CATALYTIC SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLES (A REVIEW)

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The process of the catalytic synthesis of a number of nitrogenous heterocyclic compounds based on the utilization of reactions involving the amination of oxygen-containing heterocycles, the dehydration cyclization of amino alcohols, the deamination of di- and polyamines, and the intermolecular dehydration cyclization of glycols with diamines have been considered.

The first heterogeneous-catalytic methods for the vapor-phase synthesis of nitrogen-containing heterocycles were based on the amination of acetylene and the intermolecular dehydration cyclization of the simplest aliphatic aldehydes and ammonia. Using aluminum oxide as a catalyst, A. E. Chicibabin obtained pyridine bases from acetylene or acetaldehyde and ammonia [1, 2]. However, due to the low selectivity of the formation of the individual members of this class, this reaction did not undergo further development for many years.

In the last few years the interest of scientists around the world in the catalytic synthesis of pyridine bases has again been raised owing to the expanding areas for their application and their low content in coal tar [3-6].

In the fifties there were a number of reports on the heterogeneous-catalytic cyclization of amino alcohols, diamines, and polyamines to form piperazine derivatives with the use of both oxide (vapor-phase processes) and metallic (liquid-phase processes) catalysts [7, 8].

The material presented in reviews [7, 8] covers the literature data only up to 1975, inclusively. The data on the catalytic synthesis of nitrogen-containing heterocycles on the basis of the exchange of the heteroatom in oxygen-containing heterocyclic compounds were beyond the scope of those reviews. Below we shall attempt to analyze the catalytic reactions that have been described on the basis of the nature of the functional groups in the molecule of the compound being converted and the properties of the catalyst used, and generalize the data which have appeared during the last few years as well.

The literature material has been arranged in accordance to the structure of the original compounds and the nature of the conversions which they undergo and is divided into sections devoted to the conversion of oxygen-containing heterocycles, the dehydration cyclization of amino alcohols, the deamination of di- and polyamines, and the intermolecular dehydration cyclization of glycols with diamines.

1. CATALYTIC AMINATION OF OXYGEN-CONTAINING HETEROCYCLES

The interconversion of heterocycles discovered by Yu. K. Yur'ev in the case of the replacement of the oxygen atom in furan and tetrahydrofuran by atoms of other elements, which is known as the Yur'ev conversion of heterocycles, is the basis of a convenient and easily performed synthesis of pyrrole and pyrrolidine derivatives [9, 10]. In its general form, this reaction may be represented in the following manner:

$n = 2, 4, 5$; $R = H, Alk$.

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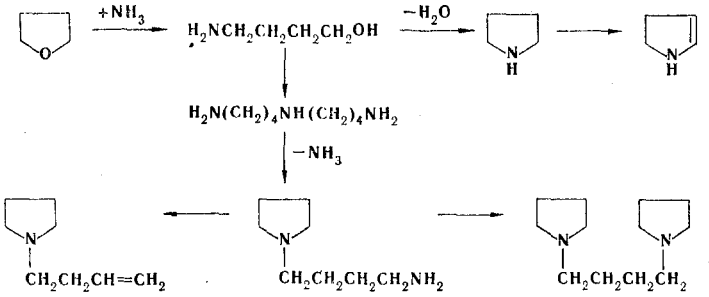
Aluminum oxide, aluminosilicates, certain types of zeolites, and metal phosphates are used as catalysts. The yield of the nitrogenous heterocycles ranges from 27 to 80%, depending on the composition of the catalyst [9, 41]. The best results were obtained on modified and bicationic phosphates, modified aluminum oxide [31], and zeolite L in the hydrogen form [28]. The conversion of tetrahydropyran into piperidine has also been carried out on the latter. The reaction of derivatives of furan and tetrahydrofuran with ammonia and amines afforded the corresponding pyrroles and pyrrolidines with high yields [17, 19, 20].

Investigations in the last few years [31] carried out with the use of highly sensitive methods of analysis have made it possible to establish the presence of compounds with an open carbon chain along with the products of heteroatom substitution. For example, up to 37% (3-butenyl)pyrrolidine (as calculated relative to the amount of the original compound reacted) forms in the reaction of tetrahydrofuran with ammonia. 1,4-Dipyrrolidinobutane and N-(4-aminobutyl)pyrrolidine were also detected. The formation of 4-amino-1-butanol and dibutylenetriamine as intermediates was also postulated in these conversions:



The products of the amination of ethylene oxide [32-34, 37, 40, 41] were found to contain cyclic nitrogenous bases (pyridine, α-picoline, γ-picoline, and piperazine) and compounds of linear structure (acetaldehyde, α-aminoethanol, β-aminoethanol, and ethylenediamine), whose formation was interpreted on the basis of a step of ring opening in the original molecule. On the basis of a thermodynamic investigation of the possible paths for the ammonolysis of ethylene oxide to form ethylenimine it has been postulated that ethylenimine forms predominantly through the $\cdot CH_2CH_2O^-$ biradical and the amination product of the latter, i.e., β-ethanolamine [42].

Thus, the analysis of the data on the catalytic amination of cyclic ethers makes it possible to view the cyclization of amino alcohols as a step in the formation of nitrogenous heterocycles from the corresponding oxygen analogs. The data on the catalytic conversions of amino alcohols will be the subject of the next section of the review.

2. CATALYTIC CYCLIZATION OF AMINO ALCOHOLS

The formation of heterocycles in the catalytic conversion of amino alcohols most often occurs as a result of intermolecular dehydration cyclization (aminoethanol and aminopropanols) or intramolecular dehydration (aminobutanol, hydroxyethylethylenediamine, hydroxyethylpiperazine, etc.). Reactions of both types, however, take place on most catalysts, causing comparatively low selectivity with respect to each of the products.

2.1. Dehydration Cyclization of Amino Alcohols

The largest number of studies has been devoted to investigations of the dehydration cyclization of β-aminoethanol. Depending on the conditions of the reaction (vapor-phase or liquid-phase processes) and the catalyst (oxides or metals), products of intra- and intermolecular cyclization, dehydrogenation, hydrogenolysis, and cracking are detected in the catalysates. Over the course of a number of years, the intermolecular cyclization of aminoethanol to form piperazine was at the center of attention [7, 8]. Aluminum oxide, aluminosilicates, and metals supported on aluminum oxide were employed as catalysts [43-58]. However, the yield of piperazine did not exceed 50%, and the catalysate contained considerable amounts of various secondary reaction products [43, 44], such as 2,5-dimethylpiperazine, ethylene, pyrrole, and morpholine. It was postulated that the conversion of ethanolamine on aluminum oxide takes place in three main directions: 1) intramolecular cyclization due to the elimination of two water molecules formed as a result of the interaction of the hydroxyl groups with hydrogen atoms of the amino groups in two ethanolamine molecules, which is assigned a reversible character (on the basis of the detection of ethanolamine among the products of the

conversion of piperazine in an aqueous medium over the same catalyst); 2) the intramolecular dehydration of ethanolamine, which takes place with the same probability both when a hydroxyl group interacts with a hydrogen on the adjacent carbon atom and with a hydrogen atom in the amino group and results in the formation of vinylamine or aziridine, respectively, whose further conversions are the sources of pyrrole or 2,5-dimethylpiperazine; 3) intramolecular deamination, which causes the formation, first, of ethylene oxide and ammonia, which are converted into diethanolamine and morpholine, as well as into ethylenediamine and piperazine. The composition of the gaseous products was not given in [43, 44]. Using GLC, Anderson [45] found about 20 compounds in a similar catalysate; besides the aforementioned compounds he identified, methyl- and ethylamine, ethylenimine, 2,5-dimethylpyrrole, pyrazine, methylpyrazine, 2,5-dimethylpyrazine, N-ethyl-2,5-dihydropyrazine, N-ethyl- and N,N'-diethylpiperazine, triethylenediamine, β-aminoethylpiperazine, and β-hydroxyethylpiperazine. In the liquid-phase process Balandin et al. [46-49] established the presence of hydroxyethylenediaminine, N-β-hydroxyethyl- and N-β-aminoethylpiperazine, diethylenetriamine, N-ethylethylenediaminine, N,N'-bis(aminoethyl)piperazine, N-aminoethylaminoethylpiperazine, 4-hydroxyethyldiethylenetriamine, 1-hydroxyethyldiethylenetriamine, dipiperazineethane, and N,N'-dihydroxyethylpiperazine in addition to piperazine in the conversion products of aminoethanol on cobalt supported on aluminum oxide and on other catalysts.

The formation of considerable amounts of triethylenediamine attests to the occurrence of processes with the participation not only of two, but even of three ethanolamine molecules [50, 51]. The modification of aluminum oxide by acids, for example, by phosphoric acid, has a favorable influence on the formation of triethylenediamine [52]. Ethanolamine undergoes deamination to a small extent: Morpholine forms with a yield no higher than 4%.

The predominant occurrence of the intramolecular dehydration of ethanolamine has been established on certain catalysts. Ethylenimine forms as the only reaction product over tungsten trioxide under the conditions of dilution of the ethanolamine vapor with nitrogen (4.5 mole per mole of the amino alcohol) at 400°C, the extent of conversion of the original compound not exceeding 4% [53]. Catalysts on which the extent of conversion of aminoethanol is significantly higher have been obtained by supporting tungsten oxide on pumice, aluminosilicates, magnesium oxide, and silica gels, as well as the modification of tungsten oxide by additions of oxides of nickel, lithium, molybdenum, bismuth, and tin, but the selectivity of the formation of ethylenimine then decreased. The extent of conversion of aminoethanol reached 45% with a selectivity with respect to aziridine of the same order on a catalyst consisting of tungsten trioxide (42%), molybdenum trioxide (3%), and an aluminosilicate (55%). Acetonitrile was found as the main conversion product on an aluminum–chromium catalyst in [54], i.e., dehydrogenation occurs along with dehydration. A dehydrogenation reaction accompanies the dehydration reaction associated with deamination in the conversion of ethanolamine on an aluminum–zinc–chromium catalyst, i.e., pyrrole was obtained with a 10% yield, and the conversion of diethanolamine (deamination does not occur) into pyrrole takes place with a higher yield [55].

The favorable effect of the dilution of the vapor of the alcohol with ammonia, hydrogen, and water vapor on the course of the conversion of aminoalkanols has been noted [56]. At an elevated pressure the main direction of the reaction in an aqueous solution is the exchange of the hydroxyl group by an amino group, and ethylenediamine is obtained as the main product [57]. On zeolites X, Y, and A and on mordenite modified by rare-earth elements the main product obtained from aminoethanol in the presence of ammonia is triethylenediamine, while the main product from diethanolamine is piperazine [58]. In the liquid-phase process the alkyl and hydroxyalkyl derivatives of ethanolamine are converted on oxide catalysts into nitrogenous heterocyclic compounds with a higher yield than in unsubstituted ethanolamine [59-78]. N-Methylaminoethanol also undergoes demethylation in the vapor phase. The favorable influence of substituents on the cyclization reaction is more strongly displayed when the process is carried out in the liquid phase [62], N- and C-alkylpiperazines being obtained respectively. N-alkyl- and N-phenylmorpholines have been obtained from the corresponding derivatives of diethanolamine with yields up to 67% [61]. Diethanolamine and diisopropanolamine are converted on Raney nickel at 200°C in the presence of ammonia into piperazine and 2,5-dimethylpiperazine with 33 and 82-68% yields, respectively [62, 63]. In the vapor phase the selectivity of the conversion of diethanolamine into morpholine is increased to 98%, if morpholine is added to the reaction medium instead of ammonia [64]. A similar effect was also observed for the conversion of hydroxyethylpiperazine [65]. Like ethanolamine, under certain conditions diethanolamine is dehydrogenated to form pyrrole [55, 66]. O-Hydroxyethylethanolamine is converted predominantly into morpholine [67, 68]. Significant amounts of morpholine

have also been obtained in the case of the conversion of N-(β-hydroxyethyl)ethylenediamine [69, 70], and 2-methylpiperazine has been obtained from N-(β-hydroxypropyl)ethylenediamine [71].

Derivatives of aminoethanol in which the nitrogen of the amino group is incorporated into a piperazine ring undergo intramolecular dehydration and cyclization [72-75]. The conversion of mixtures containing hydroxyethylpiperazine, aminoethylpiperazine, and diethylenetriamine results in the formation of methyl- and ethylpiperazines, which are hydrogenolysis and cracking products [65].

2-Aminocyclooctanol is converted on Raney nickel into the 2,3,5,6-bis-(hexamethylene) derivatives of piperazine and pyrazine with yields equal to 66 and 8 and to 7 and 82%, respectively, depending on the nature of the diluent [77]. N-Methyl-N-(3-aminopropyl)aminoethanol gives homopiperazine and N-methylhomopiperazine on a dehydration catalyst under an elevated pressure [78].

The catalytic dehydration of 1-amino-2-propanol in the liquid phase on nickel catalysts results in the formation of 2,5-dimethylpiperazine, whose yield is higher in all cases than the yield of piperazine from aminoethanol [79-82]. The ratio between the stereoisomers varies as a function of the catalyst. According to the total yield of both isomers, the most efficient catalyst is Raney nickel, which surpasses both Raney cobalt and the iron–copper–cobalt catalyst in [84].

Besides dimethylpiperazine, a certain quantity of dimethylpyrazine was also detected in the reaction products, and for this reason various opinions regarding the sequence of their formation have been advanced. According to [85], the primary conversion product on the nickel catalyst is 2,5-dimethylpyrazine, which is hydrogenated to 2,5-dimethylpiperazine. However, there are also data which indicate the predominant formation of the piperazine derivative in comparison to the pyrazine derivative [86] when nickel on a support serves as the catalyst. On phosphate catalysts in the presence of ammonia, 1-amino-2-propanol is converted not only into 2,5-dimethylpiperazine, but also into a mixture of isomers of trimethyltriethylenediamine [87]. Under similar conditions 1-N-(β-hydroxypropyl)amino-3-aminopropane gives mono- and dimethylhomopiperazines [88]. Homopiperazine and N-methylhomopiperazine have been obtained from the corresponding β-hydroxyethyl derivatives of 1,3-diaminopropane and N-methyl-1,3-diaminopropane [89]. It has been shown in the example of the conversions of 1-amino-2-propanol that dehydration cyclization with a higher yield of the piperazine base occurs on nickel supported on diatomaceous earth [90] than on Raney nickel [91].

4-Amino-1-butanol is converted in the vapor phase on aluminum oxide at 400°C in a nitrogen atmosphere, as well as in the presence of ammonia, into pyrrolidine (with 37 and 29% yields, respectively) and pyrrole (with yields up to 10%). Strong carbonizing of the catalyst was noted in this case [92].

2.2. Mechanism of the Dehydration Cyclization of Aminoalkanols

Products of intermolecular or intramolecular cyclization form as the main products in the catalytic process, depending on the structure of the amino alcohol. 1-Amino-2-alkanols usually cyclize intramolecularly to form piperazine, its alkylated derivatives, and triethylenediamine. If the carbon atoms of the functional groups are separated by two methylene groups, the predominant process is intramolecular cyclization.

Up to 40% acyclic amines (ethylamine, ethylenediamine) forms along with the cyclization products from ethanolamine in the vapor phase, depending on the reaction conditions, viz., the temperature, dilution with inert gages, and the time of contact with the aluminum oxide [45, 52], while amino- and hydroxyethylpiperazine, triethylenetetraamine, and tetraethylenepentaamine are the main by-products in the liquid phase on nickel- and cobalt-containing supported catalysts. Such products, which can be recovered from the catalysts and which may be considered as intermediates in the formation of heterocycles, for example, N-(β-hydroxyethyl)ethylenediamine, are of special interest. Back at the very beginning of the search for a method for the catalytic synthesis of piperazine it was shown that N-(β-hydroxyethyl)-ethylenediamine is converted into piperazine with a 50-60% yield when it is passed over catalysts such as the oxides of aluminum, thorium, titanium, and zirconium at 400-500°C [69]. Since the formation of piperazine is realized by intramolecular dehydration in this case, the reaction proceeds fairly readily when the water is distilled off from the melt [93]. The

application of a catalyst such as nickel on kieselguhr makes it possible to increase the yield of the heterocycle. In the presence of a copper–chromium oxide catalyst under elevated pressure, the yield of piperazine reaches 78.2% [76]. 2-Methylpiperazine has been obtained with an 80% yield from N-(β-hydroxypropyl)ethylenediamine on a nickel catalyst. An increase in the yield of the 2-alkylpiperazines occurs in the conversion of N-(β-hydroxyalkyl)-1,2-alkylenediamines when water vapor or hydrogen is added to the reaction mixture [92].

The role of N-(β-hydroxyethyl)ethylenediamine in the process of the conversion of aminoethanol into piperazine on a Co/Al_2O_3 catalysate in the liquid phase was studied by A. A. Balandin et al. [47], who discovered that the plots of the accumulation of hydroxyethylethylenediamine, ethylenediamine, and diethylenetriamine in the catalysate passes through a maximum and that these compounds may, therefore, be viewed as intermediates in the formation of piperazine.

It is interesting to note that both in the liquid-phase process and the vapor-phase process the yield of piperazine increases when ammonia is introduced into the reaction zone. This effect may be attributed, on the one hand, to the expulsion of the heterocycle from the surface of the catalyst and the prevention of its further conversions and, on the other hand, to the fact that an ammonia excess inhibits the exchange of nitrogen for oxygen, which might occur on the catalysts used as a result of the interaction of the water formed in the dehydration process with the amino groups in both the original and intermediate compounds. The latter hypothesis is supported by the presence of certain amounts of aminoethanol in the conversion products of hydroxyethylethylenediamine [48].

3. DEAMINOCYCLIZATION OF DI- AND POLYAMINES

The formation of heterocycles from amino compounds occurs either by means of the dehydrogenation cyclization of secondary amines or as a result of the deaminocyclization of di- and polyamines.

The catalytic dehydrogenation cyclization of secondary amines usually does not affect the amino groups, and its mechanism is similar to the catalytic aromatization of hydrocarbons [94-96], which is realized in a complete cycle of consecutive dehydrogenation steps [97, 98]. The conversion of secondary amines has been studied on the model reactions of dimethylamine [99] and diethylamine [100-102]. The catalysts for the dehydrogenation cyclization of diethylamine include platinum, iridium, ruthenium, osmium, rhodium, and palladium supported on charcoal. The dehydrogenation cyclization of α,δ-diamines on an aluminum–chromium–potassium catalyst underlies a method for the synthesis of alkylpyrazines [103-105]. Primary amines are converted into secondary amines on nickel, platinum, and other metallic catalysts as a result of intermolecular deamination [106].

The catalytic deaminocyclization of amines containing two primary amino groups has been studied most extensively in the model conversion of diethylenetriamine into piperazine [8]. Raney nickel [107-121], as well as Raney cobalt [110, 111], and nickel in the form of the boride [116] or supported on various oxides [115, 119, 121, 122] have been employed most often as catalysts in the liquid-phase process. On nickel supported on chromium oxide and on nickel boride the rate of the conversion of diethylenetriamine is directly proportional to the quantity of the catalyst, but the activity of the nickel boride catalyst is 1.5 times lower than that for nickel supported on chromium oxide, while the selectivity with respect to piperazine is comparable [122].

The main conversions taking place under the conditions of the liquid-phase process are the intramolecular deamination of diethylenetriamine, the bimolecular distribution of the amino groups, and multimolecular deamination. Both the original diethylenetriamine and the piperazine also undergo hydrogenolysis to a small extent [107].

The deaminocyclization of diethylenetriamine in the vapor phase was studied in the presence of typical dehydration catalysts, for example, aluminum oxide, aluminosilicates, and the oxides of thorium, titanium, and zirconium [123-146]. However, the extent of conversion of diethylenetriamine into piperazine in the 300-600°C range did not exceed 25%. The synthesis of piperazine from diethylenetriamine and of triethylenediamine from N-(β-aminoethyl)-piperazine has also been carried out on aluminum phosphate [124], on aluminosilicates [125-127], and on silicate cracking catalysts under elevated pressure [128]. Methylpiperazines form when methylethylenediamine, its dimers, and its trimers are converted on aluminosilicate at 330-370°C [129]. On tungsten trioxide the intramolecular deaminocyclization of aminoethylpiperazine takes place with a low selectivity [130, 131]. Triethylenediamine has been obtained on the basis of the higher oligomers of ethylenediamine on kaolin [132, 133]. The

synthesis of triethylenediamine has been carried out on the phosphates of aluminum, calcium, lithium, and zinc by converting N-(β-aminoethyl)piperazine, as well as N-(β-hydroxyethyl)-piperazine [88].

The study of the conversions of diethylenetriamine on aluminum oxide modified by various additions, as well as on silica gel coated with magnesium oxide, on a phosphate glass, and on Prosyanaya kaolin revealed the formation of comparable quantities of piperazine and ethylenediamine and a certain quantity of pyrazine [134]. The secondary products of the conversion of diethylenetriamine include polyethylenepolyamines, whose yield decreases with increasing temperature with a simultaneous increase in the yield of the low-molecular-weight gaseous products.

The modification of aluminum oxide by molybdenum trioxide causes enhancement of the dehydrogenating activity of the catalyst, i.e., the yield of pyrazine increases. On a catalyst containing 5% molybdenum oxide on aluminum oxide, pyrazine becomes the main conversion product of diethylenetriamine [135]. An especially high yield of pyrazine bases is obtained when heteropoly acids of molybdenum or tungsten are supported on aluminum oxide, while modification of the support by phosphoric acid or boric acid causes an increase in the yield of triethylenediamine [136], a similar pattern being observed in the dependence of the nature of the conversions on the composition of the catalyst for ethylenediamine [137]. Ethylenediamine is more reactive than diethylenetriamine, but the nature of the conversions of both compounds is identical [138]. A new catalyst for the synthesis of pyrazine bases from diethylenetriamine consisting of Al_2O_3 with additions of 0.65% P_2O_5, 15% MoO_3, and 0.5% CuO, which causes a total yield of pyrazines on the order of 70% with a pyrazine–methylpyrazine ratio equal to 1.5:1, was proposed in [138]; the replacement of phosphorus pentoxide by boron trioxide or silicon dioxide in this catalyst makes it possible to increase the fraction of unsubstituted pyrazine in the total pyrazine bases.

A comparison of the values of the energies of formation of the intermediate complexes of the deamination, dehydrogenation, and hydrogenolysis reactions on aluminum oxide and molybdenum oxide showed that the probability of the occurrence of deamination and hydrogenolysis at the C–N bond is high on both catalysts. On aluminum oxide the ratios between the main types of conversions of ethylenediamine and diethylenetriamine are similar, but lower temperatures are required for the former [139]. The study of the conversions of diethylenetriamine on individual oxides supported on a catalytically inert support (Chromosorb W) under pulse chromatographic conditions made it possible to establish the occurrence of the bimolecular disproportionation of the amino groups and dehydrogenation deaminocyclization [140]; N-ethyl- and N,N'-diethylpiperazine, ethylenediamine, and triethylenetetraamine were detected along with piperazine. On anhydrides of polyvalent acids and oxides of variable-valence metals, the deamination of diethylenetriamine is accompanied by reactions involving the redistribution of the hydrogen atoms, which become more intense as the temperature of the process is increased. Below 400°C on all the catalysts tested, viz., CuO, CoO, NiO, B_2O_3, Cr_2O_3, MoO_3, WO_3, kaolin, (MoO_3 + SiO_2), (MoO_3 + P_2O_5), (WO_3 + SiO_2), and (WO_3 + B_2O_3 + CoO), redistribution of the amino groups between two diethylenetriamine molecules with the formation of N-(β-aminoethyl)piperazine (triethylenediamine), ethylenediamine, and one (or two) moles of ammonia takes place. On boric anhydride, phosphoric anhydride, kaolin, and mixtures of the oxides of molybdenum or tungsten with silicon dioxide, the intramolecular deaminocyclization of diethylenetriamine is predominant [140]. On a catalyst containing molybdenum trioxide and silicon dioxide on Chromosorb W, the conversion of ethylenediamine is accompanied by cracking at the C–C bond, as is evinced by the presence of methylamine and methylpyrazine in the catalysate [141]. On the basis of a comparison of the results of the investigations of the conversions of ethyleneamines under flow and batch conditions it has been established that the formation of the products of particular deamination and deaminocyclization reactions and dehydrogenation deaminocyclization and hydrogenolytic deamination reactions takes place in parallel and simultaneously on different sites.

At low extents of conversion of ethyleneamines, their interaction with a surface occurs only with the participation of the most active sites, for example, Brønsted acids, on which determination mainly occurs [142]. More uniform catalysts provide for the synthesis of increased yields of the cyclization products. N-(2-Aminoethyl)piperazine undergoes 87% conversion on zeolite A at 390°C with the formation of about 70% cyclic products, i.e., triethylenediamine an piperazine [143]. However, the literature data regarding the application of different forms of zeolites for the realization of deamination and deaminocyclization are very sparse, and for this reason at the present time it is difficult to draw a definite

conclusion regarding the prospects of the use of catalytic systems based on zeolites not only in deaminocyclization reactions, but also in the more readily occurring dehydration cyclization reactions. When the distance between the primary amino groups in the molecule of the original diamine is increased, the probability of the occurrence of intramolecular deaminocyclization with increased selectivity for the formation of a cyclic imine increases. Hexamethylenediamine is converted on ruthenium dioxide on charcoal [144], as well as on aluminum oxide [145], into hexamethylenimine, while trimethylenediamine undergoes intermolecular diaminocyclization on both platinum metals [146] and tungsten oxide [147] with the formation of pyrimidine bases and their hexahydro derivatives as the main products.

One of the factors determining the selectivity of the formation of the nitrogen-containing heterocycles is their stability under the conditions of a catalytic process. Piperazine undergoes hydrogenolysis on Raney nickel and on nickel supported on chromium oxide under the conditions of a liquid-phase process, the products being N-ethyl- and N,N'-diethylpiperazine. The hydrogenolysis of piperazine is inhibited when unreacted diethylenetriamine is present in the reaction medium [148]. When the catalytic synthesis of piperazine is carried out in the gaseous phase, piperazine undergoes dehydrogenation [142]. The dehydrogenation of the heterocycle has also been postulated in the scheme of the mechanism of the conversions of 1,3-diaminopropane: The primary products are 2-ethyl- and 2-methylhexahydropyrimidine, which are dehydrogenated to the corresponding tetrahydro derivatives [147] or to pyrimidine bases [146] as the temperature is increased. The dependence of the features of the course of the dehydrogenation reaction on the composition of the catalyst will be considered in greater detail in section 5 of this review.

4. INTERMOLECULAR DEHYDRATION CYCLIZATION OF GLYCOLS WITH AMMONIA AND AMINES

An examination of the work in this area should unquestionably begin with the classical reactions of 1,4-glycols with ammonia on aluminum oxide investigated by Yu. K. Yur'ev [149], in which the formation of pyrrolidine was established. It may be postulated that the glycol at first undergoes intramolecular dehydration to form tetrahydrofuran, from which pyrrolidine forms as a result of the exchange of the heteroatoms with ammonia. A subsequent investigation of the intermolecular dehydration reactions of glycols and their derivatives with amines was carried out on objects for which a step of preliminary cyclization is unlikely. Both oxide and metallic catalysts with the compositions usually used in dehydration reactions (aluminum oxide and Raney nickel) served as the catalysts [149-159]. On a copper–chromium–nickel catalyst at 257-260°C, propylene glycol is converted with ammonia into dimethylpiperazine [150], and 2,3-butylene glycol is converted into 2,3,5,6-tetramethylpiperazine [152], while di- and trimethylpiperazine form from butylene glycol on Raney nickel [154]. Di(β-hydroxyethyl) ether is converted in a mixture with ammonia on a ruthenium catalyst (5% Ru/Al_2O_3) into 2-hydroxyethylethanolamine and morpholine [153]. Thus, the hydroxyl groups react with ammonia, while the ethereal oxygen atom remains intact. The amination reactions of 1,4-butanediol and ethanediol at 300-400°C on natural aluminosilicates and zeolite [155] resulted in the formation of significant amounts of pyrrolidine (and up to 3.3% tetrahydrofuran) in the former case and a large quantity of different products in the latter case. The main product of the reaction of propylene glycol with ethylenediamine on aluminum oxide when the reaction mixture was diluted with water vapor was 2-methylpiperazine [156]. In a number of studies devoted to the condensation of glycols with diamines, aluminum oxide modified by additions of alkali metal oxides, whose introduction should promote an increase in the yields of the cyclization products, was employed [157, 158]. The amination reaction of 1,2-ethanediol on Raney nickel gives aminoethanol and diethanolamine, which undergo further conversions to an insignificant extent under the conditions given [159], possibly due to the increased adsorbability of the glycol on the active sites on the surface.

5. DEHYDROGENATION IN DEHYDRATION-CYCLIZATION AND DEAMINOCYCLIZATION PROCESSES

As has previously been shown, dehydration-cyclization and deaminocyclization reactions on oxide catalysts in the vapor phase are accompanied by the formation of dehydrogenation products, whose yield varies over a considerable range as a function of the composition of the catalysts and increases with increasing temperature. Dehydrogenation products can be obtained as a result of intramolecular dehydration and deamination with the formation of olefinic compounds, which have an increased reactivity and readily cyclize, as intermediates. The formation of dehydrogenation products can also be caused by processes involving the dehydrogenation of saturated heterocycles. For example, there is extensive literature on the catalytic dehydrogenation of piperazine on palladium and on various oxides, chromates,

phosphates, and carbonates [160-178], including dehydration-cyclization and deaminocyclization catalysts. Not only the composition of the oxide systems, but also the temperature conditions of the dehydrogenation reaction of piperazine are similar to those characteristic of the reactions resulting in its formation. A high selectivity in the dehydrogenation of piperazine can be achieved when the reaction mixture is diluted by water vapor, vapors of aromatic hydrocarbons, as well as quinoline, and inert gases.

The dehydrogenation of piperazine has most often been carried out on chromite, as well as on copper oxide and copper carbonate [78, 160, 161, 164-173, 175]. A high extent of conversion of piperazine into pyrazine was observed with the use of palladium catalysts [163, 174]. It is noteworthy that the dehydrogenation of pyrazine takes place with a high yield of pyrazine (90%) on phosphorus pentoxide [172, 173]. High dehydration-cyclization and deaminocyclization temperatures promote not just the elimination of the functional groups and the hydrogen atoms. Thermolysis not only of the original amino alcohols and diamines, but also of the products of both the main and secondary reactions occurs under the conditions of a catalytic reaction. For example, morpholine is converted into pyrrole (22% yield) and acetonitrile on an aluminum–chromium catalyst at 400-440°C [178].

Thus, under the conditions of the catalytic synthesis of heterocycles there is a possibility for further conversions, whose proportions are determined by the nature and concentrations of the active sites on the surface of the catalyst, the composition of the reaction medium, and the equilibrium adsorption interactions of its components with the active sites.

6. INTERACTIONS OF AMINO ALCOHOLS, DIAMINES, AND POLYAMINES WITH CATALYSTS

Alkanols, aminoalkanols, and diamines are known to interact with metal oxides and ions to form chemical compounds of the alkoxide and ammonium-salt types of various complex compounds [179], which are attributed to playing the role of intermediates in the catalytic reaction. Nitrogen-containing heterocycles (pyrrolidine, piperazine, and morpholine) also form complexes, for example, complexes with the general formula $L_nM(CO)_{6-n}$ with carbonyls of the group VI metals [$Mo(CO)_6$ or $W(CO)_6$] [180].

A series of investigations of the interaction of amino alcohols with catalysts under the conditions of the liquid-phase synthesis of piperazine was carried out by E. I. Karpeiskaya. It was found that the conversion of aminoethanol on Co/Al_2O_3 is accompanied by the formation of soluble complexes of cobalt, which do not have catalytic activity themselves, although if such a complex is added to a catalyst, an increase in the yield of piperazine is observed [181]. It has been postulated that the conversion of such a complex takes place according to a mechanism of nucleophilic substitution in the ethanolamine molecule with the elimination of ammonia and water molecules, and the desorption of the reaction products occurs as a consequence of ligand substitution in the complex. The reaction of ethanol coordinated at its amino group with an ammonia molecule was postulated as one of the first steps. In a number of studies it was pointed out that the hydroxyl group not participating in a coordinate bond with the metal in the complexes of ethanolamine does not have any reactivity [182, 183]. The chemical inertness of the hydroxyl group in derivatives of N-hydroxyethylethylenediamine derivatives coordinated to a cobalt ion is attributed to the formation of an intramolecular hydrogen bond or the positioning of the oxygen atom near the cobalt(III) ion [183]. Attempts to determine the participation of the hydroxyl group in 1,3-diamino-2-propanol in complexation with Cu(II) and Ni(II) ions have not yielded reliable results [184]. In the case of the interaction of N-(β-hydroxyethyl)ethylenediamine with cobalt, Sarma et al. revealed the dependence of the mode of coordination of the molecule on the ambient pH, which is the reason for the observation of the variation of the reactivity of the hydrogen group in the complex compounds formed [185]. A systematic study of the complexes of aminoethanol and its derivatives with Co(III), Ni(II), Cu(II), and Pd(II), as well as the analogous complexes of N-(2-hydroxyethyl)- and N-(2-hydroxypropyl)ethylenediamine was carried out by E. I. Karpeiskaya et al. [187-192], who conducted the acylation at the hydroxyl group of hydroxyamides coordinated to cobalt ions [189]. They postulated that the dehydration cyclization of aminoethanol to piperazine on a cobalt catalyst involves the continuous synthesis and decomposition of a cobalt complex with the substrate that is soluble in the reaction medium, metallic cobalt being continually renewed on the catalyst surface. It was established by IR spectroscopy that the interaction of the components of the reaction medium with the catalyst is accompanied by protonation of the amino group owing to the acid sites of aluminum oxide and the formation of Co–N and Al–N bonds (with the participation of the Lewis sites) and –C–O–Al and C–O–Co– alkoxide bonds. Compounds of low stability of the

ethylenediamine-chelate type also form on the surface. The formation of a complex compound of the substrate with nickel was also established on a nickel catalyst for the deaminocyclization of diethylenetriamine in [193].

The deaminocyclization of ethyleneamines on oxides has been represented in the form of three different variants of interactions of the substrate with the catalyst, depending on the type of active site [8, 142]. When the amine molecules are oriented toward active sites of the Brønsted-acid type, it is postulated that the amino group is protonated and that its elimination is thereby facilitated. The interaction of a substrate with sites of the Lewis-acid type includes the formation of a nitrogen–metal bond and a hydrogen bond at the α-methylene group with a bridging oxygen atom on the surface, i.e., the elimination of an ammonia molecule results in the formation of an unsaturated compound (this is similar to the mechanism for the formation of ethylene from ethanol). In this case, the deamination reaction takes place according to an ammonium–carbonium mechanism.

It was found in IR spectroscopy in [194, 195] that 4-amino-1-butanol undergoes partial dehydration when it is adsorbed on tungsten oxide already at room temperature (absorption maxima characteristic of pyrrolidine and water adsorbed on the surface appear). It was also shown that the reaction products are removed from the surface only when the temperature is increased and that aminoalkanols displace the heterocycles from the surface, since they have a strong adsorption capacity. The hydroxyl and amide groups formed on the surface as a result of the interaction with aminobutanol are removed only at temperatures equal to 400°C or more, and this is the reason for the high temperatures of the catalytic reaction on oxides.

The foregoing material actually exhausts the hypotheses which have been advanced regarding the mechanisms of the dehydration cyclization of amino alcohols and the deaminocyclization of di- and polyamines. The reactions considered are complicated, have many paths, and take place on nonuniform catalytic surfaces, making it difficult to establish the mechanism for their occurrence. Since, however, the catalytic synthesis of nitrogeneous heterocycles is of considerable practical interest and a number of processes have been brought up to the level of industrial implementation, it should be assumed that the investigations into the kinetic laws and the mechanisms of the dehydration of aminoalkanols and the deamination of di- and polyamines will be continued both in the USSR and in other countries.

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