SELECTIVE REDUCTION OF ADIPONITRILE TO ϵ-AMINOCAPRONITRILE ON A NICKEL BORIDE CATALYST

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An investigation of the selectivity of catalysts in the hydrogenation of adiponitrile is of interst in two respects: for determining the steps of the process

$$NC(CH_2)_4CN \xrightarrow{H_2} NC(CH_2)_4CH_2NH_2 \qquad (1)$$

$$NC(CH_2)_4CH_2NH_2 \xrightarrow{H_2} H_2NCH_2(CH_2)_4CH_2NH_2 \qquad (2)$$

and as a method of preparing the nitrile of an amino acid, which is readily converted to an ϵ-amino acid by hydrolysis. A brief review of literature data on this problem is given in [1].

As was shown previously, in hydrogenation under pressure on a highly active skeletal nickel catalyst, it is difficult to stop the process at the formation of the aminonitrile (1). The selective hydrogenation of the dinitrile to the aminonitrile was found to be possible in the presence of partly deactivated skeletal nickel catalysts if the reaction was stopped after the absorption of 2 mol.-equiv. of hydrogen [1]. The process proceeds specifically on the nickel boride catalyst used in the present work, in contrast to skeletal nickel: The aminonitrile formed is not hydrogenated under certain conditions, but not all the dinitrile taken for the reaction can be converted to aminonitrile. It was found that this is explained by adsorption displacement of the dinitrile by the aminonitrile accumulating in the reaction mixture. On the other hand, the aminonitrile is not displaced from the catalyst by hexamethylenediamine. The latter indicates that the greater difficulty in effecting stage (2) is caused by the different reactivities of the CN groups in the dinitrile and aminonitrile molecules.

Considerably less secondary amine was formed in experiments on partial hydrogenation of the dinitrile than in its complete hydrogenation. In accordance with this, the yield of secondary amines was the same whether dinitrile or aminonitrile was used for the reaction. Thus, secondary amines are formed in stage 2. When the reaction was carried out in the absence of ammonia, the yield of secondary amines increased still further. These results confirm the aldimine mechanism for the formation of secondary amines [2].

EXPERIMENTAL

The hydrogenation was carried out in a 0.5 liter steel autoclave, which was charged with 50 ml (0.455 mole) of the dinitrile and the required amount of catalyst and ammonia. Hydrogen was introduced to an initial pressure of 100 atm, heating was begun, and when the given temperature was reached, the autoclave was rotated. The reaction products were separated from the catalyst and distilled to give fractions with the following boiling points: I – 137° (hexamethyleneimine), the boiling point of the azeotrope with water is 95°; II – 95-100° (20 mm) (hexamethylenediamine); III – 118-120° (20 mm) (ϵ-aminocapronitrile). The high-boiling residue consisted mainly of unreacted dinitrile with some bis-hexamethylenetriamine (triamine). The amine content of all the fractions was determined acidimetrically. The refractive index of the aminonitrile fraction was also determined. The catalysts were prepared by exhaustive extraction of powdered Ni–Ti–Al alloys with 10% aqueous sodium hydroxide solution for 2 hr at 95°; after being washed with water until neutral to phenolphthalein they were stored under alcohol at 1-5°.

The nickel boride catalyst was obtained by the following procedure [3]. With stirring, 60 ml of a 20% aqueous solution of sodium borohydride was gradually added to a mixture of 250 ml of a 10% aqueous solution of nickel chloride (or acetate) and 10 ml of a 10-30% solution of chromium nitrate (or sulfate) at such a rate that the temperature of the reaction mixture did not exceed 50°. The dark precipitate obtained was transferred to a funnel with a porous glass filter, washed until neutral to phenolphthalein, and stored under alcohol at 1-5°. The compositions of the alloys used, the experimental conditions, and the results of analyzing the reaction mixture are given in the tables.

TABLE 1. Experimental Conditions: Hydrogen Pressure 100 atm, Molar Ratio of Dinitrile: Ammonia, 1: 2, Catalyst 10 g

Expt. No.	Composition of alloy, wt. %		Experimental conditions		Composition of reaction products in fractions, wt. %				
			temp., °C	time, min	I	II	III	residue	
								tri-amine	di-nitrile
1	Ni–Al	50—50	80	25	5	27	53	3	12
2	Ni–Al–Ti	48—48—4	80	20	4	22	53	6	15
3	The same	46—47—7	80	40	3	17	57	4	19
4	»	30—50—20	80	55	4	13	51	4	28
5	»	30—50—20	60	210	4	14	51	4	27

TABLE 2. Experimental Conditions: Molar Ratio of Dinitrile: Ammonia 1: 2-1: 3

Expt. No.	Nickel boride catalyst	Experimental conditions				Composition of reaction products in fractions, wt. %				
		temp. °C	initial hydrogen pressure, atm	amount of catalyst, g	expt., time, hr	I	II	III	residue	
									tri-amine	di-nitrile
6	Unmodified									
		50	100	10	2,5	6	14	49	4	27
7	The same	80	100	10	2,5	6	16	52	4	23
8	Modified	75	95	10	6	4	2	45	4	45
9	»	80	100	10	4	3	3	61	3	30
10	»	90	95	10	4,5	5	17	54	2	22
11	»	120	120	10	4	13	75	0	10	2
12	»	80	50	10	2	0	0	10	—	90
13	»	80	75	10	4,5	3	3	40	6	48
14	»	75	95	20	1,5	17	74	0	7	22
15	»	80	100	20	0,8	5	7	45	3	40
16	»	65	100	20	5,5	5	7	49	4	35
17		110	100	5	4	3	7	52	4	34
18	Cobalt boride, modified	80	100	20	1,5	4	17	41	2	36

Hydrogenation over Ni–Ti catalyst. In experiments 1-7, 15, and 18, the reaction was stopped after the absorption of approximately 2 mol.-equiv. of hydrogen (when hydrogenation was half complete). Experiments 1-4, which were carried out at 80° and 100 atm (Table 1), show that the addition of 4% of Ti to the catalyst had little effect on the rate and direction of the reaction. With an increase in the amount of titanium in the catalyst to 7 and 20%, the reaction time increased by a factor of 1.5-2. At the same time the aminonitrile content of the catalyzate hardly changed, while the diamine yield fell from 27 to 17 and 13%, and the amount of unreacted dinitrile increased correspondingly from 12% (experiment 1) to 19% (experiment 3) and 28% (experiment 4). The catalyzate obtained in experiment 5, which was carried out at a lower temperature (60°), did not differ in composition from the catalyzate of experiment 4, but the reaction time increased considerably.

Hydrogenation over nickel boride catalyst. As experiments 6 and 7 show, the activity of the nickel boride catalyst was very much lower than that of the skeletal nickel: The time for half hydrogenation was 6 times greater in the presence of the former (Table 2). The catalyzates from these experiments, which were stopped when approximately 2 mol.-equiv. of hydrogen had been absorbed, were found to contain 49-52% of aminonitrile and 14-16% of diamine. The nickel boride catalyst modified with chromium was found to be even less active: The time for half hydrogenation increased by a factor of approximately 2. In contrast to the cases of all the catalysts we tested previously, with this catalyst, the fall in pressure stopped after the absorption of approximately 2 mol.-equiv. of hydrogen, i.e., the reaction stopped (experiments 8-14, 16, and 17). Experiments 8 and 9 show that at 75-80° and 100 atm, the reaction mixture with promoted catalyst contained mainly ε -aminocapronitrile (45 and 61%) and unreacted dinitrile (45 and 30%),and little hexamethylenediamine (3 and 5%) was formed. When the temperature was raised to 90°, the diamine yield increased to 17% (experiment 10). Four moles of hydrogen was absorbed at 120° and the diamine yield was 75%, while aminonitrile was absent from the reaction products. At the same time, 13% of cyclohexamethyleneimine and 10% of triamine were formed (experiment 11). The effect of pressure was studied in experiments 12-14. At 50 atm, the reaction stopped after the absorption of 7.5% of the required amount of hydrogen. The catalyzate from this experiment contained 10% of aminonitrile and 90% of unreacted dinitrile, while no diamine or cyclic imine was present. In an experiment at 75 atm, we obtained 40% of aminonitrile and 3% of diamine. When twice the amount of catalyst was used there was complete hydrogenation of the dinitrile with the formation of 74% of diamine and 17% of cyclic imine. In an analogous experiment (15), which was stopped after the absorption of ~2 mol.-equiv. of hydrogen, 45% of aminonitrile and only 7% of diamine were formed. Experiment 16, which was carried out at a lower temperature (65°) and with twice the amount of catalyst, yielded 49% of aminonitrile and 7% of diamine. With a decrease in the amount of catalyst to 10% (experiment 17), the reaction began only at 110° and the composition of the half-hydrogenation products was approximately the same as in experiments 8 and 9.

TABLE 3. Experimental Conditions: Initial Hydrogen Pressure 100 atm; Catalyst — Modified Nickel Boride

Expt. No.	Compound hydrogenated	Weight ratio of mixture components	Experimental conditions				Composition of reaction products, wt. %				
			Temp., °C	substance taken: ammonia, moles	amount of catalyst, g	experiment time, hr	I	II	III	residue	
										triamine	dinitrile
19	ε -Aminocapronitrile	—	80	1:2,4	10	2	10% of hydrogen was absorbed				
20	ε -Aminocapronitrile	—	110	1:2,4	10	2	15	76	—	8	(1)*
21	Adiponitrile: ε -aminocapronitrile	5,5:4,5	80	1:2	10	2	2	5	35	3	55
22	» »	5,3:4,7	80	1:2	10	3	3	8	36	3	50
23	» »	6:4	80	1:2	20	2	2	2	65	3	28
24	ε -Aminocapronitrile : 1,6-hexamethylenediamine	1:1	85	1:2	10	1,5	8% of hydrogen was absorbed				
25	»	1:1	120	1:2	10	2	14	76	0	8	(2)*
26	Adiponitrile : 1,6-hexamethylenediamine	1:1	85	1:2	10	2	7	3	25	9	56
27	»	1:1	120	1:1,5	10	1,5	17	50	2	16	15
28	Adiponitrile	—	80	No NH_3	10	7	9	42	29	5	15
29	»	—	120	No NH_3	10	5	20	64	—	11	(5)*

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* Untitratable part, which probably consisted of high-molecular polyamines.

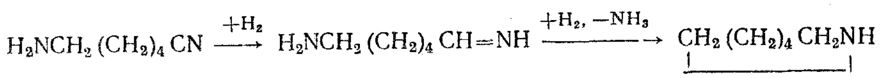
The results of experiments with modified nickel boride catalyst show very clearly that the second nitrile group of the dinitrile is hydrogenated with much more difficulty than the first; namely, at a higher temperature (110-120°) or with a larger amount of catalyst (40 weight%). Under conditions similar to experiment 15 with a cobalt boride promoted catalyst, 41% of aminonitrile and 36% of unreacted dinitrile were obtained. Thus, hydrogenation of adiponitrile proceeds in steps on a cobalt boride catalyst (experiment 18).

The data obtained led us to the conclusion that under the optimal conditions (in the presence of ammonia, 20% of catalyst, temperature 75-80°, initial hydrogen pressure 95-100 atm), the ε -aminocapronitrile formed in the reaction is not hydrogenated on a nickel boride catalyst. We confirmed this hypothesis with a special experiment, in which it was established that the aminonitrile was not reduced under these conditions: ~10% of the hydrogen required for half hydrogenation was absorbed (experiment 19). When the temperature was raised to 110°, there was further absorption of hydrogen and 76% of hexamethylenediamine was formed (experiment 20) (Table 3).

Effect of reaction products. In experiments on this catalyst (20 wt. %) at 80°, the absorption of hydrogen ceased when the reaction mixture still contained a considerable amount of unreacted dinitrile. It was important to establish what interferes with the hydrogenation of the first nitrile group of all the dinitrile molecules taken for the reaction. It may be considered that at the beginning of the process, when the dinitrile concentration in the catalyzate is high, the formation of aminonitrile does not affect the reaction rate. As the aminonitrile concentration in the reaction mixture increases, the adsorption displacement of the dinitrile by it begins and the hydrogen absorption rate falls. When the aminonitrile concentration becomes considerable (~50%), hydrogenation of the dinitrile ceases completely.

To check this hypothesis, we carried out experiments on the hydrogenation of the dinitrile mixed with the aminonitrile under conditions where the aminonitrile was hardly hydrogenated (80°, 100 atm, and 20 wt. % of catalyst). The results obtained showed that practically the whole of the dinitrile taken remained unchanged and only a small part of the aminonitrile was converted to the diamine and secondary amines (experiments 21 and 22). Even when the amount of catalyst was doubled (experiment 23), only part of the dinitrile mixed with aminonitrile was hydrogenated. The hydrogen absorption rate in the hydrogenation of the dinitrile alone in experiment 11 was 4 times greater than in its hydrogenation in a mixture with aminonitrile (experiment 21). In the first case, 20 liters of hydrogen was absorbed in an hour and in the second case, only 5 liters. The results of these experiments confirm the hypothesis that there is adsorption displacement of the dinitrile by the aminonitrile. On the other hand, the aminonitrile (stage 2) is not displaced by the diamine: In the hydrogenation of the aminonitrile mixed with the diamine (experiment 25), the same yields of diamine and cyclohexamethyleneimine were obtained as in its reduction in the absence of diamine (experiment 11). Experiment 26 shows that 45% of the dinitrile was converted at 85° in a mixture with hexamethylenediamine, while the dinitrile was hardly reduced at all in a mixture with aminonitrile under analogous conditions (experiments 21 and 22).

Mechanism of secondary amine formation. As has been reported above, secondary amines (imine and triamine) are formed together with hexamethylenediamine in the hydrogenation of the dinitrile. In accordance with the aldimine mechanism of the reaction, the imine can only be formed in stage 2:



$$H_2NCH_2(CH_2)_4CN \xrightarrow{+H_2} H_2NCH_2(CH_2)_4CH{=}NH \xrightarrow{+H_2,\,-NH_3} \underbrace{CH_2(CH_2)_4CH_2NH}$$

and should not be formed in stage 1 of the hydrogenation of the dinitrile. In actual fact, in all our experiments the imine was formed largely during complete hydrogenation of the dinitrile (13-14% yield) and in an insignificant amount (2.5%) during half-hydrogenation. The imine yield was the same whether the aminonitrile (experiment 20) or dinitrile (experiment 11) was used for the reaction. These facts indicate that the imine is formed during the hydrogenation of the aminonitrile [4]. In contrast to the imine, which is formed by an intramolecular reaction of the imino and amino groups, the triamine is formed by an intermolecular process:

$$H_2NCH_2(CH_2)_4CH{=}NH + NH_2(CH_2)_6NH_2 \xrightarrow{+H_2,\,-NH_3} H_2N(CH_2)_6NH(CH_2)_6NH_2$$

An increase in the concentration of compounds containing an amino group in the reaction mixture should therefore lead to an increase in the yield of triamine. In actual fact, during the reduction of the dinitrile in a mixture with the triamine, much more triamine than usual was formed both during half-hydrogenation (experiment 26) and during complete hydrogenation (experiment 27).

SUMMARY

1. The hydrogenation of adiponitrile to ε-aminocapronitrile on a nickel boride catalyst and on skeletal nickel with titanium added was investigated. With an increase in the amount of titanium in the skeletal nickel catalyst, the selectivity of the latter increased.

2. The dinitrile was hydrogenated selectively to the aminonitrile on the nickel boride catalyst: 50-60% of the aminonitrile and only 2-5% of the diamine were formed under the optimal conditions.

3. The reason for the incomplete conversion of the dinitrile to the aminonitrile under half-hydrogenation conditions is adsorption displacement of the dinitrile by the aminonitrile.

4. In the hydrogenation of the dinitrile, cyclohexamethyleneimine is formed during the second stage of the process, while the formation of bishexamethylenetriamine increases appreciably when the dinitrile is hydrogenated in a mixture with hexamethylenediamine. As with other catalysts, ammonia suppresses the formation of both secondary amines. These facts confirm the aldimine mechanism for the hydrogenation of the dinitrile.

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