Journal of Catalysis **206,** 263–271 (2002)
doi:10.1006/jcat.2001.3486, available online at http://www.idealibrary.com on IDEAL®

On the Role of β Hydrogen Atoms in the Hydrodenitrogenation of 2-Methylpyridine and 2-Methylpiperidine

M. Egorova, Y. Zhao, P. Kukula, and R. Prins[1]

Laboratory for Technical Chemistry, Federal Institute of Technology (ETH), 8093 Zurich-Hönggerberg, Switzerland

Received July 30, 2001; revised December 3, 2001; accepted December 6, 2001

The hydrodenitrogenation (HDN) of 2-methylpyridine and its intermediate products 2-methylpiperidine, 1-aminohexane, and 2-aminohexane was studied. The presence of most intermediates could be explained by a combination of pyridine ring hydrogenation, piperidine ring opening by elimination, and nitrogen removal by elimination, as well as by nucleophilic substitution of the amino group by a sulfhydryl group, followed by elimination of H_2S or hydrogenolysis of the C–S bond. Aminoalkenes, which are expected to be the primary products of the ring opening of alkylpiperidine, were not observed, probably because of fast hydrogenation to the corresponding amines. The ring opening of 2-methylpiperidine occurred preferentially between the nitrogen atom and the methylene group, rather than between the nitrogen atom and the carbon atom bearing the methyl group. This was confirmed by comparative HDN experiments of piperidine, 2-methylpiperidine, and 2,6-dimethylpiperidine. Although the methyl groups offer extra β hydrogen atoms, these primary hydrogen atoms are not used for elimination. Instead, the methyl groups hinder the adsorption leading to the elimination of the β hydrogen atoms on the side of the molecule bearing the methyl group.

INTRODUCTION

Heterocyclic compounds like pyridine, quinoline, and acridine are the main nitrogen-containing compounds in oil. They are removed by hydrodenitrogenation (HDN) in a hydrotreating process in which gasoline or gas oil is treated with hydrogen over a metal sulfide catalyst like nickel-promoted molybdenum sulfide (Ni–MoS_2) supported on alumina (1). Several groups have studied the HDN of pyridine (2–7), because, as the smallest nitrogen-containing heterocyclic molecule, pyridine was believed to be the simplest model molecule to study HDN. Although the network of reactions taking place in the HDN of pyridine is now well understood, the study of the kinetics of the HDN of pyridine proved to be extremely difficult. The reason for this difficulty is the occurrence of a side reaction of piperidine, the first intermediate in the HDN of pyridine. Two piperidine molecules disproportionate to *N*-pentylpiperidine and ammonia (1–5). Opening of the piperidine ring and removal of ammonia can take place from piperidine as well as from *N*-pentylpiperidine. Consequently the network of the HDN becomes very complicated and a trustworthy kinetic analysis of the separate reactions is almost impossible.

The disproportionation of piperidine to *N*-pentylpiperidine takes place by nucleophilic substitution at the carbon atom in the α position to the nitrogen atom in the piperidine ring (Fig. 1) (3, 8). It is well known that a nucleophilic attack is hindered by substitution on the α carbon atom (9). Substitution of a hydrogen atom by a methyl group on the α carbon atom might therefore hinder the disproportionation so much, that it is strongly suppressed and that it hardly interferes with the other reactions taking place during the HDN of pyridine and piperidine. Therefore we decided to study the HDN of 2-methylpyridine and 2-methylpiperidine.

2-Methylpyridine and 2-methylpiperidine were studied before by Cerny and Trka (10, 11) and Ren *et al.* (12). Ren *et al.* studied the Langmuir–Hinshelwood–Hougen–Watson kinetics of the HDN of 2-methylpyridine in a continuous-flow reactor at 4.9 MPa and 240–280°C (12). They observed 2-methylpiperidine as primary product and hexane and cyclohexane as final products. No intermediates between 2-methylpiperidine and hexane were reported. Cerny and Trka performed their investigations in an autoclave at 15.5 MPa and 250°C. Because of the high H_2 pressure, low temperature, and absence of H_2S in their experiments, mainly ring hydrogenation and only a small amount of products due to nitrogen removal were observed. They concluded that the 2-methylpiperidine ring opens preferentially on the side that does not contain the methyl group and that the HDN reactions of more substituted pyridine derivatives are slower (10). This is in disagreement with the results of Portefaix *et al.*, who observed that the HDN reaction of 2,6-dimethylpiperidine was faster than that of piperidine (13). Their result suggests that the presence of a methyl group leads to faster ring opening. Portefaix *et al.* performed their HDN work at the much lower H_2 pressure of 2 MPa and relatively high H_2S pressure of 33.3 kPa; this

[1] To whom correspondence should be addressed.

0021-9517/02 $35.00

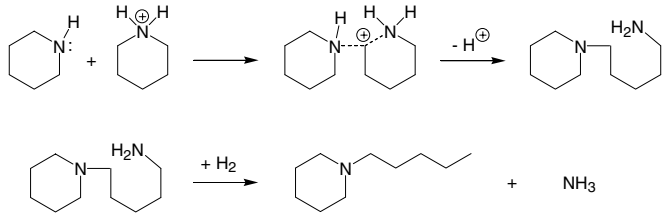

FIG. 1. Mechanism of the disproportionation of piperidine.

may explain the different results. Further study is clearly called for.

Another reason for studying the HDN of 2-methylpiperidine is the presence of three additional hydrogen atoms on the methyl carbon atom in β position relative to the nitrogen atom. HDN occurs (partly) via Hofmann elimination in which, on the one hand, the bond between the α carbon atom and the nitrogen atom is broken and, on the other hand, the bond between a hydrogen atom and the β carbon atom is broken. Portefaix *et al*. compared the HDNs of piperidine, 3,5-dimethylpiperidine, and 2,6-dimethylpiperidine and concluded that Hofmann elimination is quicker when more β hydrogen atoms are present (13). This implicates elimination of a β H atom from the methyl groups in 2,6-dimethylpiperidine as an important step in the HDN of this molecule. Portefaix *et al*. reported only the conversion of the reactant and nothing about the resulting products. Therefore, it seemed of interest to investigate if the elimination reaction of 2-methylpiperidine takes place by removal of a hydrogen atom from the methyl group and leads preferentially to 1-aminohexane.

EXPERIMENTAL

The NiMo/γ-Al_2O_3 catalyst used in this work contained 8 wt% Mo and 3 wt% Ni and was prepared by successive incipient wetness impregnation of γ-Al_2O_3 (Condea, pore volume 0.5 $cm^3\ g^{-1}$, specific surface area 230 $m^2\ g^{-1}$) with an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Aldrich), followed by an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich). The catalyst was dried in air at ambient temperature for 4 h, then dried in an oven at 120°C for 15 h, and finally calcined at 500°C for 4 h.

A sample of catalyst (0.05 g) was diluted with 8 g SiC to achieve plug-flow conditions in the continuous-flow fixed-bed reactor. The catalyst was sulfided *in situ* with a mixture of 10% H_2S in H_2 at 400°C and 1.0 MPa for 4 h. After sulfidation, the pressure was increased to 5.0 MPa (unless indicated otherwise), and the liquid reactant was fed to the reactor by means of a high-pressure syringe pump (ISCO 500D). Blank experiments with and without SiC were carried out at 573 and 623 K. The composition of the gas-phase feed in most experiments consisted of 5 kPa amine reactant, 140 kPa decane (as solvent for the amine), 20 kPa heptane (as reference for GC analysis), 20 kPa H_2S, and 4.8 MPa H_2 (unless indicated otherwise).

The reaction products were analyzed by on-line gas chromatography with a Varian 3800 GC instrument equipped with a PTA-5 fused silica capillary column (Supelco, 5% diphenylsiloxane/95% dimethylsiloxane, 30 m × 0.25 mm × 0.5 μm). Detection was performed with a flame ionization detector as well as with a pulsed flame photometric detector, which is very useful for detecting small amounts of nitrogen- and sulfur-containing compounds. Weight time was defined as the ratio of the catalyst weight to the molar flow to the reactor. The weight time was changed by varying the flow rates of the liquid and the gaseous reactants, while keeping their ratio constant.

Mass spectrometry and NMR spectroscopy were used to identify the reaction products. The MS analysis was performed with an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column (crosslinked 5% PH ME siloxane, 30 m × 0.25 mm × 0.25 μm) and with an Agilent 5973 mass selective detector. The temperature of the injector was 270°C, the initial temperature of the column oven was 80°C, and heating to 300°C started after 2 min at 20°C/min. ^1H and ^{13}C NMR spectra of isolated compounds were recorded on a Bruker DPX-300 instrument at 300 and 75 MHz, respectively, at room temperature using $CDCl_3$ as a solvent.

RESULTS

1. HDN of 2-Methylpyridine

The results of the HDN of 2-methylpyridine at 340°C, 4.8 MPa H_2, and 20 kPa H_2S are shown in Fig. 2. No products with mass higher than that of the reactant (such as condensation products) were observed and the mass balance was always better than 95%. The product selectivities show (Fig. 2b) that 2-methylpiperidine is the only primary product, as expected, since the HDN of heterocyclic N-containing aromatic molecules can occur only after ring hydrogenation (1, 3, 14, 15). The maximum yield of 34% 2-methylpiperidine and its selectivity against 2-methylpyridine conversion indicate that the ratio of the effective rate constants of formation and further reaction of 2-methylpiperidine is about 0.8 (16).

2-Hexene (*cis* and *trans*), 1-hexene, and hexane were observed as the main secondary products (Fig. 2b). These products are actually expected to be tertiary products, because HDN of aliphatic amines is generally considered to occur by Hofmann elimination or by nucleophilic substitution of the NH_2 group by an SH group followed by elimination or hydrogenolysis (1, 14). In either case, the nitrogen atom of 2-methylpiperidine is removed in two steps. The first step is a ring opening by C–N bond breaking and the second step is the removal of the nitrogen atom in the form of ammonia by breaking the other

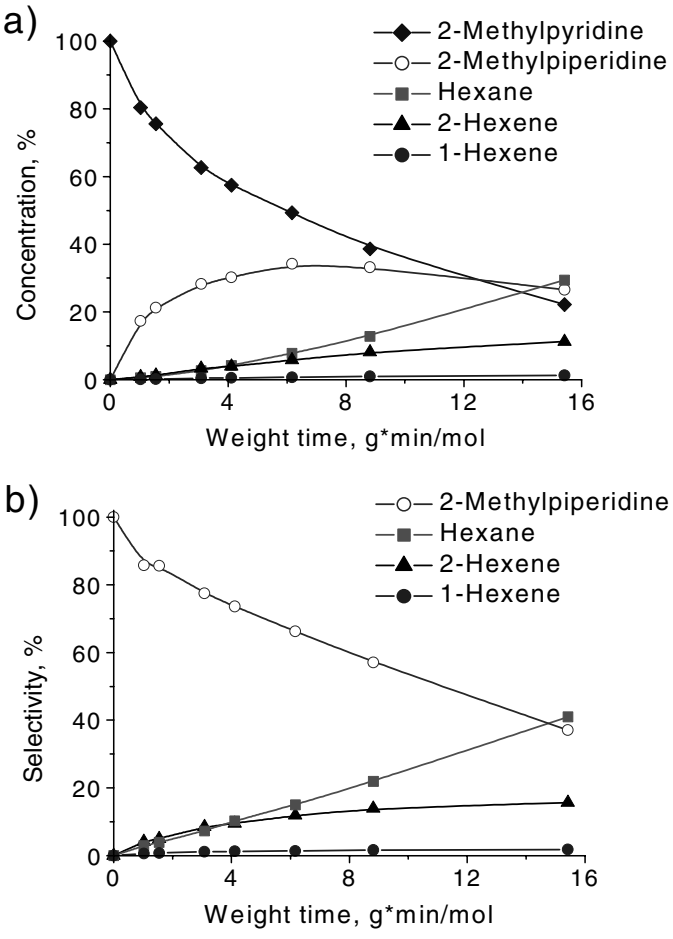

FIG. 2. Relative concentrations (a) and selectivities (b) of the products of the HDN of 2-methylpyridine as a function of weight time.

C–N bond. Of the products that are possible after the first C–N bond breakage, only traces of 1-aminohexane and 2-aminohexane were observed. The reason is that their rates of further reaction are much higher than their rates of formation, as discussed in Sections 4 and 5. These amines have a high basicity and thus larger equilibrium adsorption constants than 2-methylpyridine. Even at low concentration they may therefore have an important (inhibiting) influence on the HDN kinetics (15). For that reason, the HDN of 2-methylpiperidine, the primary product of the HDN of 2-methylpyridine, and of 1-aminohexane and 2-aminohexane, the expected secondary (or tertiary, see below) products, were studied in detail as well.

2. *HDN of 2-Methylpiperidine*

The HDN of 2-methylpiperidine was carried out at 340°C, 4.8 MPa H_2, and 20 kPa H_2S. Figure 3 shows that at least four compounds have nonzero selectivity at zero conversion of 2-methylpiperidine and thus might be considered primary products. Three of these products were identified by their GC retention times and mass spectra as 1-aminohexane, 2-aminohexane, and 2-methylpyridine. The yield of 2-aminohexane was much higher than that of 1-aminohexane. This confirms the results of Cerny (10), although they were obtained under quite different conditions, and suggests that the bond between the N atom and the methylene group is more easily broken than that between the N atom and the $CH(CH_3)$ group. This is also perfectly in line with the results of Cattenot *et al.* (8) and Vivier *et al.* (17), indicating that the amino group bonded to a methylene group cleaves very easily by nucleophilic substitution (S_N2).

GC–MS showed that the fourth compound had a molecular weight of 97, but no commercially available compound could be found that had the same retention time and a matching mass spectrum. Therefore, the product of the HDN reaction was collected and a fraction that contained the basic nitrogen-containing molecules was separated from a hydrocarbon fraction. Since pulsed flame photometric detection had shown that the fourth compound contains a nitrogen atom, it was extracted from the HDN product with an aqueous HCl solution. Neutralization of this aqueous extract and subsequent extraction with

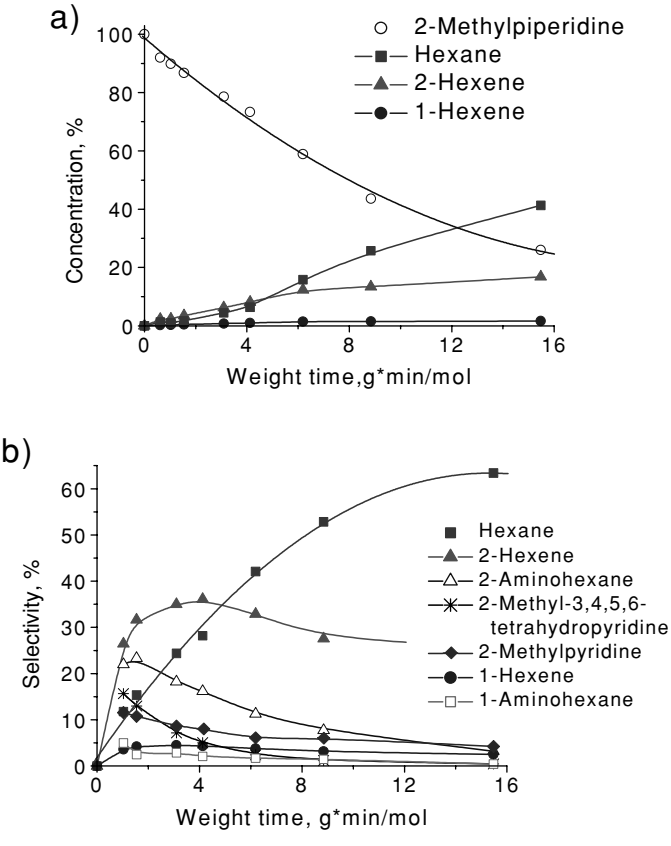

FIG. 3. Relative concentrations (a) and selectivities (b) of the products of the HDN of 2-methylpiperidine as a function of weight time.

chloroform gave a chloroform solution of all primary products as well as the remaining 2-methylpiperidine. After evaporation of the chloroform, the mixture of nitrogen-containing compounds was separated by column chromatography using silicagel and a 50 : 50 : 1 solution of $CH_3OH : CHCl_3 : NH_4OH$ (25% aqua solution of NH_3) as a mobile phase. The fraction containing the fourth unknown product was evaporated and the raw material obtained with a purity of 90% was analyzed by NMR spectroscopy. The ^1H NMR spectrum of the fourth compound in $CDCl_3$ showed peaks at δ 3.46–3.52 (m, 2H, CH_2N), 2.13 (t of t, $^3J = 6.5$ Hz, $^5J = 1.8$ Hz, 2H, $CH_2C{=}$), 1.91 (t, $^5J = 1.8$ Hz, 3H, CH_3), 1.62–1.71 (m, 2H, $C\underline{H}_2CH_2C{=}$), and 1.51–1.59 ppm (m, 2H, $C\underline{H}_2CH_2N$), while its ^{13}C NMR spectrum in $CDCl_3$ showed peaks at δ 168.45 (s, CN), 48.98 (t, CN), 30.26 (t, $\underline{C}H_2C{=}$), 27.33 (q, CH_3), 21.57 (t, $\underline{C}H_2CH_2N$), and 19.52 ppm (t, $\underline{C}H_2CH_2C{=}$). The NMR spectra together with the mass spectrum obtained (MS (EI, 70 eV) m/z 97 (M^+, 63), 96 (11), 69 (61), 68 (21), 56 (26), 55 (17), 54 (15), 42 (100), 41 (65), 39 (33), 28 (41), 27 (26)) enabled us to identify the fourth primary product as 2-methyl-3,4,5,6-tetrahydropyridine. Both NMR and mass spectra were in accord with the spectra assigned to this molecule in the literature (18, 19).

HDN experiments with 2-methylpiperidine under conditions other than 340°C and 5 MPa suggested that 2-methyl-3,4,5,6-tetrahydropyridine is formed by a catalytic as well as a thermal reaction. Experiments in the empty steel reactor and in the reactor filled with SiC only, without catalyst, showed that the 2-methyl-3,4,5,6-tetrahydropyridine yield increased by increasing the temperature from 300 to 350°C, as expected for a simple dehydrogenation reaction. Over the $NiMo/Al_2O_3$ catalyst diluted with SiC, however, the yield decreased substantially from 300 to 350°C. The 2-methyl-3,4,5,6-tetrahydropyridine yield was also lower over the catalyst than over the SiC or in the empty reactor. This suggests that in the presence of the catalyst, there occurs not only dehydrogenation but also reactions to other products, which lower the yield of 2-methyl-3,4,5,6-tetrahydropyridine. As expected, in the presence of the catalyst, decreasing the H_2 pressure from 5 to 3 MPa raised the 2-methyl-3,4,5,6-tetrahydropyridine yield.

3. *Comparison of Piperidine, 2-Methylpiperidine, and 2,6-Dimethylpiperidine*

As indicated in the Introduction, Portefaix *et al.* reported that the amount of HDN product was larger for 2,6-dimethylpiperidine than for piperidine under the following reaction conditions: 275°C, 2 MPa H_2, and 33.3 kPa H_2S (13). They related this to the presence of more β H atoms in 2,6-dimethylpiperidine, which would facilitate Hofmann elimination. These results seem to contradict those of Cerny (10) and our results for 2-methylpiperidine described in the previous section, which suggested that the ring opening occurs preferentially between the nitrogen atom and the methylene group and not between the nitrogen atom and the carbon atom bearing the methyl group. We therefore decided to repeat the measurements of Portefaix *et al.* under their conditions.

From the results presented in Fig. 4 it is clear that the conversion of piperidine is very slow and hardly reaches 2% at a weight time of 10 g · min/mol, whereas the conversion of 2-methylpiperidine is almost 20% and that of *cis*-2,6-dimethylpiperidine is more than 50% at the same weight time. The conversions at a weight time of 2.4 g · min/mol are in good agreement with those of Portefaix *et al.* (13). Analyzing the resulting products, however, we found that for piperidine the main product was not that of HDN but pyridine. For 2-methylpiperidine the main products were 2-methylpyridine (17%) and 2-methyl-3,4,5,6-tetrahydropyridine (64%), and for *cis*-2,6-dimethylpiperidine the main products were 2,6-dimethylpyridine (2%), 2,6-dimethyl-3,4,5,6-tetrahydropyridine (66%), and *trans*-2,6-dimethylpiperidine (32%), with the selectivities in parentheses.

The observed high selectivities to fully dehydrogenated pyridine molecules at low conversions are not in contradiction with thermodynamics, which indicates that the pyridine/piperidine ratio cannot be higher than 0.01 at 275°C and 2 MPa H_2 (20). The tetrahydropyridine/piperidine ratio can be much higher, however. Portefaix *et al.* apparently underestimated the latter ratio and the isomerization of *cis*-2,6-dimethylpiperidine to *trans*-2,6-dimethylpiperidine, when assuming, without any product analysis, that most of the piperidine-type molecules would convert to HDN products. At high weight time and high conversion, thermodynamic controls and HDN products will indeed dominate. At low conversion, however, kinetics may dominate the

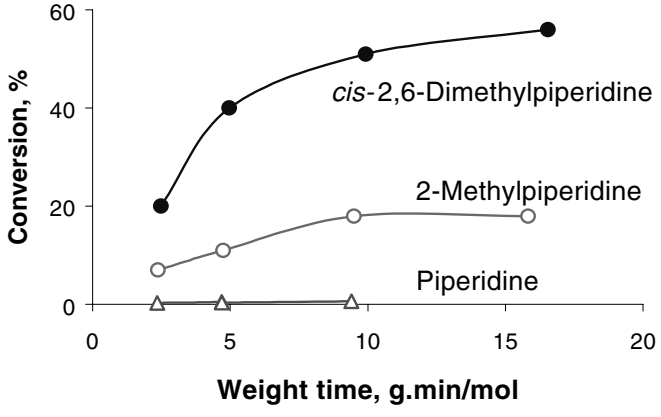

FIG. 4. Total conversions in the HDN of piperidine, 2-methylpiperidine, and *cis*-2,6-dimethylpiperidine as a function of weight time at 275°C, 2 MPa, and 33.3 kPa H_2S.

product distribution and it is in this regime that mechanistic results should be obtained.

All the compounds mentioned above are products of dehydrogenation and isomerization, and not of HDN or C–N bond cleavage. The selectivities for ring opening and HDN were calculated from the sum of the observed amines and saturated and unsaturated hydrocarbons and amounted to 9% for piperidine, 5% for 2-methylpiperidine, and 0.7% for *cis*-2,6-dimethylpiperidine at 2.4 g · min/mol. These selectivities are small; dehydrogenation and isomerization (for *cis*-2,6-dimethylpiperidine) dominate at the low H_2 pressure of 1.8 MPa. The yield (selectivity times conversion) of these ring opening and HDN products was indeed higher for *cis*-2,6-dimethylpiperidine than for piperidine, as reported by Portefaix *et al.* (13).

We also studied these three piperidine molecules under conditions in which elimination is the dominating reaction, so that a fair comparison of the HDN rates of the three molecules could be made. At 340°C, 5 MPa, and 20 kPa H_2S the 2-methylpiperidine conversion was 20% lower than that of piperidine, while the conversion of *cis*-2,6-dimethylpiperidine was higher than that of piperidine below a weight time of $\tau = 5.5$ g · min/mol and lower above this value. The reason for the high initial reaction rate of *cis*-2,6-dimethylpiperidine is fast isomerization of *cis*- to *trans*-2,6-dimethylpiperidine. For $\tau > 5.5$ g · min/mol, the equilibrium between *cis*- and *trans*-2,6-dimethylpiperidine is established, and other, slower reactions determine the reaction rate of both isomers of 2,6-dimethylpiperidine. Even at 340°C, 5 MPa, and 20 kPa H_2S, conversion to products other than obtained by HDN is not negligible for these three molecules. For piperidine the total selectivity for dehydrogenation to pyridine and disproportionation to *N*-pentylpiperidine was always below 10%. For 2-methylpiperidine and *cis*-2,6-dimethylpiperidine the selectivities to the dehydrogenation products (substituted pyridine and tetrahydropyridine) were 22 and 24% respectively, at the lowest weight time measured (1.4 g · min/mol). Taking into account only the products of hydrodenitrogenation, we found that piperidine undergoes HDN 30% faster than 2-methylpiperidine and 50% faster than 2,6-dimethylpiperidine (Fig. 5).

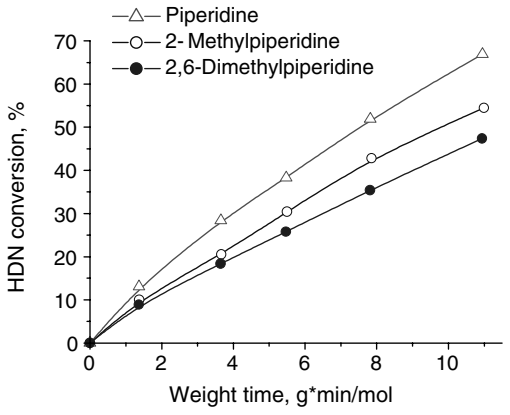

FIG. 5. HDN conversions in the HDN of piperidine, 2-methylpiperidine, and *cis*-2,6-dimethylpiperidine as a function of weight time at 340°C, 5 MPa, and 20 kPa H_2S.

4. *HDN of 1-Aminohexane*

The HDN of 1-aminohexane becomes fast above 300°C (Fig. 6) and 2-hexene and hexane are the main products. A plot of the product selectivities versus weight time (Fig. 7) shows that 1-hexene and *trans*- and *cis*-2-hexene are primary products. According to the Hofmann elimination mechanism only 1-hexene can be formed from 1-aminohexane. However, the isomerization of 1-hexene to 2-hexene is so fast above 300°C that it is difficult to distinguish if 2-hexene is a primary or secondary product. Addition of 1-pentene to the feed indeed showed that the isomerization to *cis*- and *trans*-2-pentene was fast. This means that the ratio of 1-hexene to 2-hexene above 300°C is determined mainly by thermodynamics and hardly by the kinetics of the formation of these alkenes. Consequently, the ratio of 1-hexene to 2-hexene cannot be used to distinguish between the two ways of C–N bond breakage in 2-methylpiperidine either. At 260°C the conversion of 1-aminohexane is less than 5%, even at high weight time (20 g · min/mol), versus 50% at 300°C. Comparison of the selectivity plots at 300°C (Fig. 7) and 260°C (Fig. 8) confirms that *trans*- and *cis*-2-hexene are secondary products, because the selectivities decrease at decreasing temperature and conversion.

At the higher H_2S pressure of 80 kPa, the selectivity to hexane was higher than at 16 kPa. HDN activity was hardly influenced by this change in H_2S partial pressure (at a constant H_2 pressure of 3.8 MPa), but selectivity did change. Not only was hexane selectivity higher, but 2-hexene selectivity was substantially lower and 1-hexene selectivity higher at 80 kPa H_2S. Apparently, isomerization

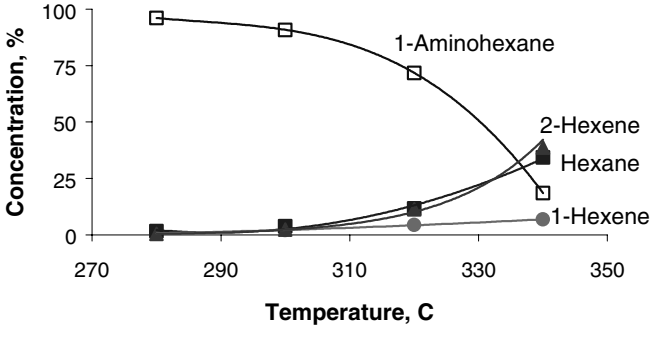

FIG. 6. Conversion and relative product concentrations in the HDN of 1-aminohexane between 280 and 340°C and at $\tau = 5$ g · min/mol.

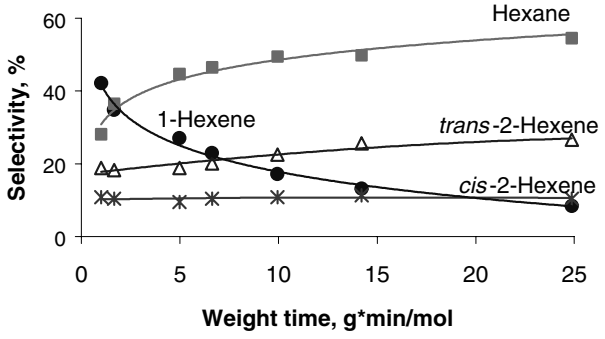

FIG. 7. Product selectivities of the HDN of 1-aminohexane at 300°C.

of 1-hexene to *cis*- and *trans*-2-hexene requires vacancies at the metal sulfide surface. The higher selectivity toward hexane formation indicates that nucleophilic attack of H_2S on 1-aminohexane must have led to hexanethiol, which very quickly reacted to hexane by hydrogenolysis and 1-hexene by elimination (1).

5. *HDN of 2-Aminohexane*

The HDN of 2-aminohexane was complicated by the formation of di-2-hexylamine, a disproportionation product of the reaction of two 2-aminohexane molecules (Fig. 1). As expected for this molecule with two chiral atoms (2-aminohexane itself has one chiral atom), the gas chromatogram showed two peaks of equal intensity, equal mass spectra, and only a small difference in retention time. One peak belongs to the (*R*,*R*)- and (*S*,*S*)-isomers, the other to the *meso* (*R*,*S*)-isomer.

Experiments between 220 and 350°C showed that not only di-2-hexylamine but also 1-hexene, and *cis*- and *trans*-2-hexene behave as a primary product (Fig. 9). Hofmann elimination explains why 1-hexene as well as 2-hexene is formed. The activation energy for elimination is higher than that of nucleophilic substitution because the hexene selectivity increased with temperature. The selectivity of di-2-hexylamine is very high at low temperature. At the lowest temperature studied (220°C), it was higher than 90% when extrapolated to zero 2-aminohexane conversion. In this case, the only other product was hexane. The formation of hexane is explained by nucleophilic substitution of the NH_2 group by an SH group, followed by hydrogenolysis of the C–S bond.

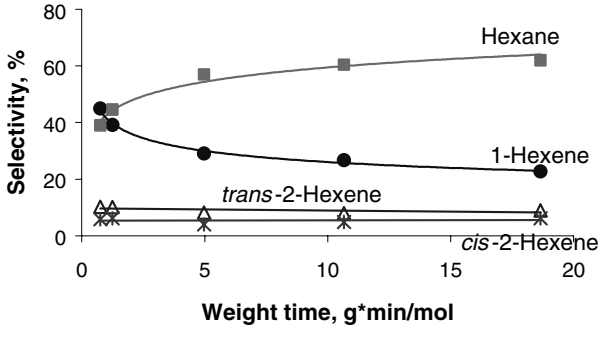

FIG. 8. Product selectivities of the HDN of 1-aminohexane at 260°C.

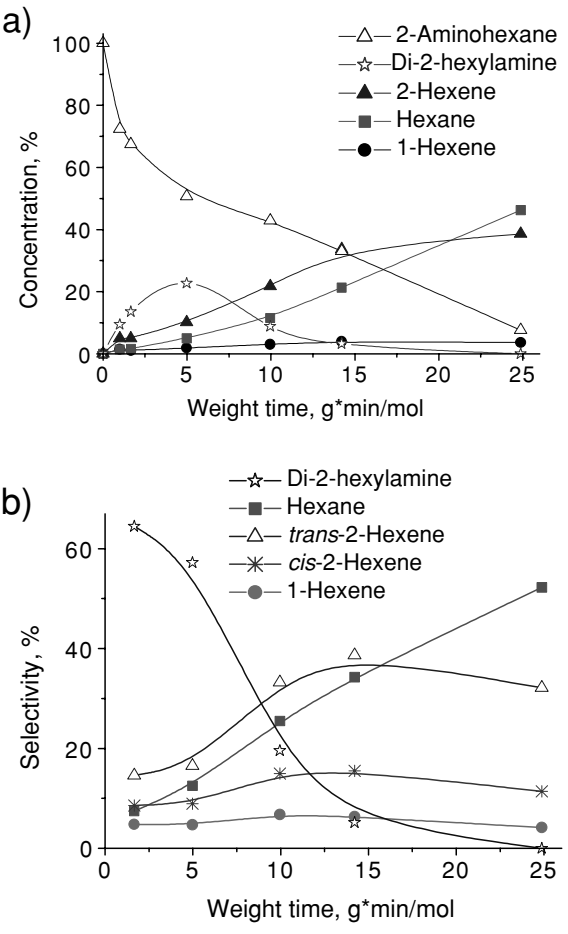

FIG. 9. Relative concentrations (a) and selectivities (b) of the products of the HDN of 2-aminohexane as a function of weight time at 20 kPa H_2S.

Increasing the H_2S pressure from 16 to 80 kPa, at the same H_2 pressure of 3.8 MPa, led to faster conversion of 2-aminohexane to hydrocarbons, while production of the disproportionation product di-2-hexylamine decreased (Fig. 10). Whereas at 16 kPa H_2S it reached a maximum yield of 25%, at 80 kPa H_2S the maximum yield was only 10%. At the higher H_2S partial pressure, a new intermediate was observed. It behaved as a primary product and was analyzed to be 2-hexanethiol. This intermediate is formed by an S_N2 reaction between 2-aminohexane and H_2S. At higher H_2S partial pressure, it will be formed faster and will hydrogenolyze less rapidly to hexane because of fewer vacancies on the metal sulfide surface. Therefore, it is easier to observe 2-hexanethiol at higher H_2S pressure.

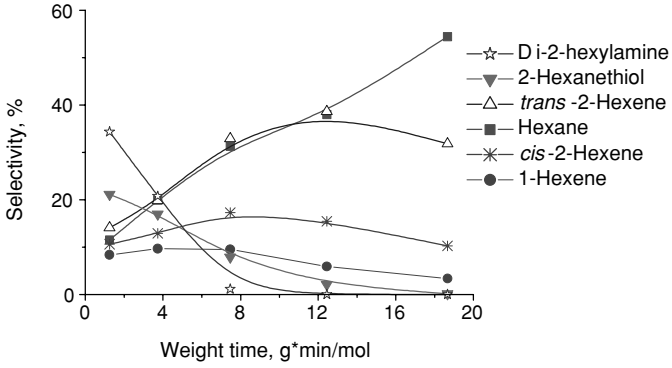

FIG. 10. Product selectivities of the HDN of 2-aminohexane as a function of weight time at 80 kPa H_2S.

DISCUSSION

Combining the results of the HDN of 2-methylpyridine, 2-methylpiperidine, 1-aminohexane, and 2-aminohexane, we arrive at the reaction scheme presented in Fig. 11. For all intermediates, except two, direct relationships between parent and daughter molecules could be established by measuring the product selectivities as a function of weight time and extrapolating to zero weight time. Thus, 2-methylpiperidine proved to be the primary product of 2-methylpyridine, while 2-methylpyridine as well as 2-methyl-3,4,5,6-tetrahydropyridine behaved as primary products of 2-methylpiperidine.

The other two apparent primary products in the HDN of 2-methylpiperidine, 1-aminohexane and 2-aminohexane, should actually be secondary rather than primary products. If opening of the piperidine ring would occur by Hofmann elimination, it would lead to 5-amino-1-hexene when the C–N bond with the methylene group is broken, and to 6-amino-1-hexene and 6-amino-2-hexene when the C–N bond with the $CH(CH_3)$ group is broken (Fig. 11). These products were not detected in the HDN of 2-methylpiperidine. The equivalent of 5-amino-1-hexene has never been observed in the HDN of pyridine either (6). The reason is most probably that these aminoalkenes adsorb strongly on the catalyst surface because of the presence of a nitrogen atom in the molecule and are very quickly hydrogenated to the corresponding saturated amines before they desorb from the catalytic site. Alternatively, if opening of the pyridine ring would occur by nucleophilic attack by H_2S, then 5-aminohexanethiol, 6-aminohexanethiol, and 6-amino-2-hexanethiol would be primary products. Thiols react very quickly by elimination to alkenes and by hydrogenolysis to alkanes. In the first and most important case, aminoalkenes should be formed; in the latter case, amines. Again, because of strong adsorption and fast hydrogenation, the aminoalkenes have not been detected. As a result, only 1-aminohexane and 2-aminohexane occur in the product, their selectivities do not go to zero at low conversion, and they behave as (quasi) primary products in the HDN of 2-methylpiperidine.

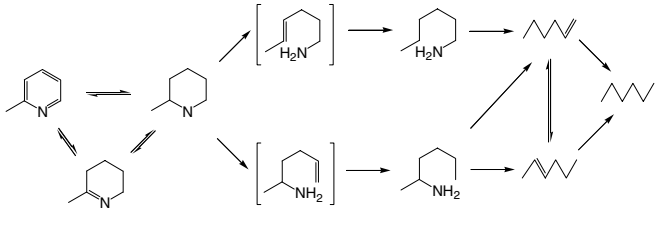

FIG. 11. Scheme of the reaction network of the HDN of 2-methylpyridine and 2-methylpiperidine.

2-Methylpyridine and 2-methyl-3,4,5,6-tetrahydropyridine both behaved as primary products in the HDN of 2-methylpiperidine. One might expect 2-methyl-3,4,5,6-tetrahydropyridine to be the dehydrogenation intermediate between 2-methylpiperidine and 2-methylpyridine, in which case it is surprising that 2-methylpyridine behaves as a primary product too. If the rate of dehydrogenation of 2-methyl-3,4,5,6-tetrahydropyridine to 2-methylpyridine is of the same order of magnitude as its rate of desorption from the catalytic site, both molecules might have nonzero selectivities at zero 2-methylpiperidine conversion. Another explanation could be that 2-methyl-3,4,5,6-tetrahydropyridine is (partially) produced by a thermal dehydrogenation reaction, while 2-methylpyridine is directly, without desorption of intermediates, produced by a catalytic reaction. We have not studied this question any further, because it is only a side effect in our study of the HDN of 2-methylpyridine and 2-methylpiperidine.

An investigation of the HDN of 1-aminohexane and 2-aminohexane is important not only to gain a better understanding of the kinetics of the HDN of 2-methylpyridine and 2-methylpiperidine, but also to understand how the ring opening of the piperidine ring takes place. Because of the methyl group in α position to the nitrogen atom, C–N bond breakage in 2-methylpiperidine can take place in two ways: between the nitrogen atom and the carbon atom of the methylene group, or between the nitrogen atom and the carbon atom carrying the methyl group. The latter possibility should prevail if, as suggested by Portefaix *et al.* (13, 21) and Cattenot *et al.* (8), the number of β H atoms determines the course of the Hofmann elimination reaction. Unfortunately, the ratio of the concentrations of 1-aminohexane and 2-aminohexane cannot be used as a direct measure of the ratio of the N–CH_2 and N–$CH(CH_3)$ bond breaks. The reason is that the concentrations of these amines depend not only on their rates of formation, but also on their rates of reaction to hexenes and hexane. Thus, the very small amount of 1-aminohexane that is produced in the HDN of 2-methylpiperidine (Fig. 3b) can be due to either slow breaking of the N–$CH(CH_3)$ bond, or rapid disappearance

of 1-aminohexane by HDN, or both. For that reason, it was necessary to investigate the HDNs of 1-aminohexane and 2-aminohexane separately.

Comparison of the conversions of 2-aminohexane (Fig. 9a) and 1-aminohexane (not shown) showed that the reactivity of 2-aminohexane is higher than that of 1-aminohexane. Despite a higher reactivity, much more 2-aminohexane than 1-aminohexane was detected in the HDN of 2-methylpiperidine (Fig. 3b). This proves that the first C–N bond break in 2-methylpiperidine occurs predominantly between the nitrogen atom and the carbon atom of the methylene group. If only the number of β H atoms plays a role, as suggested by Portefaix *et al*. (13), then 2.5 times more 1-aminohexane than 2-aminohexane should have been formed. Actually, 3 to 4 times more 2-aminohexane was formed! It is clear that the number of β H atoms is not the most important factor in Hofmann elimination. The same conclusion was reached in the HDN of 2-methylcyclohexylamine, in which the type of β H atom proved to be the most important factor (22). Thus, the β H atom at the tertiary carbon atom was removed much faster than the β H atom at the secondary carbon atom, leading to more 1-methylcyclohexene than 3-methylcyclohexene. Analogously, the results of the HDN of 2-aminohexane described in Section 5 demonstrated that 3 to 4 times more 2-hexene was produced than 1-hexene, although there are 1.5 times fewer H atoms on the CH_2 group in β position to the nitrogen atom than on the CH_3 group in 2-aminohexane. It is clear that the ease with which the C–H bond breaks plays an important role in the elimination. A hydrogen atom on a tertiary carbon atom is more easily abstracted by a base than β H atoms on secondary or primary carbon atoms. This is the basis of the Zaytzev rule, which states that elimination preferentially leads to more substituted alkenes (9).

The fact that much more 2-aminohexane than 1-aminohexane is formed in the HDN of 2-methylpiperidine further indicates that the methyl group actually has a negative rather than a positive influence on the elimination. All β H atoms on the two carbon atoms in β position to the nitrogen atom belong to methylene groups. Thus, they should have the same tendency to be eliminated. If the methyl group played no role in elimination, neither positive nor negative, then, on the basis of the number and type (methylene) of H atoms, equal amounts of 2-aminohexane and 1-aminohexane should have been formed. The fact that the rate of breakage of the N–$CH(CH_3)$ bond is lower than that of the N–CH_2 bond indicates that the methyl group hinders the adsorption of 2-methylpiperidine in a conformation in which the nitrogen atom and the β H atom of the methylene group next to the $CH(CH_3)$ group approach the metal sulfide surface. Such a steric hindrance does not exist for the adsorption of the other side of the 2-methylpiperidine molecule on the metal sulfide surface.

Our results are in good agreement with the rule that nucleophilic substitution is favored at low temperature, while elimination is favored at high temperature. The H_2S pressure may also steer the reaction in different directions. At low H_2S pressure, nucleophilic substitution is dominated by the reaction of an amine reactant with another amine molecule, leading to disproportionation products such as di-2-hexylamine (Fig. 9). In this sense, the metal sulfide surface that is depleted of sulfur behaves similarly to a metal surface, on which disproportionation of amines is important as well (23). At high H_2S pressure, H_2S becomes the dominant nucleophile that reacts with the amine, transforming the amine into a thiol molecule that reacts relatively quickly to an alkene by elimination and to an alkane by hydrogenolysis. Hydrogenolysis requires sulfur vacancies at the metal sulfide surface. Consequently, an increase in H_2S pressure has a positive effect on hexane formation at lower H_2S pressures, because more thiol is formed. At higher H_2S pressures, however, hardly any vacancies are available anymore and the thiol can undergo only elimination to an alkene.

From the higher rate of HDN conversion of *cis*-2,6-dimethylpiperidine than of piperidine, Portefaix *et al*. concluded that the rate of elimination of ammonia from an amine is larger when more β H atoms are present (13). Our analysis of all the products of the HDN reactions of piperidine, 2-methylpiperidine, and *cis*-2,6-dimethylpiperidine shows that this conclusion is not correct. Indeed, the rate of disappearance of *cis*-2,6-dimethylpiperidine is higher than that of piperidine (Fig. 4) at 275°C, 2 MPa H_2, and 33.3 kPa H_2S. However, the majority of the product at 2 MPa H_2 is not formed by elimination, but rather by dehydrogenation and isomerization. On the other hand, at 340°C and 5 MPa, dehydrogenation is much less important and the main products were formed by ring opening and HDN. Under such conditions, the rate of elimination decreases from piperidine to 2-methylpiperidine to *cis*-2,6-dimethylpiperidine. This is then in agreement with our observation that the 2-methylpiperidine ring is preferentially opened between the N atom and the methylene group. Thus, it is clear that, contrary to the proposal of Portefaix *et al*. (13), the addition of a methyl group in α position to the nitrogen atom in piperidine does not increase the HDN rate. On the contrary, the methyl group constitutes a strong steric hindrance for the right adsorption conformation of the nitrogen atom and the β H atom.

REFERENCES

1. Prins, R., *Adv. Catal.* 2001, to be published.
2. Sonnemans, J., Neyens, W. J., and Mars, P., *J. Catal.* **34**, 230 (1974).
3. Schulz, H., Schon, M., and Rahman, N. M., *Stud. Surf. Sci. Catal.* **27**, 201 (1986).
4. Hanlon, R. T., *Energy Fuels* **1**, 424 (1987).

5. Hadjiloizou, G. C., Butt, J. B., and Dranoff, J. S., *Ind. Eng. Chem. Res.* **31**, 2503 (1992).
6. Jian, M., and Prins, R., *Catal. Lett.* **35**, 193 (1995).
7. Pille, R., and Froment, G., *Stud. Surf. Sci. Catal.* **106**, 403 (1997).
8. Cattenot, M., Portefaix, J. L., Afonso, A., Breysse, M., Lacroix, M., and Perot, G., *J. Catal.* **173**, 366 (1998).
9. March, J., "Advanced Organic Chemistry," 3rd ed., Chap. 10. Wiley, New York, 1985.
10. Cerny, M., *Coll. Czech. Chem. Commun.* **44**, 85 (1979).
11. Cerny, M., and Trka, A., *Czech. Chem. Commun.* **48**, 3413 (1983).
12. Ren, S., Wang, Z., and Hu, Y., *Ranliao Huaxue Xuebo* **15**, 255 (1987).
13. Portefaix, J. L., Cattenot, M., Gerriche, M., Thivolle-Cazat, J., and Breysse, M., *Catal. Today* **10**, 473 (1991).
14. Nelson, N., and Levy, R. B., *J. Catal.* **58**, 485 (1979).
15. Perot, G., *Catal. Today* **10**, 447 (1991).
16. Levenspiel, O., "Chemical Reaction Engineering," 3rd ed., Chap. 8. Wiley, New York, 1999.
17. Vivier, L., Dominguez, V., Perot, G., and Kasztelan, S., *J. Mol. Catal.* **67**, 267 (1991).
18. Asensio, G., Gonzales-Nunez, M. E., Bernardini, C. B., Mello, R., and Adam, W., *J. Am. Chem. Soc.* **105**, 6877 (1983).
19. Hua, D. H., Shou Wu Miao, Narasimha Bharathi, S., Katsuhira, T., and Bravo, A. A., *J. Org. Chem.* **55**, 3682 (1990).
20. Cocchetto, J. F., and Satterfield, C. N., *Ind. Eng. Chem. Process Des. Dev.* **15**, 272 (1976).
21. Portefaix, J. L., Cattenot, M., Guerriche, M., and Breysse, M., *Catal. Lett.* **9**, 127 (1991).
22. Rota, F., Ranade, V., and Prins, R., *J. Catal.* **201**, 389 (2001).
23. Meitzner, G., Mykytka, W. J., and Sinfelt, J. H., *J. Catal.* **98**, 513 (1986).