On the Role of $\beta$ Hydrogen Atoms in the Hydrodenitrogenation of 2-Methylpyridine and 2-Methylpiperidine

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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$_2$S or hydrodenylation 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 $\beta$ hydrogen atoms, these primary hydrogen atoms are not used for elimination. Instead, the methyl groups hinder the adsorption leading to the elimination of the $\beta$ 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 $\alpha$ 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 $\alpha$ carbon atom (9). Substitution of a hydrogen atom by a methyl group on the $\alpha$ 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$_2$S 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$_2$S pressure of 33.3 kPa; this

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This implicates elimination of a nitrogen is quicker when more 2,6-dimethylpiperidine and concluded that Hofmann eliminated the HDNs of piperidine, 3,5-dimethylpiperidine, and methyl groups in 2,6-dimethylpiperidine as an important step in the HDN of this molecule. Portefaix et al. reported that the bond between a hydrogen atom and the nitrogen atom is broken and, on the other hand, the bond between a hydrogen atom and the 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.

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. reported 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-Al2O3 catalyst used in this work contained 8 wt% Mo and 3 wt% Ni and was prepared by successive incipient wetness impregnation of γ-Al2O3 (Condea, pore volume 0.5 cm3 g−1, specific surface area 230 m2 g−1) with an aqueous solution of (NH4)6Mo7O24·4H2O (Aldrich), followed by an aqueous solution of Ni(NO3)2·6H2O (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% H2S in H2 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 H2S, and 4.8 MPa H2 (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 13C NMR spectra of isolated compounds were recorded on a Bruker DPX-300 instrument at 300 and 75 MHz, respectively, at room temperature using CDCl3 as a solvent.

RESULTS

1. HDN of 2-Methylpyridine

The results of the HDN of 2-methylpyridine at 340°C, 4.8 MPa H2, and 20 kPa H2S 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-methylpyridine 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-methylpyridine and its selectivity against 2-methylpyridine conversion indicate that the ratio of the effective rate constants of formation and further reaction of 2-methylpyridine 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 NH2 group by an SH group followed by elimination or hydrogenolysis (1, 14). In either case, the nitrogen atom of 2-methylpyridine 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. 1. Mechanism of the disproportionation of piperidine.](image-url)
ROLE OF $\beta$ H ATOMS IN HDN OF 2-METHYLPYRIDINE

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$_2$S. 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$_3$)$_2$ 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 (SN$_2$).

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

FIG. 3. Relative concentrations (a) and selectivities (b) of the products of the HDN of 2-methylpiperidine as a function of weight time.
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 H2, and 33.3 kPa H2S (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 H2 (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
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 H2 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 H2S 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 τ = 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-2-pentene. For τ > 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 H2S, 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-pentylpyridine 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 hydrogenation, we found that piperidine undergoes HDN 30% faster than 2-methylpiperidine and 50% faster than 2,6-dimethylpiperidine (Fig. 5).

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 H2S pressure of 80 kPa, the selectivity to hexane was higher than at 16 kPa. HDN activity was hardly influenced by this change in H2S partial pressure (at a constant H2 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 H2S. Apparently, isomerization
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\(_2\)S 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.

Increasing the H\(_2\)S 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\(_2\)S it reached a maximum yield of 25%, at 80 kPa H\(_2\)S the maximum yield was only 10%. At the higher H\(_2\)S 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 SN\(_2\) reaction between 2-aminohexane and H\(_2\)S. At higher H\(_2\)S 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\(_2\)S pressure.
pyridine and 2-methylpiperidine.

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 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 H2S, then 5-aminohexanethiol, 6-aminohexanethiol, and 6-aminohexanethiol would be primary products. Thiol 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.

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 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–CH2 and N–CH(CH3) 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(CH3) bond, or rapid disappearance

![FIG. 10. Product selectivities of the HDN of 2-aminohexane as a function of weight time at 80 kPa H2S.](image)

![FIG. 11. Scheme of the reaction network of the HDN of 2-methylpyridine and 2-methylpiperidine.](image)
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 \( \beta \) 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 \( \beta \) 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 \( \beta \) H atom proved to be the most important factor (22). Thus, the \( \beta \) H atom at the tertiary carbon atom was removed much faster than the \( \beta \) 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 CH₂ group in \( \beta \) position to the nitrogen atom than on the CH₃ 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 \( \beta \) H atoms on secondary or primary carbon atoms. This is the basis of the Zaitsev 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 \( \beta \) H atoms on the two carbon atoms in \( \beta \) 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(CH₃) bond is lower than that of the N–CH₂ bond indicates that the methyl group hinders the adsorption of 2-methylpiperidine in a conformation in which the nitrogen atom and the \( \beta \) H atom of the methylene group next to the CH(CH₃) 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 H₂S pressure may also steer the reaction in different directions. At low H₂S 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 H₂S pressure, H₂S 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 H₂S pressure has a positive effect on hexane formation at lower H₂S pressures, because more thiol is formed. At higher H₂S 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 \( \beta \) 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 H₂, and 33.3 kPa H₂S. However, the majority of the product at 2 MPa H₂ 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 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 \( \alpha \) 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 \( \beta \) H atom.

REFERENCES