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The Denitrogenation Reaction Mechanism of Cyclic Amines on Pure Alumina under Normal H_2 Pressure

Different authors (*1–5*) have already studied the reactions of amines on pure alumina; we have investigated the reaction of cyclic amines under normal pressure of H_2 on a pure alumina catalyst. The analyses of the different hydrocarbons and amines formed suggest the liberation of protons and hydrides on the surface, and the intervention of classical acidic-base mechanisms of denitrogenation independent of the hydrogen pressure. In addition, the reaction of disproportionation is absent in the conditions of the reported reactions.

The following materials have been used for the study:

γ-Al_2O_3 Ketjen CK300 (S = 217 m^2/g, V = 0.62 cm^3/g). The particle diameter was 0.2–0.5 mm. The same batch of 200 mg of alumina has been used for all the experiments. Analysis: Fe 0.0173% w., Cl 0.03%, Na 0.0013%, S 0.015%. Before use, the catalyst was treated at 390°C for 24 h under normal pressure H_2 flow.

Piperidine, pyridine, and 2,6-dimethylpyridine (lutidine) (Puriss Fluka), 2,6-dimethylpiperidine (lupetidine), and 3-methylpiperidine (β-pipecoline) ≧ 99% (Aldrich) were used without further purification after checking the purity by GLC (≧ 99.8%). 2-Ethylpiperidine (Aldrich) was purified by fractionated distillation until a final purity ≧ 99.5%.

N-pentylpiperidine was prepared by the addition of 1-bromopentane to piperidine at room temperature, using benzene as a solvent, and refluxed after addition at 80°C for 2 h. The white salt formed was hydrolyzed by 2 *N* NaOH solution and, after diethylether extraction, the different products were separated by a simple distillation. The *N*-pentylpiperidine obtained by this process contained about 10% benzene and 1% other impurities. This product was only used for chromatographic retention time determination.

Information about the apparatus has been given elsewhere (*6*). All the analyses have been made when the catalyst was "stabilized," i.e., when the outlet signal of the second catharometer showed a constant outlet flow of the different products, and when the chromatographic analysis showed a constant composition with time. We are confident that in these conditions we had reached the steady state. All the products have been analyzed for the piperidine reaction and identified by mass spectrometry when necessary. For the other starting materials, we did not analyze the ammonia formed but the material balance (including all the products) was systematically checked by the thermal conductivity detection (an experiment combining an all-trapped system and the commonly used gas samplers has shown us that the impoverishment in heavy products, mainly C_9 to C_{12} hydrocarbons, during the rapid transfer was lower than 5%). The reaction rate reported in the tables has been calculated as follows:

$$r = \alpha \cdot \frac{\mu \cdot \rho}{M} \cdot \frac{10^{-3}}{60} \cdot \frac{1}{w} \text{ mol/s g}$$

where α is the conversion, μ the amine flow, ρ the mass per unit volume, M the molecular weight of the amine, and w the catalyst weight.

In Table 1 are reported the results of the piperidine reaction at 378°C under H_2 atmosphere and He atmosphere. (For this last

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TABLE 1

Reaction of Piperidine at 378°C in H_2 and He at 1 atm on 200 mg of Al_2O_3

	H_2	He
Amine flow in μl/min	1.85	0.75
Flow of H_2 or He in ml/min	87.5	36.0
% of starting compound (hydro)denitrogenated	6.7	42.70
% of starting compound reacted to dehydrogenated amine	50.32	57.23
% of starting compound reacted to aromatic amine	50.32	57.23
Mean rate of (H)DN[a]	1080	3525
Mean rate of dehydrogenation to other amines[a]	10925	5380
Mean rate of aromatization to other amines[a]	10925	5380
Hyperfine Analysis of the Hydrocarbons	mol%	mol%
C_2	3.61	5.12
C_3	1.50	2.10
Isobutene	1.20	3.25
1-Butene	2.44	
isopentenes	0.15	0.03
1-Pentene	3.46	1.84
Pentane	—	0.23
1,3-Pentadiene	1.65	0.79
1,3-Pentadiene	1.80	0.98
Cyclopentene	2.10	1.29
Benzene + Σ other C_6	1.80	1.43
Toluene + Σ other C_7	1.50	1.36
ΣC_8	3.61	
ΣC_9	12.18	81.58
ΣC_{10} (two main products)	62.99	

[a] Units of rate are [mol/s g (catalyst)] × 10^{-10}.

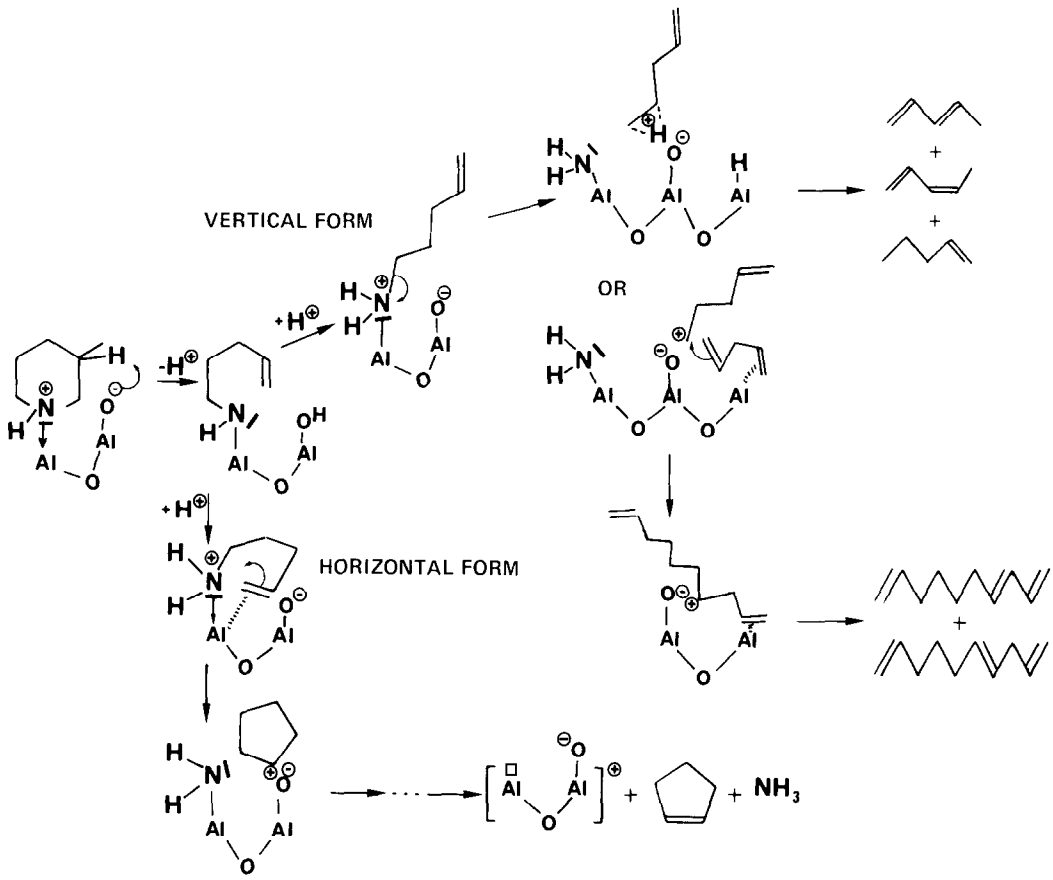
reaction the hydrogen flow was replaced 30 min before the beginning of the reaction by the helium flow.) The main product was always pyridine and we checked very carefully that *N*-pentylpiperidine was *never* formed. The absence of hydrogen increased the rate of the (H)DN reaction but decreased the rate of the dehydrogenation reaction.

The distribution of the hydrocarbons formed during the reaction shows a large amount of C_{10} products. The low resolution chromatographic analysis exhibits one peak representing about 90% of the C_{10}; the high resolution chromatography shows a double peak. The mass spectrometric analysis gives a ratio $m/e = 136$ for a linear hydrocarbon. These observations are in full agreement with the work of Sonnemans *et al.* (*5*), and the formula $C_{10}H_{16}$ (1,3,9-decatriene or 1,4,9-decatriene) which they proposed corresponds exactly to our observations. In addition, the distribution of the linear C_5 hydrocarbons is very informative for the determination of the mechanism. The main product is 1-pentene, followed by cyclopentene, *cis*-1,3-pentadiene, and *trans*-1,3-pentadiene. The *cis*- or *trans*-2-pentene and pentane are only present in a significant amount under helium atmosphere. In the light molecules, C_2 and C_4 are the most abundant. It is interesting to note the large amount of toluene and benzene formed under He atmosphere.

The reaction of pyridine at 390°C did not show any significant activity over alumina.

The formation of products is illustrated in Scheme 1. The opening of the ring leads to two adsorbed forms, one "horizontal" or two-point adsorption, due to an interaction between the double bond and the Lewis acid aluminium, one "vertical" or one-point adsorption without interaction. The "horizontal" form favors the cyclization mechanism because of the endo configuration *and* because of the proximity of O^- to stabilize the cyclic cation and to deprotonate it. This route leads to the formation of cyclopentene. The "vertical" form can lead either to the two 1,3-pentadienes by internal migration of a proton followed by deprotonation, or followed by the addition of a hydride, giving 1-pentene, or to the decatrienes by deprotonation followed by the formation of adsorbed 1,4-pentadiene which immediately reacts with another terminal cation. This dimerization is the most favored.

A similar mechanism can account for the reaction of 3-methylpiperidine which is reported in Table 2. The rate for the total (H)DN reaction, 336.10^{-10} mol/s g, shows an intermediate position between that for



SCHEME 1. Formation of 1-pentene, pentadienes, cyclopentene, and C_{10} from piperidine.

ethylpiperidine and that for piperidine and 2,6-lutidine. The dehydrogenation reaction, is occurring at the same rate as that for ethylpiperidine, 2881.10^{-10} mol/s g. The analysis of the skeletal distribution of the hydrocarbons shows the formation in decreasing amounts of $C_{12} + C_{11}$ (the distribution between C_{11} and C_{12} is often hypothetical), methylcyclopentane, 2-methylpentane, and C_2.

At 378°C, the rate for the total (H)DN reaction of 2,6-lupetidine (Table 2), namely, 1390.10^{-10} mol/s g cata., is similar to that of the piperidine degradation, viz., 1083.10^{-10} mol/s g cata. (Table 1). The dehydrogenation reactions are occurring at roughly equivalent rates, viz., 9622.10^{-10} and 10925.10^{-10} mol/s g cata.; however, the partially dehydrogenated amines (dihydro and tetrahydro) are more important than the aromatic ones, 43.0% and 7.6% for 100 molecules of starting material (the dihydroamines represented most of this 43%).

The hyperfine analysis of the hydrocarbon was impossible because of the large amounts of different olefins formed; however, the mixture was hydrogenated, allowing us to analyze the skeletal composition. The main product is C_3, followed by the methylcyclohexane, nC_7, and $C_4 + C_8$. A very precise measure of the mass balance between the amount of the inlet and outlet products gives an increase of the catharometer signal area of 1.9%; a calculation of the mass balance using appropriate correcting factors from the literature, or determined by us when not otherwise available, gives a theoretical increase of this area of 2.6%. This agreement allowed us to exclude the formation of hydrocarbons larger

TABLE 2

Reactions of 2,6-Lupetidine at 320 and 378°C, 2-Ethylpiperidine and 3-Methylpiperidine at 378°C under 1 atm of H_2 on 200 mg of Al_2O_3

Starting compound	2,6-Lup.	2,6-Lup.	2-Ethylpip.	3-Methylpip.
Temperature (°C)	320	378	375	378
Amine flow in μl/min	2.24	2.27	2.59	1.78
Flow of H_2 in ml/min	87.0	87.5	87.0	87.0
% of starting compound (hydro)denitrog.	0.16	9.7	1.1	4.4
% of start. comp. reacted to arom. amin.	0.7	7.6	1.7	18.2
% of start. comp. reacted to dehydro. amin.	7.3	50.6	16.6	18.2
Reaction rate (H)DN[a]	12	1390	132	199
Reaction rate dehydrogenation[a]	563	9622	2999	2881
Reaction rate aromatization[a]	50	1078	213	2881
Skeletal Analysis of the Hydrocarbons	mol%	mol%	mol%	mol%
C_2	0.42	0.85	14.13	4.48
C_3	28.10	34.34	4.08	10.18
Isobutane	0.08	0.41	—	3.05
n-Butane	3.89	3.96	10.38	0.41
Isopentane	0.29	0.31	0.22	6.31
n-Pentane	1.01	1.64	1.66	3.46
Cyclopentane	0.25	0.20	1.66	—
2-Methylpentane	—	—	—	12.42
3-Methylpentane	0.08	0.03	0.11	1.22
n-Hexane	0.13	0.20	2.21	1.83
Methylcyclopentane	0.46	0.38	0.22	13.03
Cyclohexane + benzene	—	0.10	0.88	0.61
2-Methylhexane	0.67	0.27	—	
3-Methylhexane	0.54	1.09	0.66	
1,2-Dimethylcyclopentane *cis* + *trans*	1.30	0.99	0.22	
1,3-Dimethylcyclopentane *cis* + *trans*	—	0.72	0.77	1.43
n-Heptane	26.72	13.53	12.14	
Methylcyclohexane + toluene	31.03	21.97	28.70	
Ethylcyclopentane	0.25	0.61	11.48	
C_8	3.69	3.42	8.17	5.70
C_9	1.09	0.20	2.32	5.70
C_{10}				1.22
$C_{11} + C_{12}$				28.92

[a] Units of rate are [mol/s g (catalyst)] × 10^{-10}.

than C_9 in noticeable amounts and the formation of nondetected amines.

At 320°C the distribution was similar. A rough calculation by Arrhenius plot gives 32 kcal/mol for the apparent activation energy of the aromatization, and 55 kcal/mol for an average (H)DN reaction.

2,6-Dimethylpyridine did not show any significant reaction over alumina at 380°C.

Table 2 also shows the results obtained from the reaction of 2-ethylpiperidine at 375°C. The rate for the (H)DN reaction, 132.10^{-10} mol/s g, and for the dehydrogenation, 2999.10^{-10} mol/s g, are much lower than for piperidine and 2,6-lupetidine.

The fine analysis of the skeletal distribution of the hydrocarbons shows the formation in decreasing amounts of methylcyclohexane, C_2, nC_7, ethylcyclopentane, C_4, and C_8. The analysis of the catharometer signal area shows again that hydrocarbons higher than C_9 are not formed in noticeable amounts.

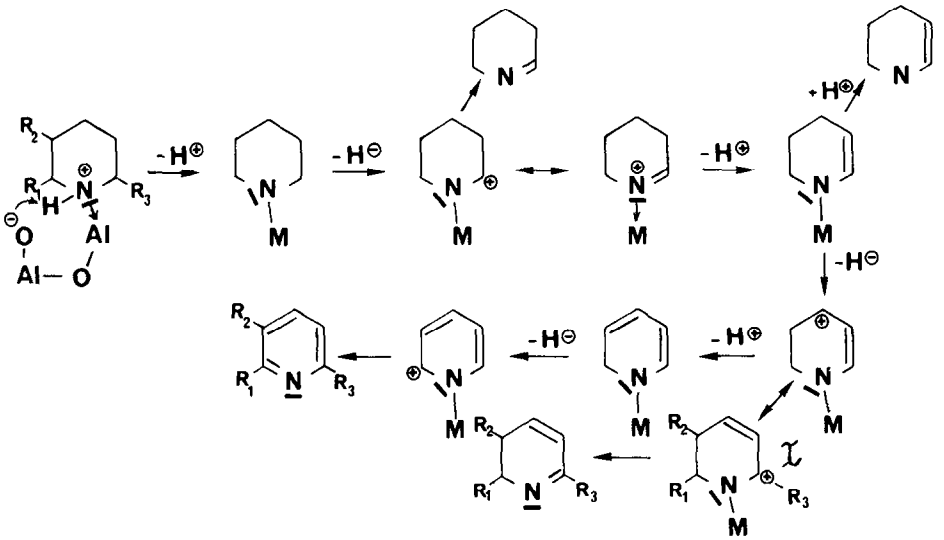
Regarding C_7 formation from 2,6-lu-

petidine, the first deprotonation leading to the ring opening occurs *on the methyl group and not on the ring*; a deprotonation on the ring, followed by cyclization, would give 1,2-dimethylcyclopentene and 1,3-dimethylcyclopentene. These products are not significant in the distribution. These observations are in full agreement with Hofmann's rule of the elimination of a quaternary ammonium leading to the less substituted olefin. The deprotonation in the "vertical" form leads to *cis*- and *trans*-1,5-heptadiene following the Markovnikoff rule, and not to 1,6-heptadiene, and excludes the dimerization to C_{14}. "The horizontal" adsorption with the endo configuration, which seems to be the most stable form, explains the large amount of methylcyclohexenes.

Regarding C_7 formation from 2-ethylpiperidine, the first deprotonation still occurs on the methylene of the ethyl group. The "horizontal" adsorption with the endo configuration is now partially destabilized by the steric effect of the methyl group, and allows 1–5 cyclization by the exo configuration to form the ethylcyclopentenes. The "vertical" adsorption excludes the formation of 1,6-heptadiene and, consequently, further dimerization.

The mechanism of the formation of the aromatic amines is shown in Scheme 2. For $R_1 = R_2 = R_3 = H$ and $R_2 = CH_3$, $R_1 = R_3 = H$, the product is the aromatic amine; if $R_1 = CH_3$ or C_2H_5 the third dehydrogenation is unfavorable because the stability of the tertiary carbocation $\mathcal{I}$ favors the desorption of the diolefinic amine (2,6-dimethyl-dihydropyridine, for instance).

To sum up, the denitrogenation reaction of the nonaromatic cyclic amines on pure alumina is easy and does not need hydrogen in the gas phase; we observe the same activity in helium. The molecule consumes its own hydrogen atoms, the protons and hydrides liberated by the reaction giving the aromatic amines. This reaction cannot therefore be called hydrodenitrogenation (HDN), but rather denitrogenation (DN). The initial step seems to be the loss of the proton located on the N atom, leading to aromatization. The aromatic amines do not possess such an atom. In fact the cyclic amine behaves like a Lewis base in the initial phase of adsorption on the Lewis acid site of alumina (Al), and like a Brønsted acid when liberating a proton which is fixed on the Brønsted basic site of alumina (O^-).



SCHEME 2. Mechanism of the formation of the aromatic amines.

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