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Abstract

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Investigation of the Dependence of the Direction of the Process of Catalytic Reduction of Dinitriles on Their Structure

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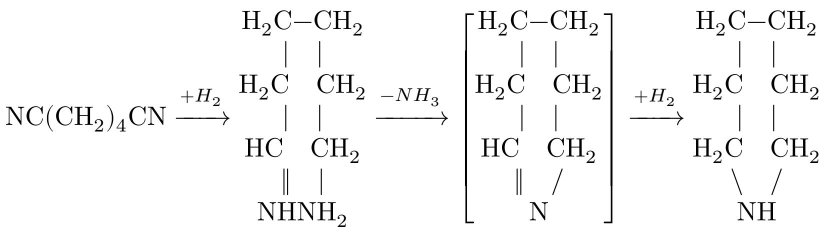
Literature data on the catalytic reduction of dinitriles of carboxylic acids are few and are represented mainly by patents. An exception is adipic acid dinitrile, the hydrogenation of which to the industrially important hexamethylenediamine has been widely studied ($^{1-8}$). Blicke and Bishop described the preparation of decamethylenediamine (yield 80%) by hydrogenation of sebacic acid dinitrile in ethanol over a skeletal nickel catalyst in the presence of ammonia at 125° and an initial hydrogen pressure of 110 atm (^{9}). A number of patents recommend hydrogenating aliphatic dinitriles with the number of carbon atoms in the chain from 3 to 20 over various cobalt and nickel catalysts at temperatures of 20—200° and a hydrogen pressure of 70—700 atm (^{10}).

Undoubtedly, the catalytic reduction of dinitriles, like that of mononitriles, proceeds by an aldimine mechanism (^{11,12}). In particular, in the course of hydrogenation of adiponitrile, the aldimine is a common intermediate in the reactions leading to formation both of the primary amine—hexamethylenediamine:

$$NC(CH_2)_4CN \xrightarrow{+H_2} H_2NCH_2(CH_2)_4CH{=}NH \xrightarrow{+H_2} H_2N(CH_2)_6NH_2, \qquad (1)$$

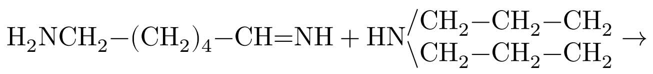
and of the secondary amine—cyclohexamethyleneimine:


(2)

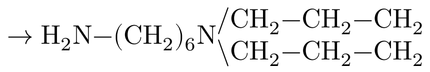
Besides reactions 1 and 2, secondary processes are possible in which the aldimine reacts with the already formed hexamethylenediamine or cyclohexamethyleneimine, giving compounds containing a secondary or tertiary nitrogen atom—bis-hexamethylenetriamine and *N*-(ε-aminocyclohexyl)-cyclohexamethyleneimine:

$$H_2N{-}CH_2{-}(CH_2)_4{-}CH{=}NH + H_2N{-}(CH_2)_6{-}NH_2 \rightarrow$$

$$\rightarrow H_2N{-}(CH_2)_6{-}NH{-}(CH_2)_6{-}NH_2$$



$$H_2NCH_2{-}(CH_2)_4{-}CH{=}NH + HN\begin{matrix}/CH_2{-}CH_2{-}CH_2\\ \backslash CH_2{-}CH_2{-}CH_2\end{matrix} \rightarrow$$



$$\rightarrow H_2N{-}(CH_2)_6N\begin{matrix}/CH_2{-}CH_2{-}CH_2\\ \backslash CH_2{-}CH_2{-}CH_2\end{matrix}$$

Thus, in the catalytic reduction of a dinitrile, along with the primary amine, cyclic products and open-chain compounds containing secondary and tertiary nitrogen atoms may be formed. The work of a number of investigators and our data have shown that the direction of the reac-

The reduction of adiponitrile depends to a considerable extent on the nature of the catalyst and on the presence of ammonia in the system. The process proceeds most selectively on cobalt catalysts and in the presence of ammonia (the yield of the primary diamine reaches 90–95% theoretical).

Recently we established that the structure of a nitrile also influences the direction of its reduction reaction ([13]). Continuing the investigation in the chosen direction, in the present work we studied the hydrogenation, under identical conditions, of the dinitriles of glutaric, adipic, pimelic, azelaic, and sebacic acids on two types of catalysts. The reaction was carried out in a 0.5-liter stainless-steel autoclave in the presence of ammonia. Nickel and cobalt catalysts were used —skeletal and boride. The skeletal nickel catalyst was prepared by exhaustive leaching of a 50% nickel-aluminum alloy with a 10% aqueous NaOH solution at 90–100°. The skeletal cobalt catalyst was prepared by cold leaching ([14]). The preparation of the nickel boride catalyst is described in ([15]), and that of the cobalt boride catalyst in ([8]). The experimental procedure was analogous to that described earlier ([16]). The discharged reaction products were separated from the catalyst and subjected to vacuum distillation in a nitrogen atmosphere. The amine content in the collected fractions was determined acidimetrically ([5]).

Table 1

Hydrogenation conditions: dinitrile charge 0.13–0.45 mole, catalyst 10–15% of the weight of the dinitrile, volume ratio dinitrile : ethanol 1 : 1, molar ratio dinitrile : ammonia 1 : 3–1 : 5, temperature 100–110°, initial hydrogen pressure 100–120 atm.

No. of experiment	Dinitrile	Catalyst	Cycloimine	Diamine	Residue
1	NC—$(CH_2)_2$—CN	Ni-skeletal	70[1]	5[2]	25
2	NC—$(CH_2)_3$—CN	Co-skeletal	35[3]	55[4]	10
3	NC—$(CH_2)_4$—CN	Co-skeletal	4[5]	93[6]	3
4	NC—$(CH_2)_4$—CN	Ni-skeletal	12	78	10
5	NC—$(CH_2)_4$—CN	Co-boride	6	90	4
6	NC—$(CH_2)_4$—CN	Ni-boride	14	74	12
7	NC—$(CH_2)_5$—CN	Co-skeletal	0.5[7]	94[8]	5.5
8	NC—$(CH_2)_7$—CN	Co-skeletal	0[9]	96[10]	4
9	NC—$(CH_2)_7$—CN	Ni-skeletal	0	91	9
10	NC—$(CH_2)_7$—CN	Co-boride	0	95	5
11	NC—$(CH_2)_8$—CN	Co-skeletal	0[11]	97[12]	3
12	NC—$(CH_2)_8$—CN	Ni-skeletal	0	89	14
13	NC—$(CH_2)_8$—CN	Co-boride	0	91	9
14	NC—$(CH_2)_8$—CN	Ni-boride	0	88	12

No. of experiment	Dinitrile	Catalyst	Cycloimine	Diamine	Residue
15	NC—$(CH_2)_8$—CN	Same[13]	0	65	35
16	NC—$(CH_2)_{10}$—CN	Co-skeletal	0	98[14]	2

1 —pyrrolidine; 2 —tetramethylenediamine; 3 —piperidine; 4 —pentamethylenediamine; 5 —hexamethyleneimine; 6 —hexamethylenediamine; 7 —heptamethyleneimine; 8 —heptamethylenediamine; 9 —nonamethyleneimine; 10 —nonamethylenediamine; 11 —decamethyleneimine; 12 —decamethylenediamine; 13 —without ammonia; 14 —dodecamethylenediamine.

The experiments were carried out under conditions which, as we had established earlier, are optimal for the hydrogenation reaction of adiponitrile. The conditions and results of the experiments are given in Table 1. Table 2 gives the constants of the diamines obtained, the melting points of their salts, and also the elemental analysis of these salts for their nitrogen content. The salts of the amines of dicarboxylic acids were obtained by mixing 10% hot alcoholic solutions of equimolecular quantities of both components; the picrates were obtained in benzene solution.

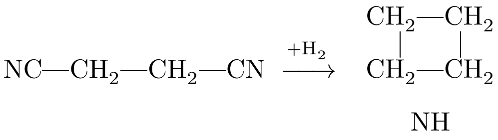
As we showed earlier ([13]), in the reduction of succinonitrile on a skeletal nickel catalyst in the presence of ammo-

Table 2

Diamine	B.p., °C/mm Hg	M.p., °C	Diamine salts	M.p., °C	Nitrogen content, %, calculated	Nitrogen content, %, found
$H_2N—(CH_2)_5—NH_2$	175—180/760	—	Azelainate	147—148	9.65	9.94
$H_2N—(CH_2)_6—NH_2$	95/18; 98—100/20	40	Succinate	171—171.5	11.33	12.15
$H_2N—(CH_2)_7—NH_2$	110—112/18	30	Picrate	222	19.50	19.59
$H_2N—(CH_2)_7—NH_2$	110—112/18	30	Azelainate	144—145.5	5.54	5.91
$H_2N—(CH_2)_9—NH_2$	98—100/4; 124/7.5; 126/8	37	Succinate	167—169	10.10	9.80

Diamine	B.p., °C/mm Hg	M.p., °C	Diamine salts	M.p., °C	Nitrogen content, %, calculated	Nitrogen content, %, found
$H_2N—(CH_2)_9—NH_2$	98–100/4; 124/7.5; 126/8	37	Azelainate	186–186.5	8.08	7.97
$H_2N—(CH_2)_{10}—NH_2$	102–103/2; 116–117/5.5; 134/8	60.5	Succinate	190–191	9.66	9.81
$H_2N—(CH_2)_{10}—NH_2$	102–103/2; 116–117/5.5; 134/8	60.5	Azelainate	127–128	5.28	5.42
$H_2N—(CH_2)_{12}—NH_2$	142–144/5	67	Terephthalate	263	–	–

at a temperature of 35–75° and with a heating duration of 2–5 hours, only the cyclic product–pyrrolidine–is obtained:



$$NC—CH_2—CH_2—CN \xrightarrow{+H_2} \begin{array}{c} CH_2—CH_2 \\ | \quad\quad | \\ CH_2—CH_2 \\ NH \end{array}$$

Only in experiment 1, given in Table 1, was 5% tetramethylenediamine also formed simultaneously with pyrrolidine. It follows from experiment 2 that, in the reduction of glutaric acid dinitrile on a skeletal cobalt catalyst prepared by cold leaching[^14], which is distinguished by high selectivity with respect to the formation of primary amines[^17], much piperidine (35%) was obtained along with pentamethylenediamine. Data similar to ours are given in a patent[^18], in which it is indicated that, in the reduction of glutaric acid dinitrile in the presence of skeletal nickel or cobalt on kieselguhr at 172°, only piperidine is formed (yield 83%). When the temperature is lowered to 125° in the presence of cobalt on kieselguhr or on alumina, 41.5% pentamethylenediamine is formed along with piperidine.

It is seen from Table 1 that, in the reduction of adipic acid dinitrile on a skeletal nickel catalyst, along with the linear diamine (yield 78%) a cyclic product was formed with a yield of 12% (experiment 4). In the absence of ammonia and on supported nickel catalysts, the yield of cyclohexamethyleneimine can increase to 30%. In the hydrogenation on skeletal nickel of the dinitriles of azelaic and sebacic acids, exclusively linear diamines are obtained, the yields of which were respectively 91 and 89% (experiments 9 and 12). In the reduction reaction on a skeletal cobalt catalyst of the dinitriles of adipic, pimelic, azelaic, sebacic, and dodecanedioic acids, the yields of diamines were respectively 93, 94, 96, 97, and 98% (experiments 3, 7, 8, 11, and 16). Some amount of cyclic imine (4%) was formed only in the hydrogenation of adiponitrile (experiment 3).

In the reduction of adiponitrile on cobalt boride or nickel boride catalysts, along with hexamethylenediamine a small amount of cyclohexamethyleneimine is also obtained (experiments 5 and 6), whereas cyclic products are not formed from the dinitriles of azelaic and sebacic acids (experiments 10, 13, and 14). When the hydrogenation of sebacic acid dinitrile is carried out in the absence of ammonia, a decrease in the yield of decamethylenediamine and an increase in the high-boiling residue are observed; however, decamethyleneimine is not formed in this case either (experiment 15).

The data obtained show that, in the catalytic reduction of aliphatic ω,ω'-dinitriles whose molecules contain 7—12 ato-

carbon atoms, only linear diamines are formed. Conversely, in the reduction of dinitriles with a shorter carbon chain (C_4—C_5), when an unstrained or slightly strained heterocycle can be formed, a cycloimine is obtained predominantly. The data obtained by us in the reduction of the dinitrile of *o*-phthalic acid are also in agreement with this conclusion. In contrast to the dinitriles of *p*- and *m*-phthalic acids, in the reduction of the dinitrile of *o*-phthalic acid, instead of the expected *o*-xylylenediamine, only isoindoline is formed (12):

$$\text{[o-phthalodinitrile]} \quad + H_2 \longrightarrow \quad \text{[isoindoline]}$$

Thus, the tendency toward formation of a cyclic imine in the reduction process decreases in the series of dinitriles of the following acids: *o*-phthalic > succinic > glutaric > adipic.

Comparison of the results of experiments on the hydrogenation of the dinitriles of succinic (^{13}), adipic, and dodecanedioic acids shows that the shorter the carbon chain of the dinitrile, the lower the temperature at which its reduction proceeds. Thus, succinonitrile, adiponitrile, and dodecanedinitrile are reduced on skeletal nickel at temperatures of 35, 80, and 120°, respectively.

The results of the present work and those obtained earlier (^{13}) show that the direction of the catalytic reduction of dinitriles depends strongly on their structure. In the reduction of ω,ω'-dinitriles in whose molecules the nitrile groups are separated by five or more carbon atoms, only primary diamines are formed. Conversely, in the case of dinitriles with two carbon atoms between the nitrile groups (when an unstrained nitrogen-containing five-membered heterocycle can be formed), only compounds containing a pyrrolidine ring are obtained. In this case, neither the use of the cobalt catalyst most selective with respect to formation of the primary amine, nor carrying out the reaction in the presence of ammonia, has any substantial effect on the direction of the process. Reduction of the dinitriles of glutaric and adipic acids leads to the formation of a mixture of secondary (cyclic) and primary (linear) amines.

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Note: Figure translations are in progress. See original paper for figures.

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