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CATALYTIC REDUCTION OF DINITRILES

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I. INTRODUCTION

As a result of the extensive industrial applications of the polymeric condensation of bifunctional compounds, a great deal of research has been done in recent years on methods of preparation of diamines. Of these, the catalytic reduction of dinitriles to diamines seems to hold the greatest promise.

Several papers have also been published on the partial reduction of dinitriles. The preparation of ω-amino-acid nitriles by catalytic hydrogenation of dinitriles may become important as a simple route to ω-amino-acids and lactams, particularly caprolactam.

In spite of the many patents and papers on the catalytic reduction of dinitriles, the field has not been reviewed up to the present.

II. REACTION CONDITIONS

The hydrogenation conditions of aliphatic, aromatic, and organosilicon dinitriles are summarised in Table 1. The reduction catalyst used is invariably a Group VIII metal: palladium activated by platinum oxide[1], Raney nickel and cobalt[2-33], nickel and cobalt catalysts on a carrier[34-39], and also nickel boride[40,41] and cobalt boride[41,42] catalysts, prepared by reduction to the metal of a salt in aqueous solution, using sodium tetrahydroborate[42].

In the presence of noble metals, the reaction proceeds rapidly at room temperature and under hydrogen pressures close to 1 atm.[1] Nickel and cobalt catalysts require elevated temperatures and hydrogen pressures. The dinitrile of adipic acid can be hydrogenated under milder conditions on a Raney nickel than on a Raney cobalt catalyst[7,8]. Cobalt catalysts are the more stable, and the more selective towards formation of a primary diamine. Raney nickel retained its activity for 30–35 h without regeneration[7] in the reduction of the adipodinitrile under flow conditions, whereas Raney cobalt and Co/Al_2O_3 retained it for ~ 500 h.[8,39]

Raney nickel–copper catalysts were found to be appreciably less active towards hydrogenation of the adipodinitrile[46]. Raney iron also has a low catalytic activity: the dinitrile of terephthalic acid is reduced to a negligible extent in the presence of this catalyst[13]. Thus the activity of metallic catalysts towards the reduction of dinitriles decreases in the sequence: Pt, Pd > Ni > Co > Fe, Cu. The reaction is usually carried out in the liquid phase, in a medium of ammonia[2-8,18-43] or of an inert solvent (alcohol, dioxan) saturated with ammonia[9-17].

By studying the catalytic reduction of the dinitriles of adipic, sebacic, terephthalic, isophthalic, and *p*- and *m*-phenylenediacetic acids it has been shown that an ammoniacal medium favours the formation of primary amines and lowers the yield of secondary and tertiary amines[10-12,17].

However, the reduction of the second nitrile group of adipodinitrile is hindered[3] at very high concentrations of ammonia, and a significant amount of the partial hydrogenation product (6-aminocapronitrile) is formed in addition to hexamethylenediamine.

In a solution of sodium acetate in acetic anhydride at 50° and under a hydrogen pressure of 3.5 atm, hexamethylenediamine was formed on Raney nickel in almost quantitative yield, but the catalyst rapidly lost its activity and disintegrated. Under the same conditions, the yield of

hexamethylenediamine was 77% and 25% on Raney Ni–Cr and Co catalysts respectively[5]. The low yield of diamine on the cobalt catalyst suggests that the reaction conditions (temperature and hydrogen pressure) were not the most favourable.

A primary diamine is either not formed at all[43], or is obtained in negligible yield[21,41,43], in the hydrogenation of dinitriles containing 2–3 carbon atoms between the nitrile groups.

There have been isolated studies of the catalytic reduction of dinitriles in the vapour phase. Under these conditions the reaction attacks the nitrile group with formation of a hydrocarbon and ammonia. Thus, 46% of *p*-xylene and 11% of *p*-tolunitrile were obtained[44] in the vapour-phase hydrogenation of the dinitrile of terephthalic acid on kieselguhr-supported Ni–Cu catalysts.

The formation of aminonitriles from dinitriles is observed when the hydrogenation is conducted under conditions milder than required to give the diamines. Therefore, the nitrile groups are reduced successively.

The conditions leading to partial reduction of diamines are set out in Table 2. It can be seen that aminonitrile formation is favoured by moderate hydrogen pressure[2] and temperature[45], high dilution with solvent[2,3], the use of low-activity Raney nickel (partly deactivated by treatment with water vapour under pressure[46] or with addition of copper or

TABLE 1.

Dinitrile	Catalyst	Medium*	Temperature, °C	Hydrogen pressure, atm	Yield of diamine, %	Reference
1	2	3	4	5	6	7
$NC-(CH_2)_3-CN$	Ni, Raney	ammonia, 7	140	120	20	21
$NC-(CH_2)_2-CN$	Ni, Raney	ammonia, 5	70	125	5	40
$NC-(CH_2)_3-CN$	Co, Raney	alcohol, 1, and ammonia, 5	100	120	55	41
$NC-(CH_2)_3-CN$	Co, Al_2O_3	ammonia, 18	125	240	42	22
$NC-(CH_2)_3-CN$	Co–kieselguhr	methanol, 0.2, and ammonia, 23	125	210	41	22
$NC-(CH_2)_4-CN$	Pd–PtO	abs. alcohol or dioxan + + H_2SO_4	room	1.6	70—80	1
$NC-(CH_2)_4-CN$	Pd–PtO	abs. alcohol or dioxan + + HCl	room	1.6	98	1
$NC-(CH_2)_4-CN$	Ni, Raney	butanol, 15	100—110	80—100	83—85	2
$NC-(CH_2)_4-CN$	Ni–Co, Raney	ammonia, 2–4	170—190	100	70	3
$NC-(CH_2)_4-CN$	Ni–Fe–Mo, Raney	ammonia, 2–4	170—190	100	70	3
$NC-(CH_2)_4-CN$	Ni, Raney	ammonia, 5–6	90—140	70	82	4
$NC-(CH_2)_4-CN$	Ni, Raney	ammonia, 3	80	100	78	41, 56
$NC-(CH_2)_4-CN$	Ni, Raney	no ammonia	80	100	52	56
$NC-(CH_2)_4-CN$	Ni, Raney	$(CH_3CO)_2O$ + NaOH	50	3.5	100	5
$NC-(CH_2)_4-CN$	Ni–Cr, Raney	$(CH_3CO)_2O$ + NaOH	50	3.5	77	5
$NC-(CH_2)_4-CN$	Co, Raney	$(CH_3CO)_2O$ + NaOH	50	3.5	25	5
$NC-(CH_2)_4-CN$	Co, Raney	methanol, 3, and ammonia, 2	85—90	100	80—85	8
$NC-(CH_2)_4-CN$	Co, Raney	ammonia, 2	110	110	94	41, 56
$NC-(CH_2)_4-CN$	Co, Raney	no ammonia	120	110	74	56
$NC-(CH_2)_4-CN$	Ni–MgO	ammonia, 3	80	120	78	56
$NC-(CH_2)_4-CN$	Ni–MgO	no ammonia	90	115	40	56
$NC-(CH_2)_4-CN$	Co–MgO	no ammonia	120	120	60	56
$NC-(CH_2)_4-CN$	Ni, alumina–silica	ammonia, 3	110	120	40	56
$NC-(CH_2)_4-CN$	Ni, alumina–silica	no ammonia	80	120	25	56
$NC-(CH_2)_4-CN$	Ni–SiO_2	ditto	100	100	17	75
$NC-(CH_2)_4-CN$	Ni–WO_2	»	95	100	24	75
$NC-(CH_2)_4-CN$	Ni–ZrO_2	»	95	100	8	75
$NC-(CH_2)_4-CN$	Ni–TiO_2	»	95	100	7	75
$NC-(CH_2)_4-CN$	Ni–Al_2O_3	»	95	100	6	75
$NC-(CH_2)_4-CN$	Ni boride	ammonia, 3	120	120	75	41
$NC-(CH_2)_4-CN$	Co boride	ammonia, 2	100	110	90—94	42, 41
$NC-(CH_2)_4-CN$	Co boride	no ammonia	100	110	71	42
$NC-(CH_2)_4-CN$	Ni boride–MgO	ditto	80	100	61	75
$NC-(CH_2)_4-CN$	Ni boride–WO_3	»	85	100	54	75
$NC-(CH_2)_4-CN$	Ni boride–MoO_3	»	85	100	28	75
$NC-(CH_2)_4-CN$	Ni boride–MoO_3–Al_2O_3	»	80	100	35	75
$NC-(CH_2)_4-CN$	Ni, Raney	ammonia, 2	50	80**	75	7
$NC-(CH_2)_4-CN$	Co, Raney	ammonia	80—85	200**	90—95	8
$NC-(CH_2)_4-CN$	Co–Al_2O_3	ammonia, 27	100	200**	95	39
$NC-(CH_2)_3-CH(OCH_3)-CH_2-CN$	Co, Raney	ammonia	not stated		90	6
$NC-(CH_2)_3-CH(OC_4H_9)-CH_2-CN$	Co, Raney	ammonia	not stated		94	6
$NC-(CH_2)_6-CN$	Co, Raney	ammonia, 3–5	100	100	94	41
$NC-(CH_2)_7-CN$	Ni, Raney	ammonia, 3	100	110	91	41
$NC-(CH_2)_7-CN$	Co, Raney, or Co boride	ammonia, 3–5	100—110	100—120	95—96	41
$NC-(CH_2)_8-CN$	Ni, Raney	ammonia, 3–5	100	120	89	9,41
$NC-(CH_2)_8-CN$	Co, Raney	ammonia, 3–5	110	120	97	41
$NC-(CH_2)_8-CN$	Ni boride	ammonia, 3–5	105	100	88	41
$NC-(CH_2)_8-CN$	Co boride	ammonia, 3–5	105	120	91	41
$NC-(CH_2)_8-CN$	Ni boride	no ammonia	105	110	65	41
$NC-(CH_2)_{10}-CN$	Ni, Raney	ammonia, 3–5	120	115	87	41
$NC-(CH_2)_{10}-CN$	Co, Raney	ammonia, 3–5	120	120	98	41
p-$NC-C_6H_4-CN$	Ni, Raney	dioxan, ammonia, 1	100	80	67	13
p-$NC-C_6H_4-CN$	Ni–Ti, Raney (24 : 1 by wt.)	n-butanol and ammonia	140—180	140	60	15
p-$NC-C_6H_4-CN$	Co, Raney	methanol and ammonia, 10	105	110	89	17
p-$NC-C_6H_4-CN$	Co, Raney	dioxan and ammonia	100—105	90	55—60	14
p-$NC-C_6H_4-CN$	Co, Raney	methanol and ammonia	100—105	90	75—77	14
p-$NC-C_6H_4-CN$	Co, Raney	aqueous NH_3 solution	60—140	105—200	80	96
p-$NC-C_6H_4-CN$	Ni–Cu–kieselguhr	***	304	atmospheric	0	44
m-$NC-C_6H_4-CN$	Ni, Raney	dioxan and ammonia, 3	100	100	79	43
m-$NC-C_6H_4-CN$	Co, Raney	methanol and ammonia	100	100	61—75	18
m-$NC-C_6H_4-CN$	Co, Raney	methanol and ammonia	100	140	84	18
m-$NC-C_6H_4-CN$	Co, Raney	no ammonia	100	100	30	18
m-$NC-C_6H_4-CN$	Co, Raney	aqueous NH_3 solution	60—140	105—200	80	96
o-$NC-C_6H_4-CN$	Ni, Raney	dioxan, ammonia, 3	100	100	0	43
o-$NC-C_6H_4-CN$	Co, Raney	dioxan, ammonia, 4	100	120	0	43
o-$NC-C_6H_4-CN$	Ni–Cu–kieselguhr	***	304	atmospheric	0	44

TABLE 1. (cont'd)

1	2	3	4	5	6	7
p-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at 20°	90—100	70—75	57	10
p-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at −7°	90—100	70—75	75	12
p-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	methanol or ethanol (3 : 2)+ammonia (10 : 1)	100—105	100	64—65	17
p-NC—CH_2—C_6H_4—CH_2—CN	Co, Raney	dioxan (3 : 1)+NH_3 (10 : 1)	100—105	100	74	17
p-NC—CH_2—C_6H_4—CH_2—CN	Co, Raney****	dioxan or methanol, ammonia (10 : 1)	100—105	100	92—94	17
m-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at 20°	90—100	70—75	57	10
m-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at −7°	90—100	70—75	78.5	12
o-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at 20°	90—100	70—75	0	10
o-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at −7°	90—100	70—75	20	11
$(CH_3)_2Si(C_6H_4CN)_2$	Ni, Raney	ammonia	125—130	350	26	19
[NC—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 5	80	110	89	92
[NC—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Co, Raney	alcohol, 1, and ammonia, 5	80	120	92	92
[NC—CH_2—CH_2—Si $(C_2H_5)_2$]$_2$O	Co, Raney	ammonia, 12	80	110	63	92
[NC—CH_2—CH_2—Si $(OC_2H_5)_2$]$_2$O	Co, Raney	absolute alcohol, 1	80	100	61	92
[NC—CH_2—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 2	75	100	92	20
[NC—CH_2—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Co, Raney	alcohol, 1, and ammonia, 15	100	120	95	92
[NC—CH_2—CH_2—CH_2—Si (CH_3) (C_2H_5)]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 2.5	75	90	87	20
[NC—CH_2—CH_2—CH_2—Si $(C_2H_5)_2$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 4	70	95	70	20
[NC—CH_2—CH_2—O—CH_2—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Co, Raney	dioxan, 1, and ammonia, 3	80	115	97	92

* The amount of solvent is shown in volumes per volume of dinitrile; the amount of NH_3 in moles per mole of dinitrile.

** Reaction carried out in a flow system.

*** Reaction carried out in the vapour phase.

**** The "cold leaching out" method was used[98].

TABLE 2.

Dinitrile	Catalyst	Medium*	Temperature, °C	Initial hydrogen pressure, atm	Yield, wt. % aminonitrile	Yield, wt. % diamine	Reference
Adipic NC—$(CH_2)_4$—CN	Ni, Raney	butanol, 15	75—80	1.5—1.7	90	**	2
NC—$(CH_2)_4$—CN	Ni, Raney	butanol, 15	75—80	1.5—1.7	50	25	48
NC—$(CH_2)_4$—CN	Ni, Raney	methanol, dioxan, or without solvent	room	5	38—51	20	45
NC—$(CH_2)_4$—CN	Ni, Raney	methylal, methanol, or dioxan, 6, ammonia, 1.9	100	70	48	5	97
NC—$(CH_2)_4$—CN	Ni, Raney treated with water vapour at 350°	ammonia, 2.5	80	100	58	14	46
NC—$(CH_2)_4$—CN	Ni–Ti, Raney, 43 : 7 by wt.	ammonia, 2	80	100	57	17	40
NC—$(CH_2)_4$—CN	Ni–Ti, Raney, 3 : 2 by wt.	ammonia, 2	60—80	100	51	13—14	40
NC—$(CH_2)_4$—CN	Ni–Ti, Raney, 12 : 1 by wt.	ammonia, 2	60	20	60	3	40
NC—$(CH_2)_4$—CN	Ni–Cu, Raney, 1 : 4 by wt.	ammonia, 5	80	100	56	16	46
NC—$(CH_2)_4$—NC	Fe–Cu, Raney, 1 : 1 by wt.	ammonia, 4.5	80	100	53	12	46
NC—$(CH_2)_4$—CN	Fe–Co, Raney, 19 : 1 by wt.	ammonia, 4	120	140—210	68	6	99
NC—$(CH_2)_4$—CN	Ni–Al_2O_3	ammonia, 4	120	140	52	22	23
NC—$(CH_2)_4$—CN	Ni–kieselguhr	ammonia, 4	120	140—210	51	17	47
NC—$(CH_2)_4$—CN	Ni-boride	ammonia, 2	80	100	61	3	40
NC—$(CH_2)_4$—CN	Co boride	ammonia, 3	80	100	41	17	40

TABLE 2. (contd)

Dinitrile	Catalyst	Medium*	Temperature, °C	Initial hydrogen pressure, atm	Yield, wt. % aminonitrile	Yield, wt. % diamine	Reference
NC—$(CH_2)_4$—CN	Co–kieselguhr	ammonia, 4	120	140—210	52	42	99
Pimelic NC—$(CH_2)_5$—CN	Ni, Raney	methanol or	room	5	40	30	45
NC—$(CH_2)_5$—CN	Co–kieselguhr	dioxan, ammonia, 4	120	175	25	**	47
Azelaic NC—$(CH_2)_7$—CN	Ni, Raney	methanol, dioxan, or without solvent	room	5	21—25	20—30	45
Sebacic NC—$(CH_2)_8$—CN	Fe–Co, Raney, 12 : 2 by wt.	ammonia, 4	120	105—175	24	37	99
NC—$(CH_2)_8$—CN	Ni–Al_2O_3	ammonia, 4	120	140	20	**	23

* The amount of NH_3 is given in moles per mole of dinitrile; the amount of solvent in volumes per volume of dinitrile.

** Yield not stated.

titanium[40,46]), the use of a nickel catalyst on a carrier[23,47], and lastly the use of nickel boride or cobalt boride catalysts[40]. Aminocapronitrile was obtained also when the reaction was carried out in the presence of insufficient catalyst[4].

Reductions on nickel and cobalt catalysts under static conditions usually give significant amounts of diamine (up to 40%) in addition to aminonitrile (25–60%) even before the absorption of sufficient hydrogen to reduce one nitrile group[45-47]. Reduction on a chromium-modified nickel boride catalyst is more selective: the yields are 61% of 6-aminocapronitrile and 3% of diamine. However, hydrogen absorption on this catalyst ceased before the whole of the dinitrile had reacted.

It has been suggested that further hydrogenation is greatly retarded by dilution of the dinitrile because of desorption

from the catalyst surface by the resulting aminonitrile. In the presence of hexamethylenediamine the extent of conversion of the dinitrile is also decreased. Reduction of the second nitrile group begins at higher temperatures [40].

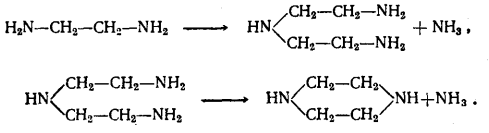
Stepwise hydrogenation of the dinitrile of adipic acid has been carried out also under flow conditions, using a nickel–titanium–alumina catalyst. The relative amounts of aminonitrile and diamine in the product were found to depend strongly on the flow rate of the dinitrile [46]. Under optimum conditions (temperature 60°, hydrogen pressure 20 atm, flow rate of dinitrile 45 ml h^{-1}) the yield of 6-aminocapronitrile was ~ 60%, and that of hexamethylenediamine only 9%.

III. DEAMINATION OF PRIMARY AMINES

It has been stated that secondary amines are formed during catalytic reduction of dinitriles by the deamination of primary amines [3,4]. Thus, secondary amines were obtained [49,50] by refluxing solutions of benzylamine or 2-phenylethylamine in the presence of palladium black, whereas reduction of benzonitrile and phenylacetonitrile on the same catalyst but under milder conditions (at 35°) gave primary amines [50].

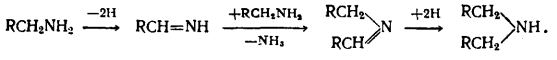
Martin and Martell [51] prepared piperazine by heating ethylenediamine and diethylenetriamine to 150–160° in the presence of Raney nickel. The deamination of diethylenetriamine in xylene, tetralin, dipentene, and without a solvent gave piperazine in yields of 17, 62, 73, and 53% respectively.

From ethylenediamine in a tetralin medium, piperazine was obtained in 39% yield. The authors suggest that diethylenetriamine is formed first, and converted into piperazine:



Heating tetramethylenediamine to 160° in the presence of nickel on kieselguhr gave pyrrolidine in 87% yield [52]. Piperidine was obtained in 62% yield [53] by the same method from pentamethylenediamine heated to 400° in the presence of acidic catalysts (SiO_2, Al_2O_3–SiO_2, BPO_4). A method has also been proposed [54] for the catalytic production of hexamethyleneimine [perhydroazepine (Ed. of Translation)] from hexamethylenediamine at temperatures above 200°.

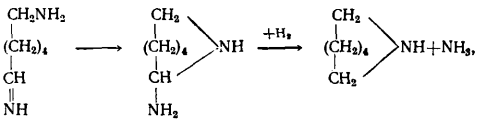
Kindler [55] suggested that aminoaldimines are involved as intermediates in the phytosynthesis of pyrrolidines and piperidines from diamines, and proposed a general scheme for the formation of secondary from primary amines:



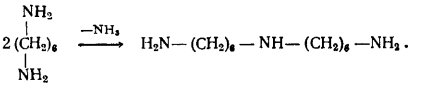
The H_2N-CH_2 group is dehydrogenated, then a Schiff's base is produced from the resulting aldimine, and the amine, and lastly the Schiff's base is hydrogenated.

Zil'berman and Skorikova [4] prepared a mixture containing 20% hexamethyleneimine, 63% hexamethylenediamine, and 17% of a high-boiling residue, by refluxing hexamethylenediamine for 12 h in the presence of a Raney nickel catalyst. On raising the reduction temperature of the adipodinitrile and extending the reaction time, the yield of hexamethylenediamine fell and that of the high-boiling residue (mainly bishexamethylenetriamine) increased. However, the yield of hexamethyleneimine remained almost constant.

The authors conclude that the cyclic secondary amine, hexamethyleneimine, is formed through an aldimine:



and that the secondary straight-chain amine, bishexamethylenetetramine, is formed by deamination of the diamine:



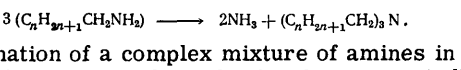
Freidlin and Sladkova [56] showed that on Raney nickel under the optimal conditions for the reduction of adipodinitrile to hexamethylenediamine (temperature 80–100°, hydrogen pressure 100 atm), hexamethylenediamine does not undergo deamination, and that under these conditions bishexamethylenetriamine and hexamethyleneimine are unchanged and do not interact. Deamination of hexamethylenediamine was observed at 140° on Raney nickel, at 160° on Raney cobalt, and at 200° on Ni/MgO. On Raney nickel the yield of hexamethyleneimine reached 32%, that of *N*-(6-aminohexyl)hexamethyleneimine reached 29%. The authors conclude from their results that the formation of secondary and tertiary amines during catalytic reduction of the dinitrile of adipic acid to hexamethylenediamine, under optimal conditions, occurs by the aldimine mechanism, and not by deamination of the primary diamine.

Thus, the optimal deamination temperature for primary amines is higher than the reduction temperature of nitriles to primary amines.

IV. MECHANISM OF THE CATALYTIC REDUCTION OF NITRILES

1. Mechanism of Reduction of Mononitriles

Sabatier and Senderens [57] obtained a mixture of primary, secondary, and tertiary amines by catalytic reduction of nitriles on a nickel catalyst at 180–350°. At the higher temperatures the yield of secondary and tertiary amines increased, and appreciable formation of hydrocarbons and evolution of ammonia was observed. The authors consider that the secondary and tertiary amines are formed by deamination:



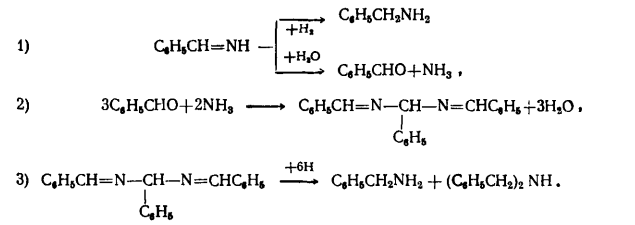
The formation of a complex mixture of amines in the catalytic hydrogenation of nitriles has been repeatedly observed [58,59].

Rosenmund and Pfankuch [60] were the first to carry out the process in an acid medium in order to discourage the formation of secondary amines: they obtained primary amines in 80% and 73% yield from benzonitrile and phenylacetonitrile respectively, using a $Pd/BaSO_4$ catalyst and

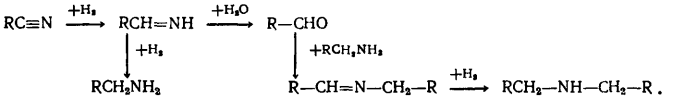
a glacial acetic acid medium. According to the authors[60], the acid reacts with the primary amine as it forms, and protects it from deamination to secondary and tertiary amines. Carothers and Jones[61] also obtained exclusively primary amines (as their acetyl derivatives) by the reduction of aromatic nitriles on Adams platinum in an acetic anhydride medium.

The use of strong acid media, though successful with platinum and palladium catalysts, is not permissible with nickel and cobalt catalysts, because these are severely attacked and lose their activity under these conditions[5,62].

Paal and Gerum[58] put forward the suggestion that the catalytic reduction of nitriles proceeds through the stage of aldimine formation, and that the formation of a secondary amine does not occur by deamination of a primary amine. The aldimine is partially hydrolysed to an aldehyde, which then reacts with ammonia to give a bis-Schiff's base. Hydrogenation of the latter produces a primary and a secondary amine:



A comparison of the composition of the hydrogenation products of benzonitrile and phenylacetonitrile on a nickel catalyst, with and without added phenylhydrazine, led Rupe and Hodel[63] to the conclusion that only step (1) can be correct in the above scheme. Formation of a bis-Schiff's base was not observed. It was also shown that the Schiff's base (benzylideneaniline) is reduced easily and almost quantitatively, under similar conditions, to a secondary amine. Hence, the authors consider that the primary amine is obtained exclusively through an aldimine, whilst the secondary amine is obtained through a Schiff's base, whose formation requires the conversion of the aldimine into an aldehyde:

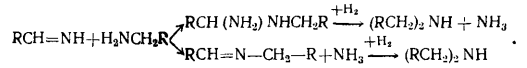


The conversion of the intermediate aldimine into an aldehyde was observed by Pietra and Trinchera[64] in the course of the reduction of aromatic nitriles on Raney nickel in aqueous-alcoholic media containing hydrazine (to precipitate the aldehydes as their hydrazones). The yield of aldehydes from benzonitrile, *o*-, *m*-, and *p*-tolunitriles, 1- and 2-naphthonitriles, was 81, 78, 82, 82, 69, and 59% respectively.

Plieninger and Werst[65] obtained aldehyde semicarbazones during hydrogenation of aliphatic and aromatic nitriles on Raney nickel and cobalt catalysts in water or aqueous alcoholic media.

Rupe and Becherer[66] obtained a Schiff's base in 70% yield during reduction of 2-naphthonitrile on a nickel catalyst in aqueous alcohol. The base was not hydrogenated to a secondary amine because it was sparingly soluble under the reaction conditions. The hydrogenation of 1-naphthonitrile under similar conditions did not produce the corresponding Schiff's base because the latter, being readily soluble, was reduced to a secondary amine. The authors' explanation for the absence of Schiff's bases among the reduction products of other nitriles is that they are usually very soluble and are therefore hydrogenated to secondary amines.

The scheme of formation of secondary amines involving reaction between an aldimine and an aldehyde was not applicable to the reduction of nitriles in anhydrous media. Yet, Braun *et al.*[67] obtained a mixture of primary and secondary amines even from the hydrogenation of nitriles in non-aqueous media. The relative yields depended on the nature and the concentration of the solvent. Hence the authors suggest that the primary amine is formed from an aldimine, whilst the secondary amine is formed by the condensation of the aldimine with the primary amine:

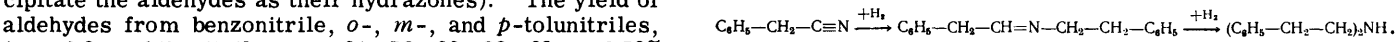


In the presence of a solvent, the formation of a secondary amine could be expected to decrease, owing to the lower probability of interaction between the aldimine and the primary amine. The experimental results were in keeping with this proposition. When the concentration of benzonitrile in decalin (or tetralin) was increased from 34% to 91% the yield of benzylamine rose from 44% to 72% and the yield of *N*-phenylbenzylamine fell from 40% to 5%. In n-pentanol, the same concentrations of nitrile produced 59% and 14% of the primary amine and 71% and 8% of the secondary amine respectively. A similar variation of the yield of primary amine with nitrile concentration was observed also in the reduction of phenylacetonitrile, 1- and 2-naphthonitriles, and *o*-, *m*-, and *p*-tolunitriles. However, the formation of a condensation product between an aldimine and a primary amine, or of a Schiff's base, was not demonstrated experimentally in this work.

Carothers and Jones[61], whilst carrying out the reduction of benzonitrile and *p*-tolunitrile over Adams catalyst in absolute alcohol, also obtained mixtures of primary and secondary amines.

Thus, the experimental results of work on the catalytic reduction of nitriles in non-aqueous media are in agreement with the mechanism for the formation of secondary amines put forward by Braun and coworkers[67].

Kindler and Peschke[68] were the first to isolate, from the hydrogenation products of phenylacetonitrile on palladium black in an anhydrous medium, the Schiff's base *N*-(β-phenylethylidene)-2-phenylethylamine. Reduction of this compound gave di-(2-phenylethylamine):

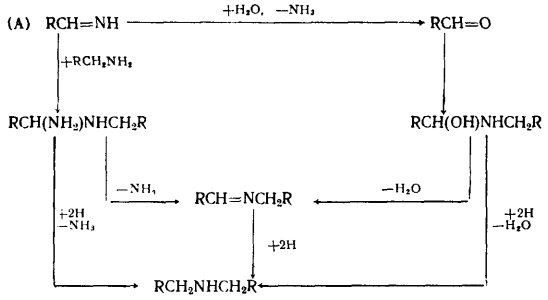


The formation of Schiff's bases in addition to primary and secondary amines during reduction of nitriles on Raney catalysts has been reported also in more recent papers.

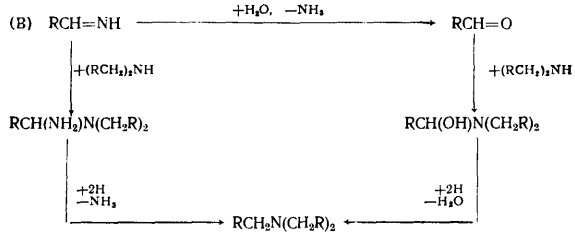
Chiavarelli and Marini-Bettolo[69] obtained 10% of a Schiff's base, besides primary (85%) and secondary amines, from the hydrogenation of 4-cyano-*N*-methyl-4-phenyl piperidine on Raney nickel.

Kindler and Hess[70] suggested possible reaction paths for the formation of secondary amines (scheme A) and tertiary amines (scheme B) during reduction of nitriles in aqueous and in anhydrous media. The secondary amine is formed by condensation of an aldimine (in anhydrous media) or an

aldehyde (in aqueous media) with the primary amine, followed by hydrogenolysis of the resulting adduct, or by conversion of the condensation product into a Schiff's base which is then hydrogenated:



Formation of the tertiary amine occurs by hydrogenolysis of the product of the condensation of an aldimine or aldehyde with the secondary amine:



Juday and Adkins[71] reduced benzonitrile on Raney nickel in the presence of aromatic amines, and obtained, among other products, a small amount of Schiff's bases mostly containing the same aromatic radical. On the other hand, the Schiff's base (and the secondary amine) obtained by hydrogenation of benzonitrile mixed with *p*-methoxybenzonitrile contained different aromatic radicals. From this the authors conclude that the formation of secondary amines during reduction of nitriles can occur, in addition to Braun's mechanism[67], by the condensation of two molecules of aldimine:

$$Ar{-}CH{=}NH + HN{=}CH{-}Ar' \rightarrow Ar{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}N{=}CHAr' \rightarrow$$

$$\xrightarrow[(-NH_3)]{+H_2} Ar{-}CH_2{-}N{=}CH{-}Ar' \xrightarrow{+H_2} Ar{-}CH_2{-}NH{-}CH_2{-}Ar'.$$

Many workers have examined the influence of the structure of the nitrile and of the preparative conditions on the yield of primary and secondary amines. Kindler *et al.*[72] showed that phenylacetonitrile is reduced much more slowly than benzonitrile on palladium black in glacial acetic acid or 96% ethanol. Secondary amines were obtained in high yield (40–68%) from phenylacetonitrile, whereas benzonitrile gave mainly the primary amine (96–99%). The authors concluded that under conditions of slow reduction of the nitrile most of the aldimine formed as an intermediate can react with the primary amine before being reduced by the hydrogen, thus giving a higher yield of secondary amine.

Winans and Adkins[73] also came to the conclusion that secondary amines can be formed by two different paths during the catalytic reduction of nitriles: deamination of two molecules of the primary amine, and reaction between an aldimine and the primary amine by Braun's mechanism[67]. Deamination of primary amines (n-pentylamine, cyclohexylamine, 2-phenylethylamine) in the presence of a nickel catalyst was carried out[73] above 160–170°. The authors point out that a catalyst is unnecessary for the formation of a Schiff's base from an aldimine and an amine, and that this reaction occurs even at room temperature, so that, in order to obtain a high yield of primary amine, nitriles should be reduced under conditions which favour hydrogenation, namely, in the presence of sufficient catalyst and under high hydrogen pressures and temperatures.

More recently, Schwoegler and Adkins[74] have suggested a more effective method of raising the yield of primary amines. On the basis of Braun's scheme for the formation of secondary amines, they point out that the yield of secondary amines should decrease in the presence of ammonia, which can react with the aldimine:

$$RCH{=}NH + NH_3 \longrightarrow \underset{\displaystyle NH_2}{\overset{\displaystyle NH_2}{\underset{|}{\overset{|}{RCH}}}} \xrightarrow{+H_2} RCH_2NH_2 + NH_3.$$

The authors confirmed this suggestion experimentally. The formation of secondary amines was almost completely suppressed when they reduced the nitriles of n-butyric acid and n-heptanoic acid in the presence of ammonia. The method has, since then, become extensively used.

Thus, a great deal of experimental work supports the conclusion that the catalytic reduction of aliphatic and aromatic mononitriles to primary and secondary amines occurs by an aldimine mechanism. At high temperatures, secondary amines can be formed also by deamination of primary amines.

2. Mechanism of Reduction of Dinitriles

The formation of aminonitriles during the catalytic hydrogenation of dinitriles convincingly proves that the two nitrile groups are not reduced at the same time:

$$NC{-}(CH_2)_n{-}CN \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+1}{-}CN \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+2}{-}NH_2.$$

The results of many investigations point to the aldimine mechanism of reduction for both nitrile groups. Plieninger and Werst[65] hydrogenated dinitriles on Raney nickel and cobalt in aqueous or aqueous-alcoholic media in the presence of semicarbazide, and obtained the semicarbazones of the following cyanoaldehydes and dialdehydes: from the succinodinitrile, the semicarbazone of 2-cyanopropionaldehyde (yield 60%) and that of the succinodialdehyde (yield 20%); from the adipodinitrile, the semicarbazone of adipodialdehyde (yield 40%); from *o*-biscyanomethylbenzene, the semicarbazones of *o*-(cyanomethyl)phenylacetaldehyde, (yield 40%) and of *o*-phenylenediacetaldehyde (yield 20%). The formation of a cyanoaldehyde as well as a dialdehyde is additional evidence for the stepwise nature of the catalytic reduction of a dinitrile.

Thus, a primary diamine is formed by the catalytic reduction of a dinitrile through the intermediate stages of aldimine formation:

$$NC{-}(CH_2)_n{-}CN \xrightarrow{+H_2} HN{=}CH{-}(CH_2)_n{-}CN \xrightarrow{+H_2}$$

$$\longrightarrow H_2N{-}(CH_2)_{n+1}{-}CN \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+1}{-}CH{=}NH \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+2}{-}NH_2.$$

Published data on the effect of ammonia on the composition of the hydrogenation products of dinitriles are in agreement

with the scheme put forward by Schwoegler and Adkins[74], according to which the aldimine formed as an intermediate reacts with ammonia to give a higher yield of primary amines in the final product.

Studies of the reduction of adipodinitrile under static conditions and in the presence of different catalysts have shown that the presence of ammonia in the reaction medium favours the formation of the primary diamine.

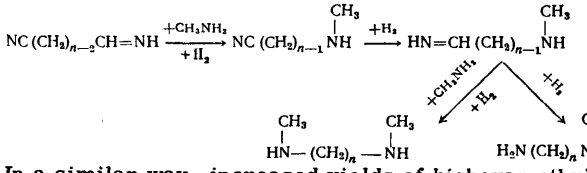
Zil'berman and Skorikova[4] established that the yield of diamine in the presence of Raney nickel is reduced from 82% to 72% by decreasing the amount of NH_3 from 9 to 3 moles per mole of dinitrile. Polkovnikov *et al.*[42] obtained hexamethylenediamine in 94% yield by the hydrogenation of adipodinitrile on a cobalt boride catalyst in the presence of ammonia: the yield fell to 71% in the absence of ammonia.

Freidlin *et al.*[75] observed a sharp increase in the yield of secondary amines, and a lower yield of hexamethylenediamine, when they carried out the reaction without ammonia on the following catalysts: Raney nickel and cobalt, nickel on magnesium oxide, and nickel on alumina–silica.

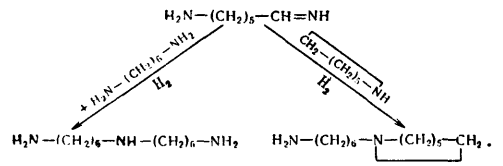
When the concentration of ammonia was increased from 10% to 20–30%, using a Raney nickel catalyst under flow conditions, the yield of hexamethylenediamine rose[7] from 40% to 65%.

The presence of ammonia in the reaction zone was found to affect the yields of primary and secondary amines in exactly the same way in the hydrogenation of adipodinitrile under flow conditions on Raney cobalt[8] and alumina-supported cobalt[39]. The yield of primary diamine has also been found to depend on the amount of ammonia present in the reaction zone in a number of investigations of the catalytic reduction of the dinitriles of terephthalic and isophthalic acids[13–16], and of the dinitriles of *p*-, *m*-, and *o*-phenylenediacetic acids[10–12] (see Table 1).

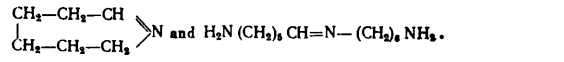
Biggs and Bishop[76], in their study of the reduction of the dinitriles of adipic and sebacic acids on Raney nickel in a medium of liquid methylamine, obtained mixed primary–secondary amines in a yield which increased with the methylamine : dinitrile molar ratio. In addition to *N*-methylhexamethylenediamine and *N*-methyldecamethylenediamine, they observed the formation of *NN'*-dimethylhexamethylenediamine and *NN'*-dimethyldecamethylenediamine. The production of mixed primary–secondary and of disecondary amines is easily explained by postulating a reaction between an aldimine and methylamine:



In a similar way, increased yields of bishexamethylenetriamine[40] and of 1,6′-aminohexylperhydroazepine[56] in the presence of added perhydroazepine have been reported for the reduction of the adipodinitrile in a medium of hexamethylenediamine:

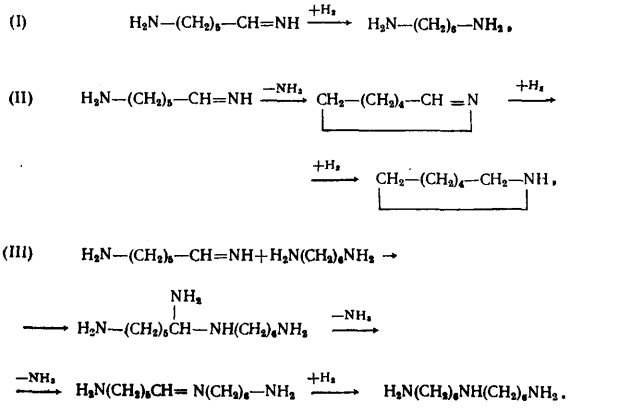


Zil'berman *et al.*[77] reported that commercial hexamethylenediamine contains small quantities of the *N*-alkylaldimines [*N*-alkylalkylideneimines (Ed. of Translation)]:

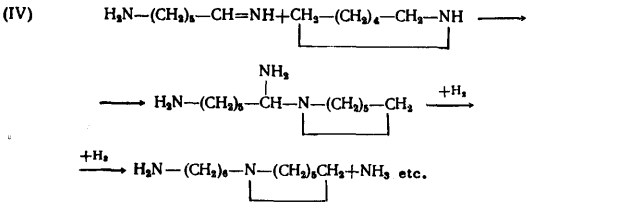


All these results indicate that secondary amines are probably formed, during catalytic reduction of dinitriles, through the stages of formation of a Schiff's base (from an aldimine and an amine) which is subsequently hydrogenated.

Secondary amine formation during reduction of dinitriles may occur either by intermolecular or by intramolecular interaction between an iminomethyl and an amino-group. Hence, cyclic as well as acyclic secondary amines can be obtained. For example, the hydrogenation of the adipodinitrile gives rise to the following amines:



A tertiary amine is formed by the reaction of an aldimine with a secondary amine:

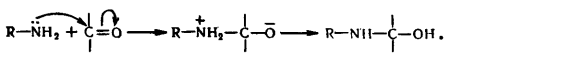


It can be seen from Eqns. (I)–(IV) that the aminoaldimine is a common intermediate product in the formation of primary, secondary, and also tertiary amines. Hence, the formation of the primary diamine and the formation of secondary and tertiary amines are competing reaction paths in the reduction of a dinitrile, and the ratio

$$\frac{\text{primary amine}}{\text{sum of secondary and tertiary amines}}$$

should depend on the relative rates of the competing reactions: hydrogenation of the aldimine and addition of the aldimine to the amine (followed by hydrogenation of the resulting Schiff's base).

The formation of a Schiff's base from an aldehyde and a primary amine is known to proceed readily even at room temperature and in the absence of a catalyst[78]. The mechanism of this reaction involves attack by the base on the electrophilic carbon atom of the carbonyl group, which shifts its π electrons towards the oxygen:



In our case, there are two bases in the solution: a stronger one (the amine) and a weaker one (the ketone). The reaction is reversible, and therefore the yield of the various products depends on the acidity (or basicity) of the medium[79,80]. Aldimines are isoelectronic with carbonyl compounds, and can therefore be assumed to react with amines or ammonia in much the same way as carbonyl compounds react with amines:

$$RNH_2 + \rangle C{=}NH \rightleftarrows R{-}NH{-}\overset{|}{\underset{|}{C}}{-}NH_2 \rightleftarrows R{-}N{=}\overset{|}{\underset{|}{C}} + NH_3,$$

$$NH_3 + \rangle C{=}NH \rightleftarrows H_2N{-}\overset{|}{\underset{|}{C}}{-}NH_2 \rightleftarrows HN{=}\overset{|}{\underset{|}{C}} + NH_3.$$

The use of strongly basic media, such as ammonia, should suppress the formation of Schiff's bases and therefore also the formation of secondary and tertiary amines.

Thus, conditions favourable to the formation of primary amines are obtained by carrying out the reduction of dinitriles in the presence of ammonia, since the tendency to form Schiff's bases is thereby decreased and the reactivity of the aldimines is increased.

V. INFLUENCE OF DINITRILE STRUCTURE ON THE COURSE OF THE REACTION

The course of the catalytic hydrogenation of dinitriles is influenced by the structure of the dinitrile as well as by the experimental conditions and the nature of the catalyst.

Benzonitrile is rapidly reduced on a nickel catalyst at 115–120°, but the naphthonitriles are reduced very slowly, and require an increase in temperature to 180–190° to give a fast reaction[67].

The position of substituents is also important. In the reduction of *o*-, *m*-, and *p*-tolunitriles the yields of primary amines were 61, 54, and 41% respectively; in the case of ω-methoxy-*o*- and ω-methoxy-*p*-tolunitriles they were 44 and 20%; and with 1,2,3,4-tetrahydronaphtho-1-nitrile and -2-nitrile they were[67] 70 and 47%. The activating influence of the phenyl group has been pointed out: under identical conditions, primary amine yields of 21, 36, and 41% were obtained by reduction from phenylpropionitrile, phenylacetonitrile, and benzonitrile respectively.

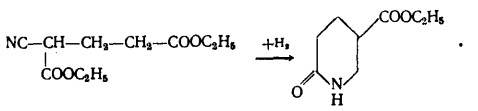
Jadot and Braine[81] showed that benzonitrile is converted into primary and secondary amines on a Raney copper catalyst at 180–200°, whereas phenylacetonitrile is not reduced even when the temperature is raised to 260°.

The effect of nitrile structure on the course of the reaction has been observed also in work on the catalytic reduction of organosilicon nitriles: under identical hydrogenation conditions a higher yield of primary amine is obtained[82] from 3-cyanopropyltriethoxysilane (81%) than from 2-cyanoethyltriethoxysilane (68%). This difference is obviously due to the different positions of the CN groups relative to the silicon atom[83].

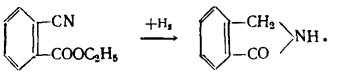
Alkyl groups on the silicon atom have a screening effect in the reduction of *sym*-tetraalkyldi-3-cyanopropyldisiloxanes: the yield of primary amine falls as the alkyl side-chain is made longer. For example, the following compounds, when hydrogenated under identical conditions, gave the corresponding *sym*-tetraalkyldi-4-aminobutyldisiloxanes in yields of 92, 87, and 70% respectively[20]:

$$[NC{-}(CH_2)_3{-}Si(CH_3)_2]_2O,$$
$$[NC{-}(CH_2)_3{-}Si(CH_3)(C_2H_5)]_2O,$$
$$[NC{-}(CH_2)_3{-}Si(C_2H_5)_2]_2O.$$

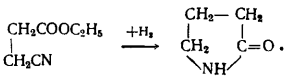
The course of the hydrogenation is particularly sensitive to the nitrile structure when a second reactive group (carbonyl, carboxyl, ethyl carboxylate, hydroxyl, or nitrile) is situated in position 3, 4, or 5 relative to the nitrile group. In this case, cyclisation occurs. There are many examples of this conversion: thus Koelsch[84] obtained ethyl 2-ketopiperidine-5-carboxylate by reducing diethyl α-cyanoglutarate on Raney nickel at 100° under 900 atm hydrogen pressure:



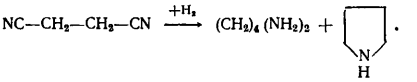
Watanabe[85] observed the formation of a cyclic product, in 73.7% yield, by the reduction of ethyl *o*-cyanobenzoate at 260° on a nickel–copper catalyst supported on silica gel:



Linn[86] obtained 2-pyrrolidone in 91% yield by reducing ethyl β-cyanopropionate on a Raney nickel catalyst at 90° and under an initial hydrogen pressure of 70 atm in an ethanol medium:



By passing the vapour of succinodinitrile in a hydrogen stream over a nickel catalyst at 180–200°, Gaudion[87] observed the formation of small amounts of tetramethylenediamine and pyrrolidine:



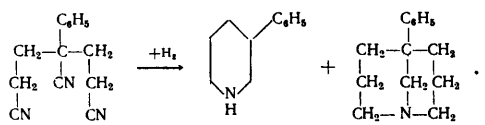
Hydrogenation of succinodinitrile in liquid ammonia on a Raney nickel catalyst at 140° gave pyrrolidine and tetramethylenediamine in 45 and 20% yield respectively[21]. Others[43] obtained pyrrolidine and tetramethylenediamine in 70 and 5% yield respectively by reducing succinodinitrile on Raney nickel at 75°.

It is claimed in a patent[22] that the reduction of glutarodinitrile in the presence of Raney nickel or cobalt on kieselguhr at 172° gives only piperidine (in 83% yield). When the temperature is reduced to 125° in the presence of cobalt on kieselguhr, pentamethylenediamine (41.5% yield) is formed as well as piperidine. Lower yields of piperidine, and the apperance of a diamine among the reaction products, were observed also upon decreasing the reaction time.

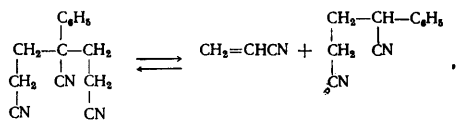
The reduction of glutaronitrile on Raney cobalt in ammonia gave[41] piperidine and pentamethylenediamine in 35 and 55% yield, whereas the primary diamines were obtained in practically quantitative yield from the dinitriles of pimelic,

azelaic, sebacic, and decanedicarboxylic acids. The yield of primary diamines was [41,88] 85–90% in the reduction (on Raney nickel) of the dinitriles of pimelic, azelaic, sebacic, nonanedicarboxylic, decanedicarboxylic, and *trans*-docos--13-enoic acids.

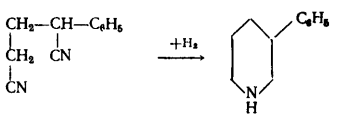
Badger *et al.*[89] hydrogenated 1,3,5-tricyano-3-phenylpentane on copper chromite at 220–230° under an initial hydrogen pressure of 175 atm, and observed the formation of 3-phenylpiperidine (10%) and 5-phenyl-1-azabicyclo-[3,3,1]nonane (15%):



The suggestion has been made[90] that the unstable tricyanide decomposes into vinyl cyanide and a dicyanide:

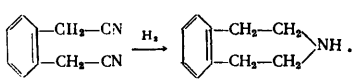


and that 3-phenylpiperidine results from reduction of the dicyanide:

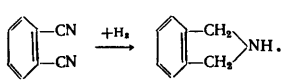


Reduction of the adipodinitrile on Raney nickel or cobalt gives rise to a mixture of the primary diamine and smaller amounts (up to 30%) of secondary diamines, both straight--chain and cyclic.

Catalytic reduction of the dinitriles of *m*- and *p*-phenylenediacetic acids produces high yields of the corresponding primary diamines [10,12,47], whereas the dinitrile of *o*-phenylenediacetic acid gives, as well as the primary diamine, up to 83% of the secondary cyclic amine "benzohexamethyleneimine" [11] [1,2,3,8,9-pentahydrobenzoazepine (Ed. of Translation)]:



The dinitriles of *m*- and *p*-phthalic acids give, respectively, *m*- and *p*-xylylenediamine [13–16,43], but the *o*-phthalodinitrile gives only the cyclic amine (a dihydroisoindole) [43]:



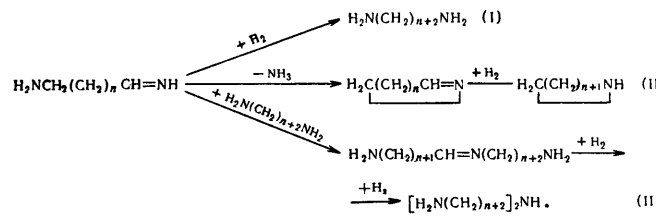
Thus, dinitriles in which the nitrilo-groups are separated by three or four carbon atoms are reduced to a mixture of cyclic and straight-chain amines. Cyclisation is greatly assisted by the presence of two carbon atoms between the CN groups, attached to a benzene ring, in aromatic (or aliphatic–aromatic) *o*-dinitriles.

When there are only two carbon atoms between the nitrilo groups, the formation of an unstrained *N*-heterocycle is favoured, and cyclic products are obtained almost exclusively [43].

Under optimum conditions, the yield of primary diamines from the dinitriles of adipic, glutaric, succinic, and *o*-phthalic acids was 90, 55, 5, and 0% respectively, whilst the cyclic secondary amine was obtained [41] in 5, 35, 70, and 90% yields respectively. Therefore, the tendency of dinitriles to give the cyclic secondary amine during reduction increases in the sequence

adipic < glutaric < succinic < *o*-phthalic.

The structure of the dinitrile appears to influence the course of the reduction by controlling the relative rates of reactions I and II: hydrogenation of the aldimine and intramolecular reaction between the iminomethyl group and the primary amino-group, followed by hydrogenation of the resulting Schiff's base:



With aliphatic α,ω-dinitriles having 7–12 carbon atoms, and also with *m*- and *p*-substituted aromatic dinitriles, hydrogenation of the aldimine is preponderant, and no intramolecular reaction between the iminoethyl and amino--groups takes place. The second reaction (formation of a cyclic amine) predominates in the reduction of dinitriles with two carbon atoms between the nitrilo-groups: neither the use of a selective catalyst (Raney cobalt) nor the use of ammonia as a reaction medium can influence the reaction in the direction of the primary amine [43].

In the intermediate case — reduction of dinitriles with 3–4 carbon atoms separating the nitrilo-groups — we observe a process occurring simultaneously by the reaction paths (I), (II), and (III).

The available data show that the structure of the dinitrile molecule has a profound influence on the course of the reaction.

VI. INFLUENCE OF THE NATURE OF THE CATALYST ON THE COURSE OF THE REACTION

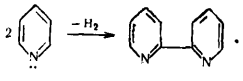
The relative yield of primary and secondary amines in the catalytic reduction of dinitriles depends on the nature of the catalyst as well as on the reaction conditions and on the structure of the dinitrile molecule.

The higher selectivity of Raney cobalt (as compared with Raney nickel) towards formation of primary amines had already been pointed out in work on the catalytic reduction of mononitriles [91,92]. Hydrogenation of aliphatic, aromatic, and organosilicon dinitriles in the presence of a Raney cobalt catalyst invariably gives a higher yield of primary diamines than hydrogenation on Raney nickel [7,8,17,41]. For example, 75–78% of hexamethylenediamine, 10–14% of hexamethyleneimine, and 10–15% of a residue consisting mainly of bishexamethylenetriamine were obtained [41,75] by the reduction of adiponitrile on nickel under the most favourable conditions. On a cobalt catalyst, hexamethylenediamine can be produced in practically quantitative yield, and the cyclic secondary amine amounts to no more than 3–5%. The yield of primary diamines from the dinitriles of pimelic, azelaic, sebacic, and decanedicarboxylic acids reaches 85 and 95% on Raney nickel and Raney cobalt respectively [41].

Cobalt catalysts act more selectively irrespectively of the method of preparation of the catalyst (Raney, boride, supported)[42,56]. Their higher selectivity persists even when the reaction is carried out in the absence of ammonia (*i.e.* under conditions which favour the formation of a secondary amine). Obviously, the selectivity of different metallic catalysts towards the reduction of dinitriles, as well as their activity, is determined mainly by their chemical nature.

Maxted and Walker[93] ascribed the deactivation of metallic catalysts by pyridine and piperidine during hydrogenation to the presence of a free electron pair on the nitrogen atom, which causes these bases to be strongly adsorbed on the catalyst. This view is in agreement with the results of Badger *et al.*[94], who found that the rate of hydrogenation of *trans*-crotonic acid on Raney nickel is significantly decreased by the presence of pyridine and 2,2′-bipyridyl. Pyridine was found to be more "toxic" than 2,2′-bipyridyl.

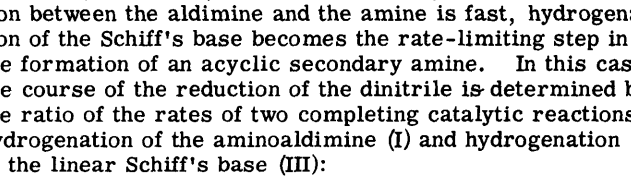
Badger and Sasse[95] obtained heterocyclic biaryls by refluxing monoheterocyclic compounds in the presence of a Raney nickel catalyst; for example, pyridine gave 2,2′-bipyridyl:



The formation of the biaryl indicates that the CH bond in position 3 with respect to the nitrogen atom is activated, probably owing to withdrawal of the electron pair from the nitrogen atom during adsorption of the reacting molecule on the catalyst.

On a Raney cobalt catalyst, on the other hand, no bipyridyl is formed[94], and the rate of hydrogenation of *trans*-crotonic acid is not depressed by the presence of pyridine and 2,2′-bipyridyl.

We have already pointed out that the yield of secondary amines (both cyclic and straight-chain) depends on the relative rate of formation of the Schiff's base and on the rate of its subsequent hydrogenation. The formation of a cyclic Schiff's base is determined almost exclusively by the structure of the dinitrile undergoing hydrogenation, whereas the rate of formation of a linear Schiff's base is largely dependent on the reaction conditions (presence of ammonia, dilution by a solvent, nature of the catalyst). If the reaction between the aldimine and the amine is fast, hydrogenation of the Schiff's base becomes the rate-limiting step in the formation of an acyclic secondary amine. In this case the course of the reduction of the dinitrile is determined by the ratio of the rates of two completing catalytic reactions: hydrogenation of the aminoaldimine (I) and hydrogenation of the linear Schiff's base (III):



The Schiff's base formed during reduction of dinitriles, being an *N*-substituted aldimine, is probably adsorbed on the catalyst less strongly than the unsubstituted aldimine. Therefore, the rate of hydrogenation of the aldimine should be different from the rate of hydrogenation of the Schiff's base. On nickel and cobalt catalysts, the main reduction product of dinitriles with more than 3 carbon atoms separating the CN groups is a primary amine. Hence, we may assume that reaction (I) is faster than reaction (III) on Ni and Co catalysts. From this point of view, the higher selectivity of the cobalt as compared with the nickel catalyst can be ascribed to a greater difference in ease of adsorption between the aldimine and the Schiff's base.

The specificity of the cobalt catalyst cannot manifest itself in the reduction of short-chain dinitriles. When $n = 2$, the tendency of the molecule towards cyclisation is so strong that reaction (II) predominates.

The nature of the catalyst support also can influence the course of the reaction[75].

It may be assumed that all the reacting species in reactions (I), (II), and (III) have activational requirements. To convert an aldimine into a primary amine, the iminomethyl group as well as the hydrogen have to be activated. On the other hand, the conversion of an aldimine into a secondary amine requires activation of two electron-donating (imino- and amino-) groups.

By choosing potential electron acceptors as carriers for the nickel catalyst, we could expect to influence the reduction of nitriles towards the formation of secondary and tertiary amines. Specifically, such a carrier should enhance the adsorption by the catalyst of =NH– and $-NH_2$ groups in the reacting molecules, and should thus affect the relative rates of the competing reactions (I), (II), and (III). In fact, nickel catalysts deposited on acidic (alumina–silica, silica gel, aluminium oxide) or amphoteric carriers (zirconium, titanium, molybdenum, or tungsten oxides) show a marked increase in the formation of secondary and tertiary amines[75].

The appreciable yield of secondary amines from nickel catalysts supported on acidic or amphoteric carriers can also be explained in terms of the very strong adsorption of the unsubstituted aldimine (catalyst poisoning) on the surface of such a catalyst, whilst the more weakly adsorbed Schiff's base is hydrogenated more rapidly.

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SOME ASPECTS OF HIGH-TEMPERATURE CHEMISTRY FROM THE VIEWPOINT OF CHEMICAL THERMODYNAMICS

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I. INTRODUCTION

In the last 10–15 years high-temperature chemistry has begun to develop rapidly into a new branch of chemistry. The concept of high temperature is relative and depends on the range of problems and phenomena considered. Some authors therefore prefer to relate high-temperature chemistry not to definite temperature limits but to various characteristics of the properties of substances and the observed relationships shown by the properties. Thus Brewer[1] defines high-temperature chemistry as the chemistry of systems at sufficiently high temperatures so that the oxidation states, compounds, and general chemical behaviour differ appreciably from those important at room temperature. Searcy[2] defines high temperatures as temperatures at which entropy differences play a major role in determining the position of equilibria of interest (under standard conditions). Using this definition, 3000°K is not a high temperature for the processes of nitrogen ionisation, but for many volatilisation processes, moderately high temperatures or even room temperature (or lower temperatures) could be regarded as high temperatures. There is some justification for this approach, but in the present paper the author prefers, in agreement with Margrave[3], to adopt, albeit arbitrarily, certain definite boundaries on the temperature scale.

In the wide range of temperatures which have now become accessible to a greater or lesser degree (10^{-6}–10^{8} °K), high-temperature chemistry concerns a relatively small interval (of 1–2 orders of magnitude) from about 1000°K to 10000°K (or possibly up to 50000°K), since at higher temperatures almost no molecules remain and atoms undergo increasing ionisation with the formation of plasma. The present paper deals chiefly with the thermodynamic properties of substances at these high temperatures. Other aspects will be touched upon, however, in the discussion of processes of vaporisation.

The marked increase in interest in the physics and chemistry of high temperatures was initially due to the demands made by certain branches of modern technology. This was further stimulated by better availability of high temperatures for experiments, development of methods of study at high temperatures, and the use of fast electronic computers for calculating the thermodynamic functions of various molecules, atoms, and ions at high temperatures using the methods of statistical thermodynamics. Statistical thermodynamics combined with new calculating techniques is widely used in high-temperature chemistry, and it is on this basis that most of the new information on the thermodynamic properties of substances at high temperatures is now obtained, partly because of the great difficulty of making calorimetric determinations even at moderately high temperatures. The methods of statistical thermodynamics are also based on experimental data, but these data are obtained from various types of spectra and by determination of the fundamental parameters of molecular structure (interatomic distances, etc.) by electron and X-ray diffraction studies, etc.

Experimental work in the field of high-temperature chemistry has been accompanied by theoretical work relating to the new experimental methods, methods for calculating thermodynamic properties, and the state of substances at high temperatures. Interest in high-temperature chemistry has also been stimulated by the fact that the previously widely-held views that all chemical relationships became progressively simpler at high temperatures and that there were no fundamentally new problems or phenomena, proved to be greatly oversimplified. The main trends observed on going to very high temperatures are an extremely marked increase in the reactivity of substances, an increase in reaction rates, and the development of processes involving the dissociation and decomposition of complex substances; these are obvious, but at the same time many elements form compounds at high temperatures corresponding to valence states (degrees of oxidation) which are not characteristic, or are unknown for these elements, at ordinary temperatures. Even the relationships between the properties of elements in the same Periodic Group are sometimes found to be more complex than those observed at ordinary temperatures. High temperatures lead to the appearance of species of new types, which may be simpler than the corresponding species at ordinary temperatures (for example CaCl, SiO, Al_2O, AlO, SO) or more complex (C_3, C_9, Na_2, Ge_8, Mg_2, Mo_5O_{15}, $Na_2(OH)Cl$, Ba_2O_3, etc.). At high temperatures, where the thermal motion of the species is capable of breaking chemical bonds, many radicals and free atoms exist in equilibrium with their parent molecules and become essentially molecules themselves. The processes by which they are formed may be quantitatively described by the thermodynamic parameters of the reaction (heat of reaction, entropy change, equilibrium constant, etc.). By determining their temperature dependence, it is often possible, by extrapolation, to obtain interesting conclusions for ordinary temperatures which cannot be arrived at by direct determination at lower temperatures. The tendency for molecules to be simpler at