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On the Formation of Pentylpiperidine in the Hydrodenitrogenation of Pyridine

Huamin Wang · Roel Prins

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Abstract The hydrodenitrogenation of 2-methylpiperidine and 2-methylpyrrolidine was studied over sulfided NiMo/γ-Al_2O_3 in the presence of dialkylamines, alkylamines, and alkenes to determine why *N*-pentylpiperidine is formed in the hydrodenitrogenation of pyridine. *N*-alkylated 2-methylpiperidine and 2-methylpyrrolidine were only formed as primary products by reaction with alkylamines and not by reaction with 2-methylpiperidine and 2-methylpyrrolidine, or by reaction with an alkene. This indicates that, in the hydrodenitrogenation of pyridine, *N*-pentylpiperidine is formed by the reaction of the secondary intermediate pentylamine with the primary intermediate piperidine, and not by reaction of two primary piperidine intermediates or by reaction of pentene, one of the final products, with piperidine.

Keywords Hydrodenitrogenation · Piperidine · Pyridine · Pyrrole · Pyrrolidine · Pentylpiperidine · Sulfided NiMo/γ-Al_2O_3

1 Introduction

Hydrodenitrogenation (HDN) is a reaction in which a nitrogen atom is removed from a nitrogen-containing molecule and is of importance for the cleaning of oil and coal-derived fuels. In these fuels most of the nitrogen-containing molecules have an aromatic structure and the nitrogen atoms have to be removed by hydrogenation of the aromatic structures and breaking of the resulting aliphatic C–N bonds. Since nitrogen-containing molecules adsorb more strongly on the catalyst surface than sulfur-containing molecules, HDN has become more and more important due to the demand for more deeply desulfurized fuels.

Pyridine is the simplest aromatic amine and thus could be the perfect molecule for model HDN studies. Indeed, several studies of the HDN of pyridine have been published [1–12]. In several of these studies substantial amounts of *N*-pentylpiperidine were observed [2, 4, 6–8, 10–12]. The formation of this molecule has been ascribed to the reaction of piperidine, the first intermediate in the HDN of pyridine, with another molecule of piperidine, to the reaction of piperidine with a pentylamine molecule, a secondary intermediate of the HDN of pyridine, and to the reaction of piperidine with pentene, one of the two final, denitrogenated products of the HDN of pyridine (Scheme 1). No proof for any of these reaction partners of piperidine has been provided, however. Because of the uncertainty about its formation and further reaction, it has been difficult to allow for the existence of *N*-pentylpiperidine in the mass balance of the HDN of pyridine as well as of piperidine. As a consequence, pyridine has not been popular as a model molecule in HDN studies. Some studies have looked for conditions to minimalize the formation of *N*-pentylpiperidine and thus avoid the mass-balance problem [8], while others have instead used 2-methylpyridine as model compound, which hardly shows the formation of *N*-hexyl-2-methylpiperidine [13, 14]. In the HDN of bicyclic nitrogen-containing molecules, the formation of *N*-alkylated compounds has not

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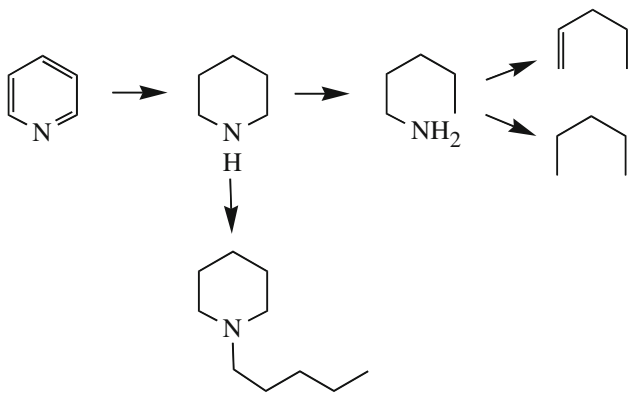
been observed and quinoline has often been used as a model molecule for HDN studies [15–17].

For several years it was believed that HDN occurs by hydrogenation of the aromatic nitrogen-containing molecules, followed by C–N bond breaking by means of Hoffman elimination or of nucleophilic substitution by H_2S [18–20]. Recent work has demonstrated that the elimination of ammonia from an alkylamine is too difficult under HDN conditions and that C–N bond breaking occurs exclusively by nucleophilic substitution [21–23]. It was furthermore demonstrated that this substitution does not occur by a classic nucleophilic substitution, but by addition of H_2S to an imine C=N or enamine CH_2=CH_2–N bond, that is formed by dehydrogenation of an alkylamine [24, 25]. Subsequent elimination of ammonia or an amine leads to an alkanethiol. This in turn quickly desulfurizes to an alkene by elimination or an alkane by hydrogenolysis (Scheme 2).

Now that the chemistry of HDN has been unraveled, it should be possible to determine which reactions are responsible for the formation of *N*-pentylpiperidine in the HDN of pyridine and piperidine. For that purpose we have studied reactions of 2-methylpiperidine and 2-methylpyrrolidine with dialkylamines, alkylamines, and alkenes.

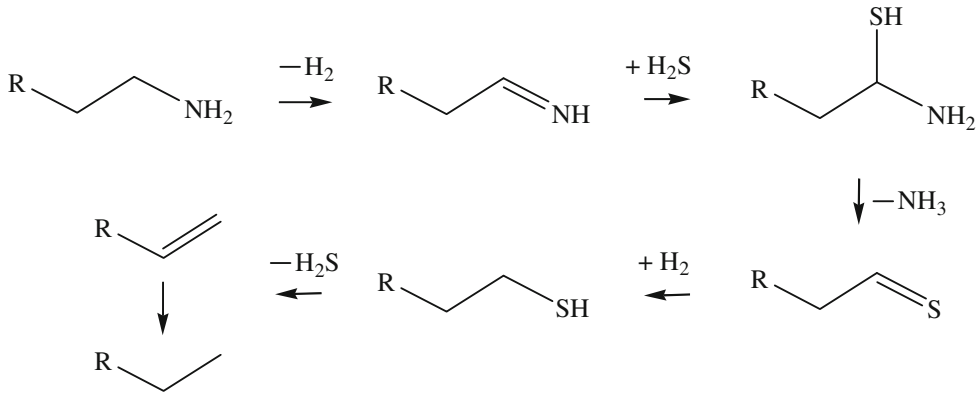


Scheme 1 Reaction network of the HDN of pyridine

2 Experimental

A NiMo/γ-Al_2O_3 catalyst (8 wt% Mo and 3 wt% Ni) was prepared [13] by successive incipient wetness impregnation of γ-Al_2O_3 (Condea, pore volume 0.5 cm^3/g, specific surface area 230 m^2/g). The catalyst was crushed and sieved to a 230-mesh (<0.063 mm) particle size. The HDN reactions were carried out in continuous mode in a fixed-bed inconel reactor that was heated by an oven and filled with 0.05 g catalyst, diluted with 8 g SiC. The catalyst was sulfided in situ with a mixture of 10% H_2S in H_2 (25 mL/min) at 400 °C and 1.0 MPa for 4 h. After sulfidation, the pressure was adjusted to the total reaction pressure of 1.0 or 3.0 MPa, the temperature was decreased to the reaction temperature of 340 °C, and the liquid reactant was fed to the reactor by means of an ISCO 500D syringe pump. The gas-phase feed consisted of 140 kPa decane (solvent for the nitrogen-containing compounds), 20 kPa heptane (GC reference for the nitrogen-containing compounds), 0.5 or 5 kPa amine reactant (2-methylpiperidine (Acros) or 2-methylpyrrolidine (Acros)), 0 or 20 kPa H_2S, and 2.8 MPa H_2. An amount of 0.5, 2, or 5 kPa 1-butylamine, 1-pentene, or 1-hexene was added to the feed in some of the experiments. The reaction products were analyzed off line by gas chromatography with a Varian 3800 GC instrument equipped with a PTA-5 fused silica capillary column and a flame ionization detector. Identification of the reaction products was done with an Agilent 6890 gas chromatograph equipped with an HP-5MS capillary column and an Agilent 5973 mass selective detector. The weight time was defined as the ratio of the catalyst weight to the molar flow to the reactor (1 g min/mol = 1.8×10^{-2} g h/L) and was changed by varying the flow rates of the liquid and the gaseous reactants, while keeping their ratio constant.

Scheme 2 Mechanism of the substitution of an alkylamine with H_2S to an alkanethiol, and then the formation of alkane and alkene by desulfurization



3 Results

3.1 HDN of 2-Methylpiperidine

The HDN of 5 kPa 2-methylpiperidine was carried out as a function of weight time at 340 °C and 3.0 MPa in the absence and presence of 20 kPa H_2S over the sulfided NiMo/γ-Al_2O_3 catalyst. The reaction profiles of the reactant and products are presented in Fig. 1. The conversion of 2-methylpiperidine at the highest weight time was 19% in the absence and 38% in the presence of H_2S. Seven products were observed: 2-methylpyridine, 2,3,4,5-tetrahydro-6-methylpyridine, 1-hexylamine, 2-hexylamine, 1-hexene, 2-hexene, and hexane. 2-Methylpyridine, 2,3,4,5-tetrahydro-6-methylpyridine, and the two hexylamines behaved as primary products. 1-Hexene, 2-hexene, and hexane (denoted as C6 products) were the final products of the HDN network. No products with mass higher than that of the reactant (e.g., *N*-hexyl-2-methylpiperidine) were detected. H_2S greatly enhanced the yield of C6 products and slightly reduced the 2-methylpyridine yield. The results are in agreement with those of Wang et al. [26].

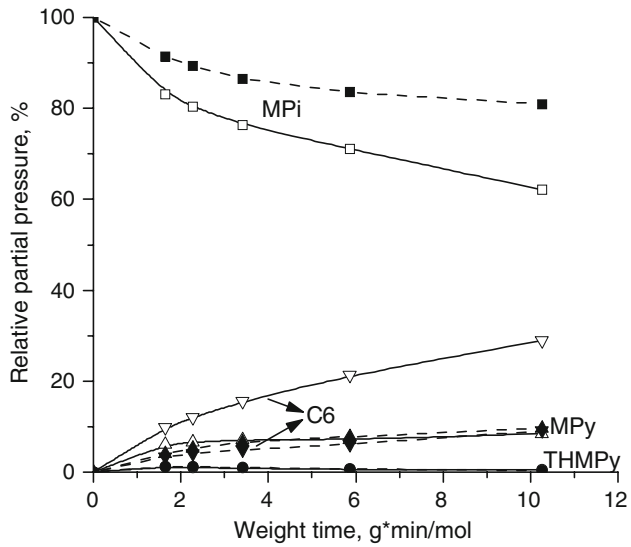
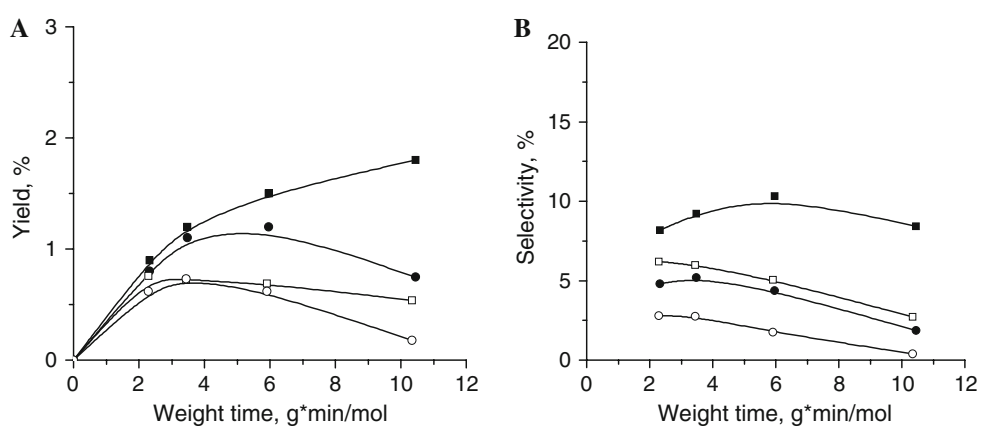


Fig. 1 Relative partial pressure of the 2-methylpyridine (MPy), 2,3,4,5-tetrahydro-6-methylpyridine (THMPy), and C6 (hexenes and hexane) products of the HDN of 2-methylpiperidine (MPi) at 340 °C and 3.0 MPa in the absence (dashed lines, closed symbols) and presence (drawn lines, open symbols) of 20 kPa H_2S

The HDN of 5 kPa 2-methylpiperidine in the presence of 2 and 5 kPa 1-butylamine was studied at 340 °C and 3.0 MPa in the absence and presence of 20 kPa H_2S (Fig. 2). The addition of 1-butylamine hardly influenced the reaction profile of 2-methylpiperidine. The conversion of 1-butylamine varied from 60 to 90% for 2.0 kPa 1-butylamine and from 55 to 80% for 5.0 kPa 1-butylamine when the weight time increased from 2.3 to 10.4 g min/mol. H_2S slightly promoted the conversion of 1-butylamine. The products of the HDN of 1-butylamine were mainly butane and 1-butene. A higher molecular weight product, *N*-butyl-2-methylpiperidine, was observed in all four reactions. In the reaction of 2-methylpiperidine with 5 kPa 1-butylamine in the absence of H_2S, the *N*-butyl-2-methylpiperidine yield increased with increasing weight time and reached 1.8% at the highest weight time, which was the highest yield in the four reactions (Fig. 2a). The *N*-butyl-2-methylpiperidine selectivity was 8–10% based on 2-methylpiperidine, and first increased until $\tau = 6$ g min/mol and then slightly decreased. It extrapolated to a nonzero value at weight time zero, suggesting that *N*-butyl-2-methylpiperidine was a primary product (Fig. 2b). In the reaction of 2-methylpiperidine with 5 kPa 1-butylamine in the presence of 20 kPa H_2S, the yield of *N*-butyl-2-methylpiperidine at low weight time was nearly the same as in the absence of H_2S (Fig. 2a). The yield went through a maximum at $\tau = 6$ g min/mol, and therefore was much lower at high weigh time in the presence than in the absence of H_2S. *N*-butyl-2-methylpiperidine behaved as a primary product and its selectivity decreased with weight time (Fig. 2b). Its selectivity was much lower in the presence than in the absence of H_2S, due to its lower yield and the two times higher conversion of 2-methylpiperidine.

Fig. 2 The yield (**a**) and product selectivity (**b**) of *N*-butyl-2-methylpiperidine in the HDN of 5 kPa 2-methylpiperidine with 2 kPa (open symbols) and 5 kPa (closed symbols) 1-butylamine at 340 °C and 3.0 MPa in the absence (● and ●) and presence (● and ●) of 20 kPa H_2S



Also in the reaction of 2-methylpiperidine with 2 kPa 1-butylamine, the *N*-butyl-2-methylpiperidine yield went through a maximum as a function of weight time, both in the absence and presence of H_2S. At high weight time the yield was several times lower than with 5 kPa 1-butylamine. Its selectivity decreased with weight time (Fig. 2b) and therefore *N*-butyl-2-methylpiperidine also behaved as a primary product in the reaction of 2 kPa 1-butylamine.

The presence of 2 kPa 1-pentene did not affect the HDN of 5 kPa 2-methylpiperidine at 340 °C and 3.0 MPa in the absence of H_2S. No higher molecular weight product, such as *N*-pentyl-2-methylpiperidine, was observed, only conversion of 1-pentene to pentane and 2-pentene occurred.

3.2 HDN of 2-Methylpyrrolidine

The HDN of 0.5 kPa 2-methylpyrrolidine was carried out as a function of weight time at 340 °C and 1.0 MPa in the absence of H_2S over the sulfided NiMo/γ-Al_2O_3 catalyst. These conditions were chosen because at high pressure or in the presence of H_2S, the reaction of 2-methylpyrrolidine and the formed *N*-alkylated amine was fast and their products were complex. 2-Methylpyrrolidine reacted fast at 340 °C and 1.0 MPa; its conversion reached 55% at the lowest weight time (Fig. 3a). 2-Methyl-1-pyrroline and 2-methylpyrrole were the major products (see Scheme 3 for their chemical structures) and the non-zero intercepts of their selectivities with the ordinate (about 80% and 20%, respectively) showed that both behaved as primary products (Fig. 3b). This indicates that dehydrogenation is the main reaction of 2-methylpyrrolidine under our conditions. The yield of 2-methylpyrrole increased with weight time and 2-methylpyrrole was the most abundant product at the highest weight time; therefore it was the final product of dehydrogenation of 2-methylpyrrolidine. The yield of 2-methyl-1-pyrroline decreased at $\tau > 1.2$ g min/mol, more or less parallel to the decrease of 2-methylpyrrolidine, suggesting that 2-methylpyrrolidine and 2-methyl-1-pyrroline have a tendency to reach equilibrium. A minor amount of 2-pentylamine was observed. Its selectivity decreased with weight time, indicating that 2-pentylamine is a primary product. Only a trace of 1-pentylamine was detected. 1-Pentene, 2-pentene, and pentane (together denoted as C5 products) were observed as the denitrogenated products. The C5 yield was low, only 4.5% at the highest weight time, demonstrating that denitrogenation is not favored under these conditions.

Six high molecular weight compounds were observed: *N*-(2-pentyl)-2-methylpyrrole, *N*-(1-pentyl)-2-methylpyrrole, *N*-(2-pent-2-enyl)-2-methylpyrrole, *N*-(1-pent-1-enyl)-2-methylpyrrole, *N*-(2-pentyl)-2-methylpyrrolidine, and *N*-(1-pentyl)-2-methylpyrrolidine (see Scheme 3 for their structures). These molecules together are denoted as NPMPs (Fig. 3) and their yield was 8.1% at $\tau = 8$ g min/mol. The yields and selectivities of *N*-(2-pentyl)-2-methylpyrrole and *N*-(1-pentyl)-2-methylpyrrole are presented in Fig. 4. *N*-(2-pentyl)-2-methylpyrrole and *N*-(1-pentyl)-2-methylpyrrole had nearly the same yield, which increased with weight time and reached 3.3% at $\tau = 8$ g min/mol. Their selectivities increased with weigh time and gave zero values by extrapolation to $\tau = 0$, indicating that the two molecules were not primary, but higher order products. The yields and selectivities of *N*-(2-pent-2-enyl)-2-methylpyrrole and *N*-(1-pent-1-enyl)-2-methylpyrrole increased with weight time and the selectivities approached zero values by extrapolation to $\tau = 0$ (Fig. 5), indicating that the two molecules were higher order products. The yield of *N*-(2-pent-2-enyl)-2-methylpyrrole was larger than that of *N*-(1-pent-1-enyl)-2-methylpyrrole. Only traces of *N*-(2-pentyl)-2-methylpyrrolidine and *N*-(1-pentyl)-2-methylpyrrolidine were observed at high weight time. The yield of *N*-(2-pentyl)-2-methylpyrrolidine was higher than that of *N*-(1-pentyl)-2-methylpyrrolidine.

The HDN of 0.5 kPa 2-methylpyrrolidine in the presence of 0.5 kPa 1-butylamine was performed at 340 °C and 1.0 MPa in the absence of H_2S (Fig. 6). The addition of 1-butylamine slightly inhibited the denitrogenation of

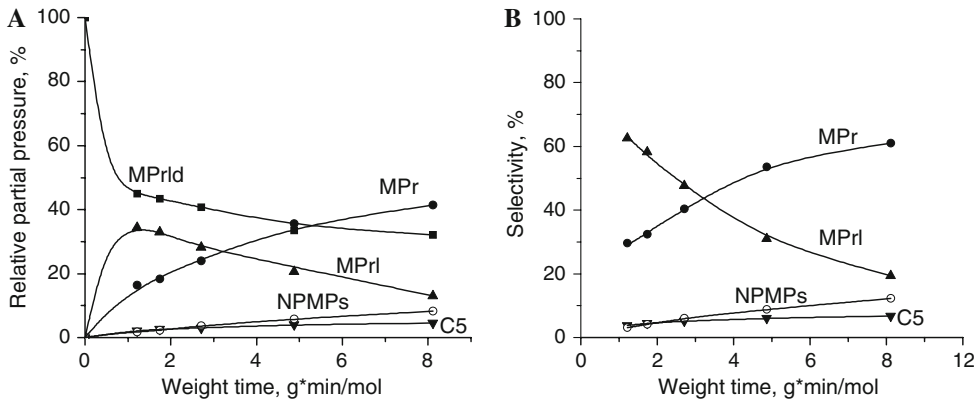
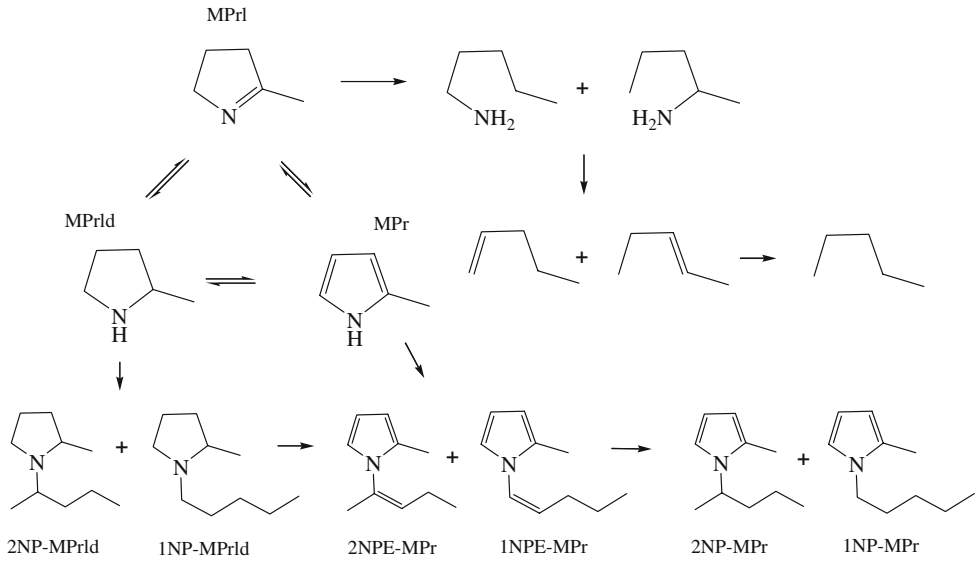


Fig. 3 Relative partial pressures (**a**) and product selectivities (**b**) of 2-methylpyrrole (MPr), 2-methylpyrroline (MPrl), NPMPs, and C5 (see text) in the HDN of 0.5 kPa 2-methylpyrrolidine (MPrld) at 340 °C and 1.0 MPa in the absence of H_2S

Scheme 3 The reaction network of 2-methylpyrrolidine over NiMo/γ-Al_2O_3



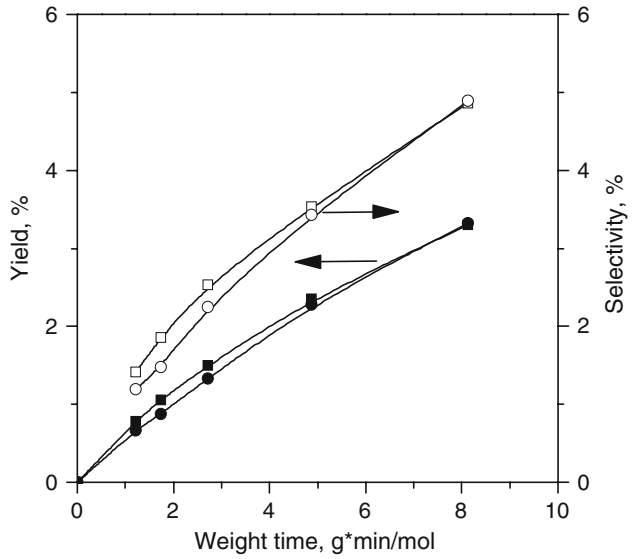


Fig. 4 Yield (closed symbols) and product selectivities (open symbols) of *N*-(2-pentyl)-2-methylpyrrole (● and ●) and *N*-(1-pentyl)-2-methylpyrrole (● and ●) in the HDN of 0.5 kPa 2-methylpyrrolidine at 340 °C and 1.0 MPa in the absence of H_2S

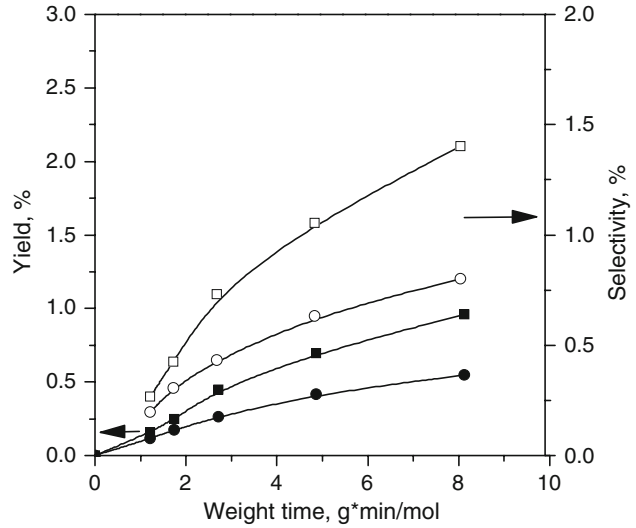


Fig. 5 Yields (closed symbols) and product selectivities (open symbols) of *N*-(2-pent-2-enyl)-2-methylpyrrole (● and ●) and *N*-(1-pent-1-enyl)-2-methylpyrrole (● and ●) in the HDN of 5 kPa 2-methylpyrrolidine at 340 °C and 1.0 MPa in the absence of H_2S

2-methylpyrrolidine. The yield of C5 at the highest weight time was 4.5% in the absence and 3.7% in the presence of 1-butylamine. A large amount of the higher molecular weight products *N*-butyl-2-methylpyrrole and *N*-butyl-2-methylpyrrolidine was observed. Their yields reached 24% and 7% at the highest weight time, respectively. As a result, the yield of 2-methylpyrrole was much lower and the yield of 2-methyl-1-pyrroline was slightly lower in the presence than in the absence of 1-butylamine (cf. Figs. 3, 6). The yield of *N*-butyl-2-methylpyrrolidine first increased and then leveled off with weight time, while the yield of *N*-butyl-2-methylpyrrole increased continuously. The selectivity of *N*-butyl-2-methylpyrrolidine (based on 2-methylpyrrolidine) first increased until $\tau = 2.5$ g min/mol and then slightly decreased, indicating that a further reaction, dehydrogenation of *N*-butyl-2-methylpyrrolidine to *N*-butyl-2-methylpyrrole, occurred. The selectivities (based on 2-methylpyrrolidine) of *N*-butyl-2-methylpyrrole and *N*-butyl-2-methylpyrrolidine extrapolated to zero at weight time zero, suggesting that they are secondary products, although *N*-butyl-2-methylpyrrolidine should be a primary product. The yield of NPMPs was much lower in the presence than in the absence of 1-butylamine, indicating that 1-butylamine inhibited their formation.

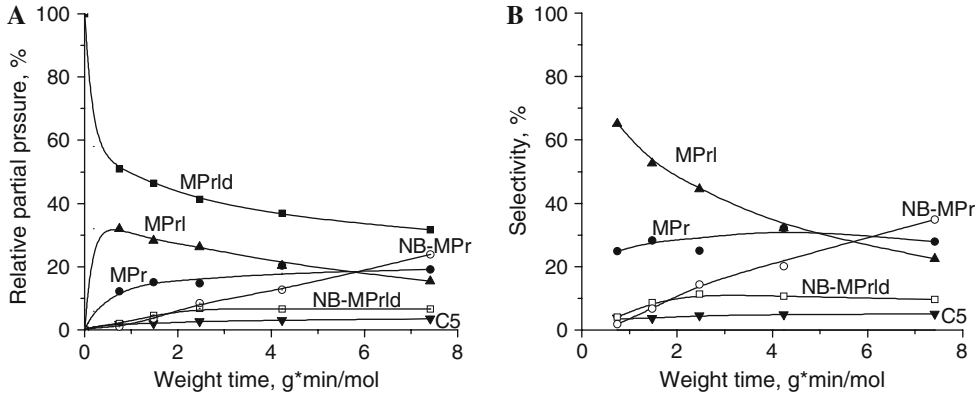


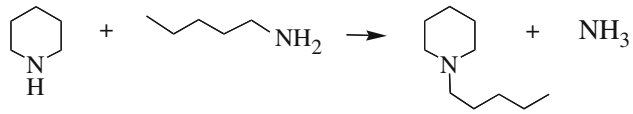
Fig. 6 Relative partial pressures (**a**) and product selectivities (**b**) of 2-methylpyrrole (MPr), 2-methylpyrroline (MPrl), N-butyl-2-methylpyrrole (NB-MPr), N-butyl-2-methylpyrrolidine (NB-MPrld), and C5 in the HDN of 0.5 kPa 2-methylpyrrolidine (MPrld) with 0.5 kPa 1-butylamine at 340 °C and 1.0 MPa in the absence of H_2S

The HDN of 0.5 kPa 2-methylpyrrolidine was also performed in the presence of 0.5 kPa 1-hexene at 340 °C and 1.0 MPa in the absence of H_2S. 1-Hexene did not affect the HDN of 2-methylpyrrolidine and no higher molecular weight product, such as *N*-hexyl-2-methylpyrrolidine, was observed; only conversion of 1-hexene to hexane and 2-hexene occurred.

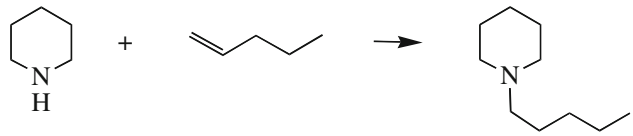
4 Discussion

Already in the first HDN study of pyridine over a metal sulfide catalyst, McIlvried established that pyridine reacts mainly by a consecutive reaction of pyridine to piperidine, of piperidine to pentylamine, and finally of pentylamine to pentene and pentane [1] (cf. Scheme 1). Sonnemans et al. were the first to report the formation of *N*-pentylpiperidine. They observed about equal amounts of *N*-pentylpiperidine and ammonia, but no pentylamine, over an oxidic $CoMoO_3/Al_2O_3$ catalyst at 300 °C and 6 MPa [2]. From these results, they concluded that the most important consecutive reaction after the formation of piperidine is not the ring opening of piperidine to pentylamine, but the disproportionation of two piperidine molecules to *N*-pentylpiperidine and ammonia (Scheme 4). They overlooked, however, that the reaction of piperidine to pentylamine, followed by a fast reaction of pentylamine with piperidine (Scheme 5), would lead to the same results. Also the reaction from piperidine to pentylamine, followed by a fast reaction of pentylamine to pentene and by reaction of pentene with piperidine (Scheme 6), would show a vanishingly low pentylamine concentration and equal amounts of *N*-pentylamine and ammonia. Furthermore, Sonnemans et al. must have assumed that the first product of the reaction of two piperidine molecules, *N*-(5-aminopentyl)piperidine (Scheme 7), loses ammonia very fast.

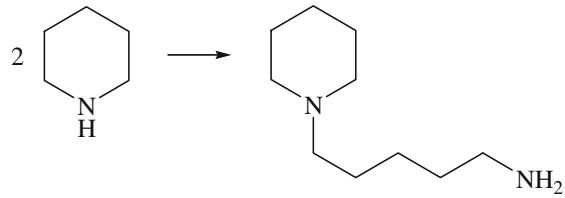
Hanlon, in his study over sulfided $NiMo/Al_2O_3$ at 310 °C and 6 MPa in the presence of 32 kPa H_2S, observed *N*-pentylpiperidine as well and stated, without further argument, that it is formed in a reaction between piperidine and pentylamine (Scheme 5) [4]. In studies over molybdenum carbide as well as a sulfided Mo/SiO_2 catalyst below 280 °C and at 3.1 MPa with 3000 ppm sulfur in the feed, Schwartz and Oyama did not observe any pentylamine, but observed substantial amounts of *N*-pentylpiperidine [12]. The same product distribution was



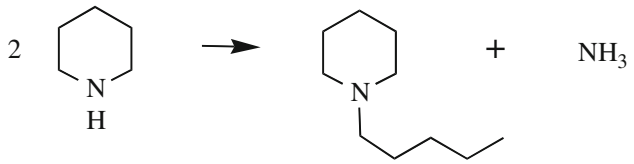
Scheme 5 The formation of *N*-pentylpiperidine by the reaction of piperidine with 1-pentylamine



Scheme 6 The formation of *N*-pentylpiperidine by the addition of piperidine to 1-pentene



Scheme 7 The formation of 1-(5-aminopentyl)piperidine from the reaction of two piperidine molecules

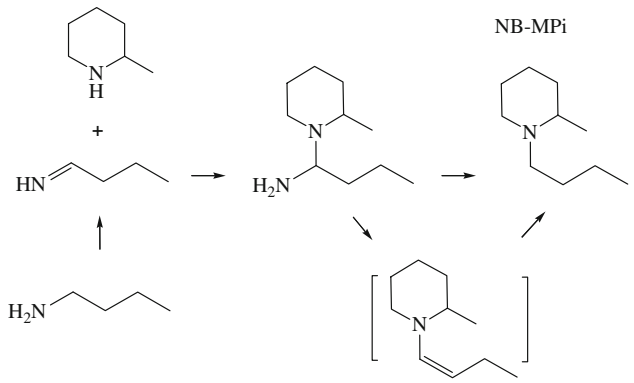


Scheme 4 The disproportionation of two piperidine molecules to *N*-pentylpiperidine and ammonia

observed over a $NiMoN_x/Al_2O_3$ metal nitride catalyst at 300 °C and 3 MPa [10] and over a $GaNiMo/Al_2O_3$ catalyst at 400 °C and 3.5 MPa [11]. Schwartz and Oyama ascribed the absence of pentylamine to the relatively fast disproportionation reaction of pentylamine with piperidine. Hajdiloizou et al. studied the HDN of piperidine around 300 °C and at the relatively low pressure of 1.3 MPa in the absence of H_2S over a CoMo/USY-silica-alumina catalyst [6], which was probably partly metallic and only partly sulfidic, because it had first been reduced and then sulfided. Over this catalyst they observed *N*-pentylpiperidine, 2-pentylpiperidine, and even decahydroquinoline, but no pentylamine and only small amounts of C_5 products. They explained the formation of *N*-pentylpiperidine by the reaction of two piperidine molecules, as well as by the reaction of piperidine with pentylamine [7]. The strong acidity of the support was probably responsible for the formation of 2-pentylpiperidine and decahydroquinoline. In a study over sulfided MoP/Al_2O_3 and $NiMoP/Al_2O_3$ catalysts at 320 °C, 3 MPa, and 9 kPa H_2S, pentylamine as well as *N*-pentylpiperidine were observed, and a third possibility for the formation of *N*-pentylpiperidine was suggested, the addition of piperidine to pentene (Scheme 6) [8]. Over sulfided Mo, CoMo, and NiMo Ledoux and Djellouli did not observe products heavier than C5 in the HDN of pyridine. This might be due to the high temperature and pressure (350 °C and 6 MPa) used in their experiments, which led to metal and acid-catalyzed cracking [5].

Our results of the HDN of 2-methylpiperidine in the absence or presence of 1-butylamine or pentene show that 2-methylpiperidine only reacts with 1-butylamine to form higher molecular weight product. No reaction of 2-methylpiperidine with itself or pentene occurred. It indicates that the formation of *N*-alkylpiperidine by the addition of piperidine to the imine of another piperidine or to an alkene molecule is not possible or slow. If two 2-methylpiperidine molecules would have reacted by the reaction of 2-methylpiperidine with 2,3,4,5-tetrahydro-2-methylpyridine, the imine of 2-methylpiperidine with no steric hindrance by the methyl group, then *N*-(5-aminohexyl)-2-methylpiperidine should be formed first, which reacts on to *N*-hexyl-2-methylpiperidine. Not even a trace of either molecule was observed. Neither was N-(5-aminopentyl)piperidine observed in the reaction of piperidine [8].

The reaction of 2-methylpiperidine with 1-butylamine must occur by the addition of the 2-methylpiperidine molecule to the imine intermediate of 1-butylamine, as shown in Scheme 8. The dehydrogenation of 1-butylamine to butylimine and addition of 2-methylpiperidine to butylimine gives *N*-(1-amino-butyl)-2-methylpiperidine. Denitrogenation occurs to form *N*-(1-but-1-enyl)-2-methylpiperidine, followed by fast hydrogenation to *N*-butyl-2-methylpiperidine. Alternatively, *N*-(1-but-1-enyl)-2-methylpiperidine undergoes hydrogenolysis directly to *N*-butyl-2-methylpiperidine.



Scheme 8 The reaction of 2-methylpiperidine with 1-butylamine by the addition of 2-methylpiperidine to the imine intermediate of butylamine

The reverse reaction, the addition of 1-butylamine to 2,3,4,5-tetrahydro-6-methylpyridine, the imine of 2-methylpiperidine, did not occur, because no ring-opened products were observed. This must be due to steric hindrance in the attack of the nitrogen atom of 1-butylamine on the C_2 atom of 2,3,4,5-tetrahydro-6-methylpyridine. The reason why 2-methylpiperidine did not react with its own HDN product hexylamine must be the low reactivity of 2-methylpiperidine with an alkylamine. Only about 1% of 1-butylamine reacted to *N*-butyl-2-methylpiperidine in the reaction of equimolar (5 kPa) amounts of 1-butylamine and 2-methylpiperidine. In the HDN of 2-methylpiperidine the yield of hexylamine is only a few percent [13] and thus, if this hexylamine reacts with 2-methylpiperidine, the yield of *N*-hexyl-2-methylpiperidine would be very low. The low yield of *N*-butyl-2-methylpiperidine is not only due to the steric hindrance of the methyl group in the reaction of 2-methylpiperidine with 1-butylimine and the low concentration of butylimine in equilibrium with 1-butylamine, but also to the fast further reaction of *N*-butyl-2-methylpiperidine. The yield of *N*-butyl-2-methylpiperidine passed through a low maximum as a function of weight time (Fig. 2), indicating that its rate of consumption is higher than its rate of formation. The maximum was lower in the presence of H_2S. Indeed, trialkylamines were shown to react fast to dialkylamines and alkanethiols, especially in the presence of H_2S [21, 25].

The HDN of 2-methylpyrrolidine was much faster than that of 2-methylpiperidine under the same conditions and led to a greater extent of denitrogenation. This must be due to the fact that the five-membered ring of 2-methylpyrrolidine possesses a higher electron density than the six-membered ring of 2-methylpiperidine [27]. Furthermore, the steric hindrance of the methyl group is smaller in

2-methylpyrrolidine than in 2-methylpiperidine, because the bond angle between the methyl group and the lone pair of the nitrogen atom is larger in 2-methylpyrrolidine than in 2-methylpiperidine [27]. The reaction network of 2-methylpyrrolidine is similar to that of 2-methylpiperidine, except for a fast formation of higher molecular weight products (Scheme 3). The imine 2-methyl-1-pyrroline (or the 2- or 5-methylpyrroline isomer) (MPrl) was formed by dehydrogenation of 2-methylpyrrolidine (MPrld) or hydrogenation of 2-methylpyrrole (MPr). Ring opening of the imine leads to 1- and 2-pentylamine, which are denitrogenated to pentene and pentane. Breaking of the two C–N bonds occurs by addition of H_2S to pentylimine, NH_3 elimination, and hydrogenation, as indicated in Scheme 2 and described for 2-methylpiperidine [26].

In the HDN of 2-methylpiperidine more 2-hexylamine than 1-hexylamine was produced, because the addition of H_2S to the imine 2,3,4,5-tetrahydro-6-methylpyridine is sterically hindered and the addition of H_2S to 2,3,4,5-tetrahydro-2-methylpyridine is not hindered [13, 26]. For the same reason more 2-pentylamine than 1-pentylamine was observed in the HDN of 2-methylpyrrolidine. This in turn (Scheme 3) resulted in a higher yield of *N*-2-pentenyl-2-methylpyrrole (2NPE-MPr) than of *N*-1-pentenyl-2-methylpyrrole (1NPE-MPr) and a higher yield of *N*-2-pentyl-2-methylpyrrole (2NP-MPr) than of *N*-1-pentyl-2-methylpyrrole (1NP-MPr).

Higher molecular weight products were observed in the HDN of 2-methylpyrrolidine and they showed that 2-methylpyrrolidine as well as 2-methylpyrrole reacted with amines to the corresponding *N*-alkylated compounds. 2-Methylpyrrole possesses an N–H bond and can therefore add to an imine. It also shows that 2-methylpiperidine, 2-methylpyrrole, and 2-methylpyrrolidine react by addition to the alkylimine, and not by the reverse addition of the alkylamine to 2,3,4,5-tetrahydro-6-methylpyridine or 2-methyl-1-pyrroline. Small amounts of *N*-2-pentenyl-2-methylpyrrole (2NPE-MPr) and *N*-1-pentenyl-2-methylpyrrole (1NPE-MPr) were observed, which should be the intermediates of the reaction of 2-methylpyrrole with 2-pentylamine and 1-pentylamine, respectively. As shown in Scheme 8 for the reaction of 2-methylpiperidine with butylamine, the denitrogenation of *N*-(1-amino-pentyl)-2-methylpyrrole, formed in the reaction of 2-methylpyrrole with pentylamine, produces *N*-(1-pent-1-enyl)-2-methylpyrrole by elimination. The conjugation of the double bond with the pyrrole ring in *N*-1-pentenyl-2-methylpyrrole (1NPE-MPr) and *N*-2-pentenyl-2-methylpyrrole (2NPE-MPr) explains why these molecules were observed, but *N*-1-pentenyl-2-methylpyrrolidine and *N*-2-pentenyl-2-methylpyrrolidine were not observed. The yield of *N*-alkyl substituted 2-methylpyrrole was higher than that of 2-methylpyrrolidine, probably because the aromaticity of the pyrrole ring makes the hydrogen connected with the nitrogen atom a weak acid ($K_a = 10^{-15}$). Therefore, the addition of pyrrole to an imine is more favored than that of pyrrolidine.

1-Butylamine reacted with 2-methylpyrrolidine and 2-methylpyrrole. The yield of NB-2-methylpyrrole was about fourfold higher than the sum of the yields of *N*-1-pentyl-2-methylpyrrole and *N*-2-pentyl-2-methylpyrrole, because the concentration of 1-butylamine was much higher than that of the pentylamines. The yield of *N*-butyl-2-methylpyrrolidine was nearly the same as that of *N*-butyl-2-methylpyrrole at low weight time although the concentration of 2-methylpyrrolidine was much higher than that of 2-methylpyrrole, proving that the reaction of 2-methylpyrrole with 1-butylamine is favored. At high weight time, *N*-butyl-2-methylpyrrolidine converted to *N*-butyl-2-methylpyrrole, because the dehydrogenation of 2-methylpyrrolidine to 2-methylpyrrole was favored under our conditions. 2-Methylpyrrolidine did not react with hexene, proving again that high molecular weight compounds are formed by reaction of 2-methylpyrrolidine and 2-methylpyrrole with amines, not by reaction with themselves or with an alkene.

5 Conclusion

To explain the formation of *N*-pentylpiperidine in the HDN of pyridine and piperidine, the reactions of 2-methylpiperidine and 2-methylpyrrolidine with dialkylamines, alkylamines, and alkenes were studied over sulfided NiMo/γ-Al_2O_3. 2-Methylpiperidine only reacted with 1-butylamine to form *N*-butylpiperidine, but not with another 2-methylpiperidine molecule or with 1-pentene. *N*-Pentyl-substituted 2-methylpyrrole and 2-methylpyrrolidine were observed in the HDN of 2-methylpyrrolidine, indicating that 2-methylpyrrolidine and 2-methylpyrrole react with the secondary pentylamine products because of their higher electron density and smaller steric hindrance of the methyl group compared with 2-methylpiperidine. 2-Methylpyrrole and 2-methylpyrrolidine also reacted with 1-butylamine, but not with 1-hexene. The reactivity of 2-methylpyrrole with an alkylamine is higher than that of 2-methylpyrrolidine.

Our results explain why *N*-alkylated products are not or hardly observed in the HDN of pyridine and piperidine alkylated in the 2 position and of quinoline and decahydroquinoline. These molecules have in common that a carbon atom neighboring the nitrogen atom carries an alkyl substituent and this makes the addition of an alkylamine to the imine of these cyclic amines sterically demanding. The reverse reaction, between the cyclic amine and the alkylimine, has a low probability because of the low alkylimine concentration.

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