a material containing a substantial amount of mono - amino - mononitro - product; and, if desired, the process may be stopped at this point, or the product drawn off and the process thus used to reduce the aromatic dinitro compound to the corresponding mononitro-monoamino-compound. Also, while it is preferred to start with an aromatic dinitro compound, it should be understood that the process is operable, and effective for the reductions of aromatic compounds containing two nuclear nitrogen substituents, in which the nitrogen is present in a reducible form. Thus, in addition to aromatic dinitro compounds, the process may be employed with partially reduced aromatic dinitro compounds in which one or both of the nitro groups is present in the nitroso-, hydroxylamino-, azoxy-, azo-, or hydrazo-stage.

Aromatic nitro compounds have long been reduced to the corresponding aryl amines by a number of methods, such as, for example, by the use of iron borings and dilute acid. In addition, zinc, tin and stannous chloride, with or without acid, alkaline sulfides, and a variety of other reducing agents have been used. In addition, the direct reduction of nitro compounds with hydrogen and a catalyst has been used to a substantial extent, since it offers appreciable advantages over the foregoing methods, with respect to economy, separation of the products, operating complexities, versatility, and the ease of adaptation to continuous processing. Such catalytic hydrogenations have been quite successful in the reduction of mononitro aromatic compounds to the corresponding aromatic amine; e.g., reduction of nitro benzene to aniline. However, a number of problems have, heretofore, beeen encountered in attempting to effect the catalytic hydrogenation of dinitro or a higher polynitro aromatic compound to corrseponding aromatic diamines or higher polyamines.

In large measure, the difficulties encountered in the catalytic hydrogenation of aromatic dinitro compounds to the corresponding aromatic diamines are attributable to the water, which is formed in the reduction. Thus, when such catalytic hydrogenation is carried out using the usual solvents which have, heretofore, been suggested, such as methanol, ethanol, propanol, and butanol,

the water formed in the course of the reaction dilutes the alcohol and decreases the solubility of the aromatic nitro compound being reduced so as to precipitate it from the solution. This produces poor reaction conditions because of the presence of two liquid phases, and a solid catalyst phase. Other suggested solvents, such as ether, hydrocarbons, and the aromatic amine products of the reduction, also frequently give rise to two liquid phases with the water formed during the reduction, so as to give rise to poor reaction conditions.

Among the difficulties encountered, due to the presence of two liquid phases, are the fact that the catalyst often becomes wet with the wrong liquid phase, and, thus, the reaction is slowed down, or even stopped. Even with good agitation, such a 2-phase system causes finely divided active catalyst to become pasted to the reactor, thus giving a short catalyst life.

While many of these difficulties are also encountered in the reduction of mononitro compounds, to the corresponding monoamines, they are accentuated in the case of the catalytic reduction of dinitro compounds to corresponding dinitro amines. In addition, many of the solutions for these problems, which have been proposed and are effective for the catalytic reduction of mononitro compounds, are either not as effective, or are else not readily applied to the catalytic reduction of the dinitro aromatic compounds. Thus, in U.S. Patent 2,292,879, it is suggested that the ill-effect of the presence of the water phase during catalytic hydrogenation of aromatic nitro compounds, can be overcome by operating at conditions which remove the water as vapor as fast as it is formed. This procedure, however, is not readily applied to the catalytic reduction of aromatic dinitro compounds, due to the increased hazard of handling the dinitro compounds, as compared with the mononitro compounds; and, also, due to the comparative instability of the aromatic diamines, as compared with the monoamines. Thus, the temperature and pressure conditions, which are preferably employed for the production of aromatic diamines, are frequently such that water cannot readily be removed as vapor as it is formed.

Due to the potentially hazardous (explosive) character of the aromatic dinitro compounds, it is highly advisable in any process involving the catalytic hydrogenation of such aromatic dinitro compounds, that care should be exercised to insure that there is not formed a separate phase having a high concentration of aromatic dinitro compound. At the same time, it is desirable, from a commercial standpoint, in order to cut down the amount of material which must be handled and for other commercial and economic reasons, to employ as high a concentration as possible of aromatic dinitro compounds as the feed to the process. While aromatic dinitro compounds appear to be catalytically reduced without the necessity of using solvents, the explosion hazards in such an operation are too great to permit its use. Such hazards are disclosed, for example, by Gage, in U.S. Patent 2,430,421, which suggests that dinitro aromatic compounds should be removed from mononitroaromatic compounds which are to be subjected to catalytic hydrogenation, in order to decrease the hazard.

Further evidence of the potential hazardous character of dinitro aromatic compounds is found in an article by Brown, Smith and Scharmann, Ind. Eng. Chem. 40 1538 (1948), where mention is made of the fact that a specification of 3% dinitro xylene in mononitroxylene feed stocks was set by the U.S. Army Ordnance Department in the production of xylidene for aviation gas blending agents. In the course of my own investigation, I have found that explosions occur, and the process is potentially quite hazardous, when aromatic dinitro compounds,

such as dinitro toluene, m-dinitro benzene, etc., are catalytically hydrogenated under any conditions in which a separate phase, containing a high proportion of aromatic dinitro compound, can be formed. While it has been suggested that the catalytic hydrogenation of aromatic dinitro compounds can be carried out effectively in a water suspension, or emulsion, and, at the same time moderate the explosion hazards (Benner and Stevenson, U.S. Patent 2,619,503), it will be apparent that this procedure does not, inherently, completely remove the essential hazards of the possibility of a separate phase being formed in which there is a high concentration of aromatic dinitro compounds. In order to prevent any substantial accumulation of such a separate phase, which would give rise to an explosion hazard, special agitation is required; and, also, careful design of the equipment, in order to avoid the possibility of any area of poor agitation, since any shut-down or interruption of the agitation, or any region of poor agitation, could quickly result in a dangerously explosive concentration of the aromatic dinitro compound.

I have now found that, by operating in accordance with the present invention, it is possible to effect the catalytic hydrogenation of aromatic dinitro compounds to the corresponding diamines in an efficient manner, and, in such a way that the entire process is carried out in a single liquid phase so thot the explosive hazard of a separate phase of an aromatic dinitro compound is inherently overcome.

In accordance with the present invention, the aromatic dinitro compound to be hydrogenated is dissolved in a solvent, which is capable of dissolving at the desired operating conditions, both the aromatic dinitro compound used as a feed stock, as well as the products formed in its catalytic hydrogenation, i.e., water and the desired aromatic diamine, so that a homogenous single liquid phase is maintained throughout the reaction.

The solvent to be used in this process should be one which permits a relatively high concentration of the aromatic dinitro compounds to be hydrogenated, as well as of the products of the reaction, and should, preferably, be relatively inexpensive, easy to separate from the product, and inert to hydrogenation or inter-reaction with the aromatic diamine, or aromatic dinitro compounds. I have also found it to be desirable that the solvent used be capable of being diluted with water, for economic purposes.

Among the solvents, which I have found suitable for this process, may be mentioned morpholine, N-alkyl morpholines, butyrolactone, ethylenediamine, piperidine, N-alkyl piperidine, pyridine, N, N'-dialkylamides, such as dimethyl formamide and dimethyl acetamide, pyrrolidone, methyl pyrrolidone, ethyl ether of ethylene glycol ("Cellosolve"), methyl ether of ethylene glycol ("methyl Cellosolve"), ethyl ether of diethylene glycol ("Carbitol"), methyl ether of diethylene glycol ("methyl Carbitol"), dimethyl ether of ethylene glycol, diethyl ether of ethylene glycol, dimethyl or diethyl ethers of diethylene glycol, and monomethyl, monoethyl, dimethyl or diethyl ethers of polyethylene glycols. All of these solvents may be used alone, in admixtures with each other, or diluted with water. In addition, I have found that the aromatic diamine product of the reaction can be used as a solvent if diluted with sufficient water—about 15% to about 50% by weight—in order to form a liquid solvent. While many of the aromatic diamines formed on reduction of aromatic dinitro compounds are water-soluble, they are usually solid at desirable temperatures of reaction, and under the conditions under which they are formed in the prior art, have not given liquid reaction conditions. While it has been found that a wide variety of inert solvents, which will dissolve the nitro compound to be hydrogenated—the amino compound produced on hydrogenation and water are operative in the process, certain solvents, particularly those containing an ether linkage, such as the lower alkyl ethers of ethylene glycol (Cellosolves) have the desirable property of enhancing the reaction rate, and/or prolonging the catalyst's life; and are, therefore, to be preferred in most instances.

The remaining conditions employed for the catalytic hydrogenation of the aromatic dinitro compounds are those known in the art; i.e., temperatures of 20° C. to 100° C., or slightly higher, are employed. Lower temperatures are less desirable, since the reaction becomes excessively slow, and above 100° C. undesired reactions, such as hydrogenolysis, ring hydrogenation, and polymerization may take place. Optimum temperatures and pressures of reaction may be obtained for each specific dinitro compound, and the particular catalyst employed. However, in general, it has been found that satisfactory reaction rate is obtained within the range of 40 to 100° C. At 100° C. some decomposition of the diamine may take place, although this usually does not become serious, or hazardous until temperatures above 100° C. are reached.

The pressure employed for the reaction is preferably about 25 to 80 pounds per square inch gauge; although pressures from about atmospheric to about 150 pounds per square inch gauge may be used.

The catalysts which are preferably employed in the reduction comprise nickel and the platinum metals' group of the periodic system; preferably palladium and platinum—either supported on carriers, or unsupported. Any of the standard preparations of catalysts may be used. The supported catalysts may be pelleted, granular or powdered. The catalyst may be on the outside of the support or throughout it. Some of the useful catalysts which may be employed together with references to their preparation are given below:

Platinum black—Sabatier-Reid, Catalysis in Organic Chemistry. D. Van Nostrand Co., New York, 1922.

Platinum oxide—Adams, Voorhees and Shriner, Organic Syntheses, Coll. vol. 1, p. 452. John Wiley & Sons, New York, 1932.

Raney nickel—Covert, J. Am. Chem. Soc. 54 4116 (1952).

Palladium on charcoal—Mannich & Thiele, Ber. Deutches pharm. Ges. 26 36–48 (1916).

Platinum on charcoal—Ellis, U.S. Patent 1,174,245.

Nickel on kieselguhr—Covert and Conner, J. Am. Chem. Soc. 54 165 (1932).

Platinum or palladium on alumina—Schwarcman, U.S. Patent 1,111,502.

It should be understood that, when operating a batch process, the catalyst recovered from one batch of material may be reused a number of times before its activity decreases markedly. Similarly, if the process is operated in a continuous manner, the catalyst has a relatively long period of useful life. When the activity of the catalyst, either in batch or continuous operation, has dropped below a desirable level, the catalyst may be reactivated by means known in the art. Since noble metal catalysts, such as platinum and palladium, are preferred catalysts, the recovery and regeneration of the catalysts, after its deactivation is normally justified economically.

The details of the present invention will be apparent to those skilled in the art, from consideration of the following specific examples, in which the parts are by weight:

Example 1

A solution of 30 parts of m-dinitrobenzene as a 90% aqueous paste (solidification point, 89° C., of the dry material), was made in 170 parts m-phenylenediamine, S.P. 62.8° C., and 34 parts water at 40° C. To the solution was added 5 parts of a commercial 5% palladium on charcoal catalyst (0.25 part palladium).

The above mixture was placed in a 1-liter steel shaker-type autoclave, and the system purged of air with hydrogen gas. Hydrogen gas was then fed in with shaking to

maintain a pressure of 100 p.s.i.g. The temperature was maintained at 45° C. Almost the theoretical hydrogen was absorbed in 14 hours, at which time the pressure was released. The catalyst was filtered from the solution and the solution subjected to distillation, first at atmospheric pressure to remove water, then at reduced pressure to obtain 181 parts of m-phenylenediamine or 11 parts produced from 30 parts of charged m-dinitrobenzene which is a yield of 57% of the theoretical. The S.P. was 63.1° C.

Example 2

A solution of 30 parts m-dinitrobenzene as 90% aqueous paste was made in 170 parts dimethylformamide at 45° C. This mixture was hydrogenated as in Example 1, using 5 parts of the same catalyst as described in Example 1, at 50 p.s.i.g. hydrogen pressure and 45–50° C. The hydrogenation was complete in 2 hours. After removing the water and solvent dimethyl formamide from the filtered batch by distillation, a m-phenylenediamine fraction of 16.5 parts, having a solidification point of 62.5° C. was obtained. This is an 86% of theory yield.

Example 3

80 parts of m-dinitrobenzene as 90% aqueous paste was dissolved in 320 parts dimethylformamide at 40° C. To this solution was added 30 parts of a reduced and stabilized nickel on kieselguhr catalyst (sold by Harshaw Chemical Co. as Ni 0104T⅛).

The mixture was hydrogenated as in Example 1 and Example 2, at a temperature of 100° C. and hydrogen pressure of 150 p.s.i.g. The reduction was complete in 25 hours. After working up the hydrogenation mixture as described in Example 2, a yield of 36.5 parts of m-phenylenediamine of S.P. 61° C. was obtained. This is a 71% of theory yield.

Example 4

80 parts of m-dinitrobenzene of S.P. 89° C. was dissolved in 320 parts of commercial methyl ether of ethylene glycol (methyl Cellosolve). To this solution was added 2 parts of a commercial 10% palladium on charcoal catalyst (0.20 part palladium), obtained from Baker & Co.

The above mixture was hydrogenated in the same manner as Example 2, but at a temperature of 65° C. and a hydrogen pressure of 40 p.s.i.g. The hydrogenation was complete in 2 hours. After removing the water and methyl Cellosolve from the filtered batch by distillation, a m-phenylenediamine fraction of 47 parts, having a solidification point of 63.0° C. was obtained. This is a 91.3% of theory yield of a high purity product.

Example 5

80 parts of m-dinitrobenzene (S.P. 89° C.) was dissolved in 320 parts of pyrrolidone. This solution was hydrogenated with 10 parts of the 10% palladium on charcoal catalyst, described in Example 4, at a temperature of 60° C. and a hydrogen pressure of 50 p.s.i.g. The reduction was complete in 31 hours with an absorption of 95% of the theoretical hydrogen. The resultant solution after filtration from the catalyst was assayed by coupling with diazotized p-toluidine and found to contain 45.4 parts of phenylenediamine. This is 88.2% of the theoretical yield.

Example 6

80 parts of m-dinitrobenzene (S.P. 89° C.) was dissolved in 320 parts of butyrolactone. This solution was hydrogenated with 12.5 parts of the same 5% palladium on charcoal catalyst, described in Example 1, at 50° C. and 50 p.s.i.g. hydrogen pressure. The reduction took 5 hours and absorbed 75% of the theoretical hydrogen. Assay of the solution, filtered from the catalyst, by coupling with diazotized p-toluidine gave a yield of 36.2 parts of phenylenediamine or 71.5% of the theoretical yield.

Example 7

A solution of 80 parts of m-dinitrobenzene (S.P. 89° C.) in 320 parts of methyl pyrrolidone was hydrogenated at 50° C. and 50 p.s.i.g. hydrogen pressure, using as catalyst 5 parts of the same 5% palladium on charcoal catalyst described in Example 1. The reduction took 31 hours, and absorbed 105% of the theoretical hydrogen. Coupling with diazotized p-toluidine indicated a yield of 47.9 parts of m-phenylenediamine or 93.2% of the theoretical yield. Isolation of the m-phenylenediamine by fractional distillation yielded 46 parts or 89.3% of the theoretical yield of m-phenylenediamine having a solidification point of 62.9° C.

Example 8

80 parts of m-dinitrobenzene (S.P. 89° C.) was dissolved in 320 parts of 2% pyridine and the solution hydrogenated at 50° C. and 50 p.s.i.g. hydrogen pressure, using 5 parts of the 5% palladium on charcoal catalyst described in Example 1. The reduction took 17 hours and 89% of the theoretical hydrogen was absorbed. Coupling the filtered solution with diazotized p-toluidine indicated a yield of 13 parts of phenylenediamine or 25.2% of the theoretical.

Example 9

A solution of 80 parts m-dinitrobenzene (S.P. 89° C.) in 320 parts dimethyl formamide was hydrogenated at 50–60° C. and 50 p.s.i.g. hydrogen pressure using 10 parts of a commercial 0.3% palladium on silica gel catalyst (0.03 part palladium), supplied by the American Platinum Works. The reduction took 13 hours and absorbed 106% of the theoretical hydrogen. Workup of the reaction products, as described in Example 2, gave 46.1 parts or 89.5% of the theoretical yield of m-phenylenediamine having a solidification point of 63.0° C.

Example 10

This was run exactly as Example 9, except as catalyst was used 10 parts of a 0.5% palladium on alumina (0.05 part palladium) supplied by American Platinum Works. The hydrogenation took 5 hours and absorbed 102% of the theoretical hydrogen. Workup of the reaction products yielded 47 parts or 91.3% of the theoretical of m-phenylenediamine having an S.P. of 63.05° C.

Example 11

160 parts of mixed dinitrotoluenes having an S.P. of 55.8° C. and approximately the following composition: 75% 2,4-dinitrotoluene, 21% 2,6-dinitrotoluene, and 4% other isomers, was dissolved in 640 parts of dimethyl formamide. This solution was hydrogenated at 50° C. and 50 p.s.i.g. hydrogen pressure, using as catalyst 10 parts of the 5% palladium on charcoal catalyst described in Example 1 (0.5 part of palladium). The reduction was made in a 2 l. stirred autoclave, and was complete in 3 hours with a hydrogen absorption of 105% of the theoretical. Isolation of the mixed toluenediamines by filtration from the catalyst and fractional distillation gave 95.3 parts or 89.3% of the theoretical yield of mixed toluenediamines. This product had an S.P. of 85° C. and a purity of 99% by coupling with diazotized p-toluidine.

Example 12

80 parts of the mixed dinitrotoluenes, described in Example 11, was dissolved in 320 parts of the ethyl ether of ethylene glycol (Cellosolve) at 50° C. and the mixture hydrogenated at 70° C. and 25 p.s.i.g. hydrogen pressure using 10 parts of a 1% palladium on charcoal catalyst (0.1 part palladium) supplied by the American Platinum Works. The reduction took 3 hours and absorbed 105% of the theoretical hydrogen. Isolation of the mixed toluenediamines as in Example 11 gave 47.5 parts or 89% of the theoretical yield.

Example 13

A solution of 80 parts of m-dinitrobenzene in 320 parts of the methyl ether of ethylene glycol was hydrogenated at 80° C. and 100 p.s.i.g. hydrogen pressure, using 5 parts of Raney nickel (supplied by the Raney Catalyst Co.) as catalyst. The reduction was complete in 5 hours, with the absorption of 103% of the theoretical hydrogen. Assay of the products as in Example 5 showed a yield of 46.7 parts or 91% of the theoretical phenylenediamine.

Example 14

80 parts of 2,4-dinitrotoluene was dissolved in 320 parts of the methyl ether of ethylene glycol (methyl Cellosolve). This solution was hydrogenated at 40° C. and 25 p.s.i.g. hydrogen pressure, using, as catalyst, 1 part of the same 5% palladium on charcoal catalyst described in Example 1. The reduction took 10 hours, and absorbed the theoretical hydrogen. After filtering from the catalyst, pure 2,4-diaminotoluene was recovered by fractional distillation. This amounted to 50 parts, 93.2% of theory, of a pure product having a melting point of 98–101° C., and a purity of 99.8% by coupling with diazotized p-toluidine. The filtered catalyst was reused several times with comparable results.

Example 15

80 parts of ortho-dinitrobenzene was dissolved in 320 parts of the methyl ether of ethylene glycol. This solution was hydrogenated at 50° C. and 50 p.s.i.g. hydrogen pressure, using 2 parts of the 5% palladium on charcoal catalyst described in Example 1. The reduction took 2½ hours and absorbed the theoretical hydrogen. After filtering from the catalyst, pure orthophenylene diamine was recovered by fractional distillation. This amounted to 46.3 parts or 90% of theory yield of the pure orthophenylene diamine having a melting point of 100–101° C. (Lit. 102° C.)

Example 16

60 parts of the mixed dinitrotoluene described in Example 11 was dissolved in 240 parts of the methyl ether of ethylene glycol. This solution was hydrogenated at atmospheric pressure and 25° C. in a stirred round-bottom glass flask, using 1 part of a 5% palladium on charcoal catalyst (.05 part palladium). This was a commercial catalyst obtained from Baker & Co. The theoretical hydrogen was absorbed in 20 hours. Isolation of the mixed toluenediamines, as in Example 11, gave 48 parts, or 90% of the theoretical yield. The product was 99.5% pure by coupling with diazotized p-toluidine.

Example 17

This was the same as Example 16, except that 3 parts of a 0.5% platinum supported on alumina pellets was used as catalyst. This was a commercial "platforming" catalyst. The reduction took 12 hours, and gave the same yield and quality of product described in Example 16.

Example 18

80 parts of a mixture of dinitroethylbenzenes, produced by the nitration of orthonitroethylbenzene and containing essentially isomeric m-dinitroethylbenzenes, was dissolved in 320 parts of the methyl ether of ethylene glycol (methyl Cellosolve). This solution was hydrogenated at 60° C. and 50 p.s.i.g. hydrogen pressure, using as catalyst 2 parts of the same 5% palladium on charcoal catalyst, described in Example 1. The reduction was completed with the absorption of 105% of the theoretical hydrogen. After filtering from the catalyst, the production of mixed diaminoethylbenzenes was established by coupling an aliquot of the solution with diazotized p-toluidine.

It will be apparent that the foregoing examples are illustrative of the present invention, and that substantial modifications may be made therein without departing from the scope thereof. Thus, in the foregoing examples, while the hydrogenation reactor was charged with the total amount of dinitrobenzene to be hydrogenated, it would be possible to prepare a solution of the dinitrobenzene to be hydrogenated in a solvent of the type contemplated, and add additional quantities of said solution during the course of the hydrogenation, so long as throughout the course of the hydrogenation there was a homogenous solution of the dinitrobenzene present for hydrogenation, the diamine formed in the hydrogenation and any water formed in the hydrogenation, the only separate phase being the solid catalyst.

While the foregoing examples describe batch operation of the process of the present invention, it will be apparent that the process is adaptable to continuous operation, and has been successfully operated in a continuous manner. In such a continuous operation, the catalyst may be present as a fixed bed, or, if desired, fluidized bed may be employed. The catalyst may either be maintained in the reactor, or continuously added to the reactor (for instance, along with the feed) and withdrawn from the reactor along with the product, separated from the product and returned to the reactor. If it is desired to operate in a continuous manner, the feed to the reactor advantageously could be a solution of a polynitro aromatic compound to be hydrogenated in a solvent, which will also dissolve the diamine formed, and the water formed in the hydrogenation. From the reactor there can be withdrawn a solution in the solvent of the diamine and water formed in the reaction, along with any unhydrogenated material. In the event that there is any unhydrogenated material in the material withdrawn from the reactor, this can be separated by suitable means, such as distillation, and returned to the feed.

It will also be apparent that, while dinitro benzene, particularly, m-nitrobenzene, and other dinitro benzenes, and their isomers or mixtures of isomeric dinitrobenzene and simply substituted dinitrobenzenes, e.g., dinitrotoluenes, and dinitro ethyl benzenes were employed in the foregoing examples, that the process of the present invention is of general applicability to the catalytic hydrogenation of polynitro aromatic compounds, and, if desired, products, intermediate of the aromatic nitro compounds and the corresponding aromatic amines, may be employed. As previously indicated, substantial advantages are obtained so long as the nitrogen compounds being reduced are in a monomolecular form, i.e., the nitrogene substituents on the ring are in the nitroso or hydroxylamine form (higher than the azoxy stage).

Also, as previously indicated, the reduction of the several nitro groups present as substituents on the polynitro compound, proceeds in a substantially step-wise manner, so that, if, for example, a dinitro benzene is being reduced, there is first obtained a substantial amount of product consisting of mononitro aniline, before any substantial amount of the diamino-benzene is obtained. If desired, the process may be carried only so far as the mononitro-monoamino stage, and the mononitro-monoamino compound recovered as the desired product for use, or, since the explosibility of the monoamine-mononitro compound is, substantially less than that of the dinitro compound, further reduction to the diamine may be effected in some other manner, since, so far as reducing the danger of explosion is concerned, it may no longer be necessary to have only one liquid phase present during the reaction. While such operations are feasible, it is ordinarily not economically justified if the diamine is the desired product.

The reduction of a dinitro compound to the mononitro-monoamino compound is illustrated by the following example of the production of meta-nitro aniline from dinitrobenzene:

Example 19

Meta-dinitrobenzene was reduced, as in Example 4, in solution in the methyl ether of ethyleneglycol (methyl Cellosolve), using 10% palladium on charcoal hydro-

genation catalyst. The hydrogenation was stopped when 75% of the amount of hydrogen, theoretically necessary for the production of the meta-diaminobenzene, had been absorbed. The reaction mixture was then worked up as follows:

The reaction mixture was filtered to remove the catalyst, and the solvent then removed by distillation. A small amount of water was added to the residue, and it was then filtered. This removed the diamine formed in the reaction. The residue was then extracted with dilute hydrochloric acid, and filtered. The filtrate contained the meta-nitro aniline hydrochloride, and was neutralized with caustic soda, whereby the meta-nitro aniline was precipitated and recovered by filtration and dried. The thus recovered meta-nitro aniline had a melting point of 109°–110° C., and the yield amounted to 65%, based on the amount of meta-dinitrobenzene charged, or 80% of theoretical, based on the amount of dinitrobenzene charged, and the amount of meta-phenylenediamine produced.

I claim:

1. In a process for the catalytic hydrogen reduction of aromatic polynitro compounds to form the corresponding polyamine compounds, wherein a polynitro compound and hydrogen are introduced into a hydrogenation zone, and therein reacted in the presence of a hydrogenation catalyst selected from the group consisting of nickel and the platinum group of metals, to thereby form an amino compound corresponding to the polynitro compound introduced; the improvement which comprises introducing in the said hydrogenation zone a solution, liquid at the temperature and pressure maintained in such zone, of said polynitro compound in an inert solvent therefor, said solvent being also a solvent for the polyamine and water formed in the hydrogenation, the concentration of polynitro compound in said solvent being such that there is maintained in said hydrogenation zone throughout the hydrogenation, a single-phase liquid solution of said solvent, polynitro compound, corresponding polyamine and water, removing from said hydrogenation zone a solution in said solvent containing the polyamine and water formed therein, and recovering the polyamine from said solution.

2. The process as defined in claim 1, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic polyamines formed in the reaction.

3. In a process for the catalytic hydrogen reduction of aromatic dinitro compounds to form the corresponding diamines, wherein a dinitro compound and hydrogen are introduced into a hydrogenation zone, and therein reacted in the presence of a hydrogenation catalyst selected from the group consisting of nickel and the platinum group of metals, to thereby form the diamines corresponding to the dinitro compound introduced; the improvement which comprises introducing in the said hydrogenation zone a solution, liquid at the temperature and pressure maintained in such zone, of said dinitro compound in an inert solvent therefor, said solvent being also a solvent for the diamines and water formed in the hydrogenation, the concentration of dinitro compound in said solvent being such that there is maintained in said hydrogenation zone throughout the hydrogenation, a single-phase liquid solution of said solvent dinitro compound and diamines, and water formed therein, removing from said hydrogenation zone a solution in said solvent containing the diamines and water formed therein, and recovering the diamines from said solution.

4. The process as defined in claim 3, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the diamines formed in the reaction.

5. The process as defined in claim 3, wherein the dinitro compound specified is a benzenoid dinitro compound.

6. The process defined in claim 3, wherein the dinitro compound specified is a benzenoid dinitro compound, and wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkylethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic diamines formed in the reaction.

7. The process as defined in claim 3, wherein the dinitro compound specified is dinitro benzene.

8. The process as defined in claim 7, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic diamines formed in the reaction.

9. The process as defined in claim 3, wherein the dinitro compound specified is dinitro toluene.

10. The process as defined in claim 9, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic diamines formed in the reaction.

11. The process as defined in claim 3, wherein the dinitro compound specified is dinitroethylbenzene.

12. The process as defined in claim 11, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and a corresponding aqueous solution of the aromatic diamines formed in the reaction.

13. In a process for the catalytic hydrogen reduction of aromatic polynitro compounds, wherein at least one of the nitro groups is reduced to an amino group, and wherein a polynitro compound and hydrogen are introduced into a hydrogenation zone, and therein reacted in the presence of a hydrogenation catalyst selected from the group consisting of nickel and the platinum group of metals; the improvement which comprises introducing into the said hydrogenation zone a solution, liquid at the temperature and pressure maintained at such zone of said polynitro compound, and an inert solvent therefor, said solvent being also a solvent for the amino compound and water formed in the hydrogenation, and the concentration of polynitro compound in said solvent being such that there is maintained in said hydrogenation zone, throughout the hydrogenation reaction, a single phase liquid solution of said solvent, polynitro compound, amino compound and water formed; removing from said hydrogenation zone a solution in said solvent, containing the amino compound and water formed in such zone, and recovering such amino compound from such solution.

14. The process as defined in claim 13, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic polyamines formed in the reaction.

15. In a process for the catalytic hydrogen reduction of an aromatic dinitro compound to form the corresponding mono-nitro-monoamino compound, wherein the aro-

matic dinitro compound to be reduced, and hydrogen, are introduced into a hydrogenation zone and, therein, reacted in the presence of a hydrogenation catalyst selected from the group consisting of nickel and the platinum group of metals to thereby form the monoamino-mononitro compound corresponding to the dinitro compound introduced; the improvement which comprises introducing into said hydrogenation zone a solution, liquid at the temperature and pressure maintained in such zone, of said dinitro compound in an inert solvent therefor, said solvent being also a solvent for the amino compounds and water formed in the hydrogenation, and the concentration of dinitro compound in said solvent being such that there is maintained in said hydrogenation zone, throughout the hydrogenation, a single phase liquid solution of said solvent, dinitro compound and amino compound and water formed therein; continuing the hydrogenation until a substantial amount of said monoamino-mononitro compound is formed, and then removing from said hydrogenation zone a solution of said solvent containing the mononitro-monoamino compound and water formed therein, and recovering the monoamino-mononitro compound from said solution.

16. The process as defined in claim 15, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic polyamines formed in the reaction.

17. The process as defined in claim 16, wherein the dinitro compound, which is reduced, is m-dinitrobenzene and m-nitroaniline, is recovered.

18. The process as defined in claim 17, wherein the inert solvent specified is selected from the group consisting of morpholine, N-alkylmorpholines, butyrolactone, ethylenediamine, piperidine, N-alkylpiperidine, pyridine, N,N'-dialkylamides, lower alkyl ethers of ethylene glycol and diethylene glycol, and a concentrated aqueous solution of the aromatic polyamines formed in the reaction.

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