Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 221 (2004) 441–454

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Investigation of the mechanism of the hydrodenitrogenation of *n*-hexylamines over sulfided NiMo/γ-Al_2O_3

Yonggang Zhao, Pavel Kukula, and Roel Prins *

Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology (ETH), 8093 Zurich, Switzerland

Received 17 March 2003; revised 7 July 2003; accepted 8 September 2003

Abstract

The hydrodenitrogenation (HDN) of *n*-hexylamine, dihexylamine, and trihexylamine was studied between 300 and 340 °C, 3 and 5 MPa total pressure, 5 and 20 kPa amine pressure, and 10 and 150 kPa H_2S pressure over a sulfided Ni–Mo/γ-Al_2O_3 catalyst. The conversion increased with the H_2 pressure and decreased with increasing partial pressure of the hexylamines. The conversion of hexylamine and dihexylamine decreased slightly with H_2S pressure, but that of trihexylamine increased substantially. The contributions of elimination and nucleophilic substitution to the HDN were determined by the initial product selectivities at short weight time. The initial alkene selectivities were low and accounted for only a minor part of the *n*-alkylamine conversion. Since the hexene/hexane branching ratio in the HDN of the alkylamines was almost equal to that in the hydrodesulfurization of pentanethiol in the presence of an alkylamine, it was concluded that the majority of hexene in the HDN of the hexylamines originates from hexanethiol. Nucleophilic substitution of the hexylamines with H_2S to give an alkanethiol is the predominant HDN reaction of all three *n*-hexylamines.

Keywords: Hydrodenitrogenation; Elimination; Nucleophilic substitution; Disproportionation; Hexylamine; Dihexylamine; Trihexylamine; Hydrogen sulfide; Ni–Mo/γ-Al_2O_3

1. Introduction

Reactions such as hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) take place in the hydrotreating of oil fractions, one of the most important catalytic processes in the petroleum industry. A considerable number of studies have led to a better understanding of the mechanisms involved in these reactions. It is generally accepted [1–9] that the first step in the HDN of nitrogen-containing aromatic molecules is the hydrogenation of the heterocyclic ring. Only after the breaking of the aromaticity can C–N bond cleavage in the resulting saturated molecules take place. Several mechanisms of the C–N bond scission and nitrogen removal have been proposed [1,10–12]. Nelson and Levy [1] were the first to suggest Hofmann-type elimination and nucleophilic substitution as mechanisms for C–N bond scission of aliphatic nitrogen-containing molecules. The initial step in C–N bond scission is the addition of a proton to a nitrogen lone pair with the formation of a quarternary ammonium compound, which provides a better leaving group than the amine group. C–N bond scission can then occur via elimination of a β-hydrogen atom with the formation of an alkene or via nucleophilic substitution of the amine group at the α-carbon atom by a sulfhydryl group to form an alkanethiol.

Several studies [6,13–18] have dealt with the HDN of aliphatic amines over different catalysts. Portefaix et al. showed in HDN studies at 2 MPa over sulfided NiMo/Al_2O_3 that an increase in the number of β-hydrogen atoms in pentylamines and piperidines increased the conversion of these molecules [6,13]. This was taken as proof that aliphatic C–N bond cleavage takes place by Hofmann elimination. However, they did not measure the reaction products and ascribed the total conversion of the amines to the rate of HDN. We showed that a substantial part of the conversion went to dehydrogenated molecules rather than HDN products [14]. If only the HDN products were taken into account, then the introduction of a methyl group onto the α-carbon atom of piperidine and, thus an increase in the number of β-hydrogen atoms, actually decreased the rate of nitrogen removal. Furthermore, ring opening of 2-methylpiperidine by C–N bond cleavage occurred preferentially on the CH_2–N side and not

---

* Corresponding author.
E-mail address: prins@tech.chem.ethz.ch (R. Prins).

0021-9517/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2003.09.010

on the $CH(CH_3)$–N side. This and the observation of thiol intermediates in the HDN of 2-methylpiperidine [14] and methylcyclohexylamine [19] suggest that nucleophilic substitution is even important in the HDN of aliphatic amines that contain β-hydrogen atoms.

Vivier et al. [7] were the first to prove that C–N bond cleavage by nucleophilic substitution can take place in the HDN of amines. They observed that benzylamine and α,α-diphenylmethylamine, which do not have β-hydrogen atoms and thus cannot react by elimination, react fast to toluene and diphenylmethane, respectively. Benzylamine and α,α-diphenylmethylamine react most probably by nucleophilic substitution of the amine group by an SH group followed by rapid hydrogenolysis of the intermediate thiol. The C–N bond cleavage in these molecules may be of the S_N1 and not S_N2 type, because of the stabilizing influence of the phenyl groups on the intermediate carbenium ion that results from removal of the amine group. Cattenot et al. showed that both elimination and nucleophilic substitution play a role in the C–N bond scission of pentylamines on unsupported transition-metal sulfides at atmospheric pressure [15]. The ratio of the two mechanisms depended on the type of metal sulfide catalyst and the type of amine. Over MoS_2, n-pentylamine reacted by nucleophilic substitution with H_2S to pentanethiol as well as with another n-pentylamine molecule to dipentylamine. Pentenes were observed as secondary products and supposed to be formed by elimination from dipentylamine. These findings suggest that the molecular structure is one of the most important factors in HDN and that different molecules may undergo nitrogen removal by different mechanisms.

Concurrent with the β-hydrogen elimination and nucleophilic substitution reactions, a disproportionation reaction can occur between two alkylamine molecules, and this complicates the study of the HDN reaction mechanism. This disproportionation results in the formation of a dialkylamine and ammonia in case of an alkylamine and in the formation of a trialkylamine and alkylamine in case of a dialkylamine; it takes place even on alumina at low hydrogen pressure [20,21]. Substantial amounts of the disproportionation products N-pentylpiperidine, dicyclohexylamine, and dipentylamine were observed in the HDN of piperidine [22], cyclohexylamine [23], and pentylamine [15,24], respectively.

We decided to carry out a detailed investigation of the HDN of alkylamines over sulfided $NiMo/Al_2O_3$. The aim of our work was to determine which of the different mechanisms (elimination, substitution, and disproportionation) plays the major role in the HDN of aliphatic amines. To elucidate the mechanism it is necessary to determine the primary HDN products and to compare the influence of different reaction conditions on product distribution. Accordingly, we carried out experiments at low weight times and under different reaction conditions to check the formation of primary products and, thus, to prove the mechanism of the HDN of aliphatic amines. In this work we will present our results of the HDN of the linear n-alkylamines hexylamine, dihexylamine, and trihexylamine, while in subsequent work we will publish our results of the HDN of alkylamines with the amine group attached to secondary and tertiary carbon atoms.

2. Experimental

The $NiMo/\gamma\text{-}Al_2O_3$ catalyst used in this work contained 8 wt% Mo and 3 wt% Ni and was prepared by a two-step pore-volume impregnation of $\gamma\text{-}Al_2O_3$ (Condea; pore volume 0.5 cm^3/g, specific surface area 230 m^2/g). The catalysts were crushed and sieved to a 230-mesh (< 0.063 mm) particle size. For further details about the catalyst preparation see Ref. [14].

A sample of 0.05 g catalyst was mixed with 8 g of SiC to achieve plug-flow conditions in the continuous-flow fixed-bed reactor (material: Inconel 718). The catalyst was sulfided in situ with a mixture of 10% H_2S in H_2 at 370 °C and 1 MPa for 4 h. After sulfidation, the pressure was increased to 3 or 5 MPa, 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 300 and 350 °C. Cyclohexane, decane, and octane were used as solvents and heptane as an internal standard for GC analysis. The hydrogen pressure was varied from 2.8 to 4.8 MPa. Three types of molecules were used as reactants to study the HDS, HDN, and hydrogenation reactions simultaneously. We used pentanethiol and hexanethiol as thiols, hexylamine and cyclohexylamine as amines, and 1-hexene and cyclohexene as alkenes. The choice of the alkanethiol, alkylamine, and alkene in a simultaneous HDS, HDN, and hydrogenation experiment was primarily made so as to obtain separate peaks in the GC analysis. All the chemicals were purchased as commercial standards from Aldrich and Fluka. The partial pressure of the alkanethiols and alkenes was kept at 5 kPa, while the partial pressure of the amines was 5, 10, or 20 kPa. The H_2S pressure was varied between 10 and 150 kPa and the experiments were carried out at 300, 320, and 340 °C. When changing the partial pressure of the reactant, the solvent flow was adapted to keep the partial pressure of hydrogen constant. The weight time was defined as the ratio between the catalyst weight (w_{cat}) and the total molar flow fed to the reactor (n_{feed}). As the influence of weight time on the product distribution was studied, the weight time was changed by varying the flow rates of the liquid and the gaseous reactants with respect to the amine, while their ratio was kept constant.

The product selectivity (S) was defined as the number of molecules converted to a certain product (n_P) divided by the number of converted reactant molecules (n_R), both multiplied by their number of carbon atoms, Cn_P and Cn_R respectively: $S = (n_P * Cn_P)/(n_R * Cn_R)$. With this definition, the mass balance of the carbon atoms is preserved. For instance, in the reaction $(C_6H_{13})_3N + H_2S \rightarrow (C_6H_{13})_2NH +$

$C_6H_{13}SH$, the selectivity of DHA is 66.7% and the selectivity of hexanethiol is 33.3%. The original feed was usually reentered after the set of HDN experiments to check whether the activity of the catalyst had remained constant. Then the whole reactor setup was cleaned for another series of experiments.

The reaction products were analyzed by on-line gas chromatography with a flame ionization detector and a pulsed-flame photometric detector. Mass spectrometry was used to identify the reaction products. For further details see Ref. [14].

3. Results

3.1. HDS of pentanethiol and hydrogenation of hexene

To compare the relative rates of the HDS of alkanethiols, the HDN of alkylamines, and the hydrogenation of alkenes, we performed the simultaneous conversion of octanethiol, hexylamine, and 1-pentene at 300 °C and 3 MPa in the presence of 10 kPa H_2S. It is clear from the results presented in Fig. 1 that an alkanethiol reacts very much faster than an alkylamine and an alkene. Fig. 2 shows the HDS conversion of pentanethiol at 300 °C and 3 MPa in the presence of different pressures of hexylamine and H_2S; it was equally fast as that of octanethiol (Fig. 1). The pentanethiol conversion decreased strongly with increasing H_2S pressure from 10 to 50 kPa and less strongly with increasing hexylamine pressure from 5 to 20 kPa. The nonzero selectivities at short weight time (Fig. 3) demonstrate that 1-pentene and pentane are primary products, while the low initial selectivity of 2-pentene indicates that 2-pentene is a secondary product. The pentene selectivity decreased with increasing hexylamine pressure as well as with increasing H_2S partial pressure, while the opposite dependence was observed for the complementary pentane. As a consequence, the molar pentenes/pentane ratio (pentenes stands for the sum of all the pentenes) decreased with increasing partial pressure of hexylamine and H_2S (Fig. 4).

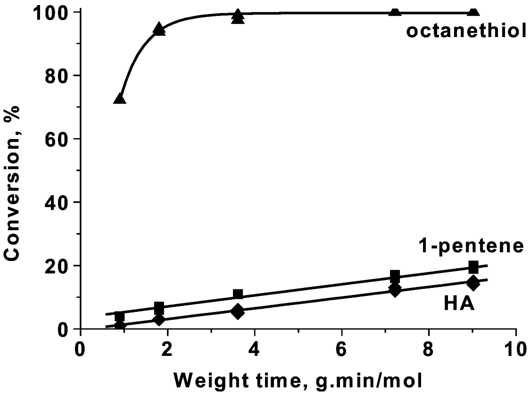


Fig. 1. Conversions of octanethiol and hexylamine, and yield of pentane in the simultaneous HDS of 5 kPa octanethiol, HDN of 5 kPa hexylamine (HA), and hydrogenation of 5 kPa 1-pentene at 300 °C, 3 MPa, and 10 kPa H_2S.

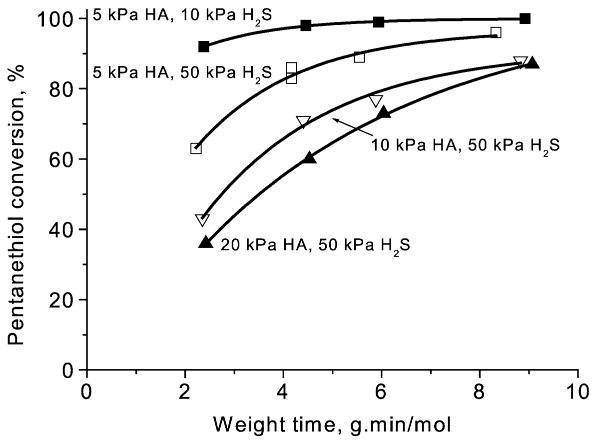


Fig. 2. Conversion of 5 kPa pentanethiol at 300 °C and 3 MPa in the presence of 5, 10, and 20 kPa hexylamine (HA), and 10 and 50 kPa H_2S.

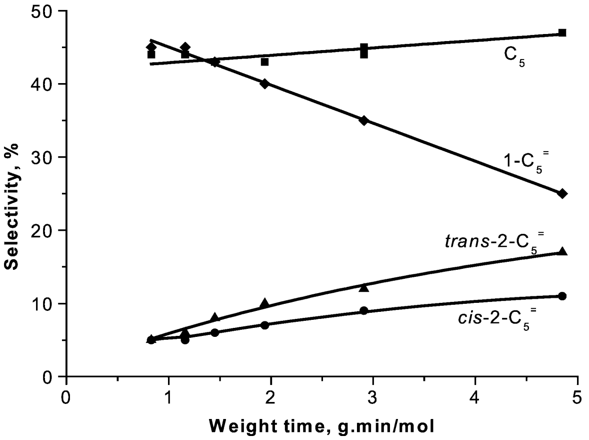


Fig. 3. Product selectivities to pentane, 1-pentene, *trans*-2-pentene, and *cis*-2-pentene in the HDS of 5 kPa pentanethiol at 300 °C and 3 MPa in the presence of 20 kPa hexylamine, 5 kPa cyclohexene, and 10 kPa H_2S.

The conversion of 1-hexene to hexane was high in the absence of alkylamine; at 300 °C in the presence of 10 kPa H_2S it was already 40% at $\tau = 0.8\ \mathrm{g\,min\,mol^{-1}}$ (Fig. 5). In the presence of 5 kPa cyclohexylamine and 10 kPa H_2S, however, it was only 8% at $\tau = 0.8\ \mathrm{g\,min\,mol^{-1}}$. At 300 °C (Fig. 1), the alkene conversion at 340 °C in the presence of an alkylamine (Fig. 5) was much lower than the conversion of pentanethiol (98%). The conversion of 1-hexene to hexane decreased substantially with increasing hexylamine and H_2S partial pressure, while in the presence of alkylamine the influence of H_2S was only moderate. This indicates that the alkylamine is more strongly adsorbed than H_2S.

3.2. HDN of hexylamine

The conversion of 5 kPa hexylamine at 300 °C and 5 MPa in the presence of 50 kPa of H_2S was 6% at low weight time ($0.9\ \mathrm{g\,min\,mol^{-1}}$) and reached 37% at high weight time ($8.7\ \mathrm{g\,min\,mol^{-1}}$). It almost doubled when the reac-

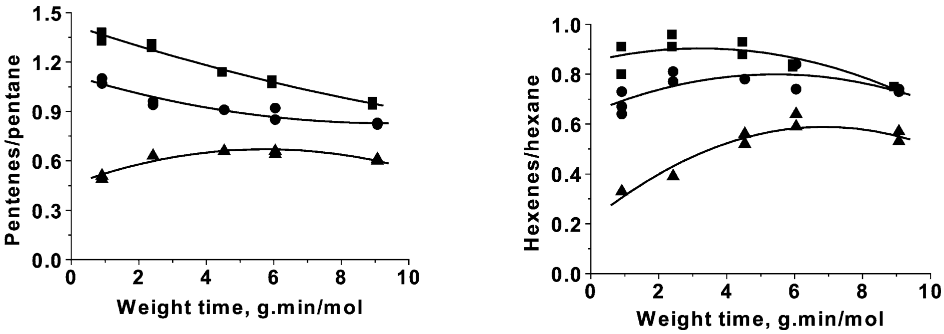


Fig. 4. Pentenes/pentane ratio and hexenes/hexane ratio in the simultaneous HDS of 5 kPa pentanethiol and HDN of 5 or 20 kPa hexylamine at 300 °C and 3 MPa, and 10 or 50 kPa H_2S. ■, 5 kPa HA and 10 kPa H_2S; ●, 20 kPa HA and 10 kPa H_2S; ▲, 20 kPa HA and 50 kPa H_2S.

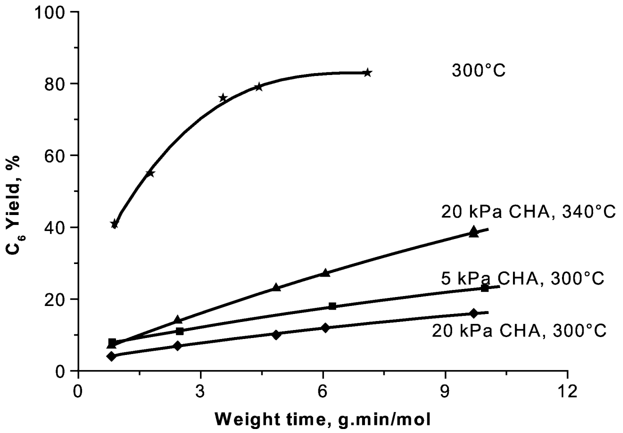


Fig. 5. Conversion of 5 kPa 1-hexene at 300 and 340 °C and 3 MPa in the presence or absence of 5 or 20 kPa cyclohexylamine (CHA), 5 kPa pentanethiol (PT), and 10 kPa H_2S. ★ 300 °C; ▲, 5 kPa PT, 20 kPa CHA, and 340 °C; ■, 5 kPa PT, 5 kPa CHA, and 300 °C; ◆, 5 kPa PT, 20 kPa CHA, and 300 °C.

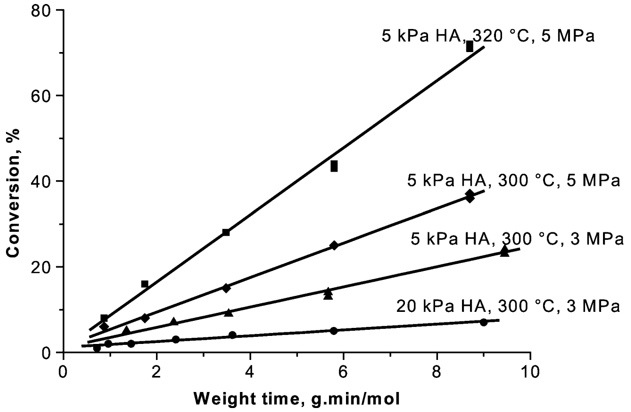


Fig. 6. Influence of the partial pressure of hexylamine (HA) on its conversion as a function of weight time at 300 and 320 °C, 3 and 5 MPa, and 50 kPa H_2S. ■, 5 kPa HA at 320 °C and 5 MPa; ◆, 5 kPa HA at 300 °C and 5 MPa; ▲, 5 kPa HA at 300 °C and 3 MPa; ●, 20 kPa HA at 300 °C and 3 MPa.

tion temperature was increased from 300 to 320 °C (Fig. 6). Fig. 7 shows the corresponding product distributions at 300 °C (Fig. 7A) and 320 °C (Fig. 7B). The main product of the HDN of hexylamine was hexane, which behaved as a primary product because the selectivity extrapolates to a nonzero value at $\tau = 0$. The selectivity of the hexenes (the sum of 1-, 2-, and 3-hexene) decreased with decreasing contact time at 300 °C, suggesting that hexene may be a secondary product or a secondary as well as a primary product. At 340 °C, hexene behaved as a primary product. The selectivity of 1-hexanethiol increased with decreasing weight time, showing that it is a primary product.

As 1-hexene is too easily hydrogenated at 5 MPa total pressure, it does not give us much information about the HDN mechanism. Therefore, the total pressure was decreased from 5 to 3 MPa to obtain less severe hydrogenation conditions. This change resulted in a decrease in the hexylamine conversion that was about proportional to the change in H_2 pressure (Figs. 6 and 8). Fig. 9 shows that, at 50 kPa H_2S and short contact time (1.4 $\mathrm{g\,min\,mol^{-1}}$), the main product was hexanethiol (45% selectivity), followed by hexane (39% selectivity) and hexenes (12%). At 3 MPa, dihexylamine was observed as well (4% at short contact time). The selectivities of 2-hexene and 3-hexene were zero. This shows that initially no isomerization of 1-hexene takes place. At $\tau = 14.2\ \mathrm{g\,min\,mol^{-1}}$, the hexanethiol selectivity decreased to 6% and the hexane selectivity increased to 62%. Isomerization had become important and the sum of the selectivities of 1-hexene, 2-hexene, and 3-hexene reached 30%. The hexanethiol selectivity was much higher at 3 than at 5 MPa (cf. Figs. 7A and 9). Some dihexylimine was observed as well. It was also observed in a blank experiment carried out without the catalyst in the empty Inconel 718 reactor. In the product mixture of the HDN of hexylamine, the yield of dihexylimine reached only 0.4% at $\tau = 1.4\ \mathrm{g\,min\,mol^{-1}}$, while during the HDN of dihexylamine and trihexylamine it amounted to 1.2% at $\tau = 1.0\ \mathrm{g\,min\,mol^{-1}}$. These small amounts of dihexylimine were ignored.

At 3 MPa and 300 °C, the hexane selectivity extrapolated to a nonzero value at $\tau = 0$ and the hexene selectivity to a zero or very low value (Fig. 9), indicating that hexane behaves like a primary and hexene like a secondary product. This ratio decreased with increasing hexylamine and H_2S partial pressure. The hexenes/hexane ratio, obtained from the HDN of hexylamine, was smaller than the pentenes/pentane ratio, obtained from the HDS of pen-

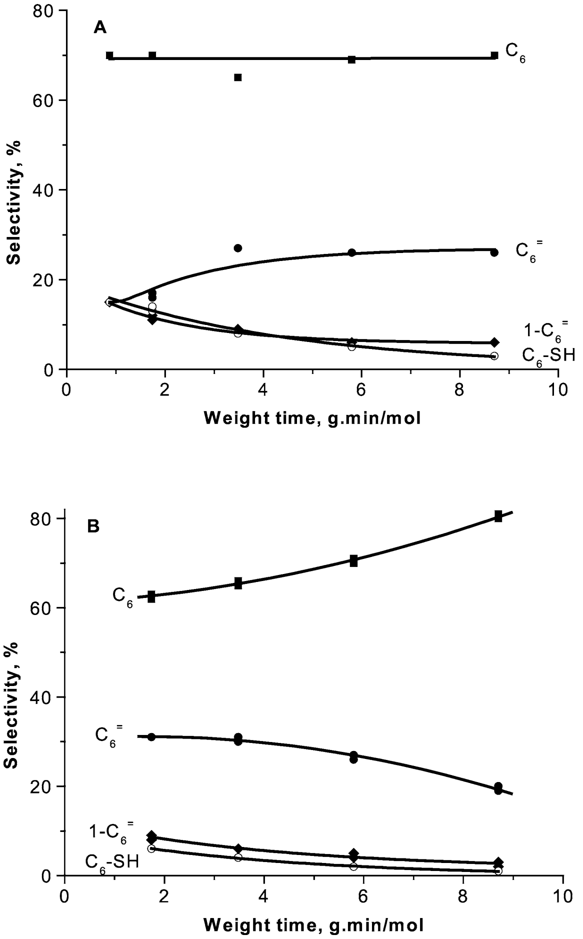


Fig. 7. Product selectivities in the HDN of 5 kPa hexylamine at 5 MPa, 50 kPa H_2S, and 300 °C (A), and 320 °C (B). ■, hexane; ●, hexenes; ◆, 1-hexene; ○, hexanethiol.

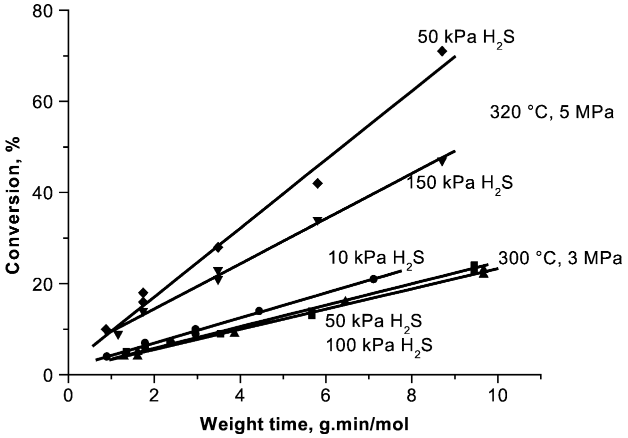


Fig. 8. Influence of H_2S on the conversion of 5 kPa hexylamine at (◆) 320 °C, 5 MPa, and 50 kPa H_2S; (▼) 320 °C, 5 MPa, and 150 kPa H_2S; (●) 300 °C, 3 MPa, and 10 kPa H_2S; (■) 300 °C, 3 MPa, and 50 kPa H_2S; (▲) 300 °C, 3 MPa, and 100 kPa H_2S.

tanethiol (Fig. 4), at small weight time, but approached the pentenes/pentane ratio at high weight time.

The conversion of hexylamine decreased by about a factor of 3 at $\tau = 5.8\ \mathrm{g\,min\,mol^{-1}}$ when increasing the hexylamine partial pressure from 5 to 20 kPa while keeping the other parameters constant at 3 MPa, 300 °C, and 50 kPa H_2S (Fig. 6). The selectivities of hexanethiol, hexane, and hexene did not change much with the change of the hexylamine partial pressure; only the initial selectivity of dihexylamine increased from 4 to 7%. At 300 °C, the hexylamine conversion decreased slightly when the H_2S pressure was increased from 10 to 50 and 100 kPa (Fig. 8). At 320 °C and 5 MPa, a stronger decrease was obtained. With increasing H_2S partial pressure, the selectivity of the hexenes decreased, the hexane selectivity was about constant, the hexanethiol selectivity increased strongly, and the dihexylamine selectivity

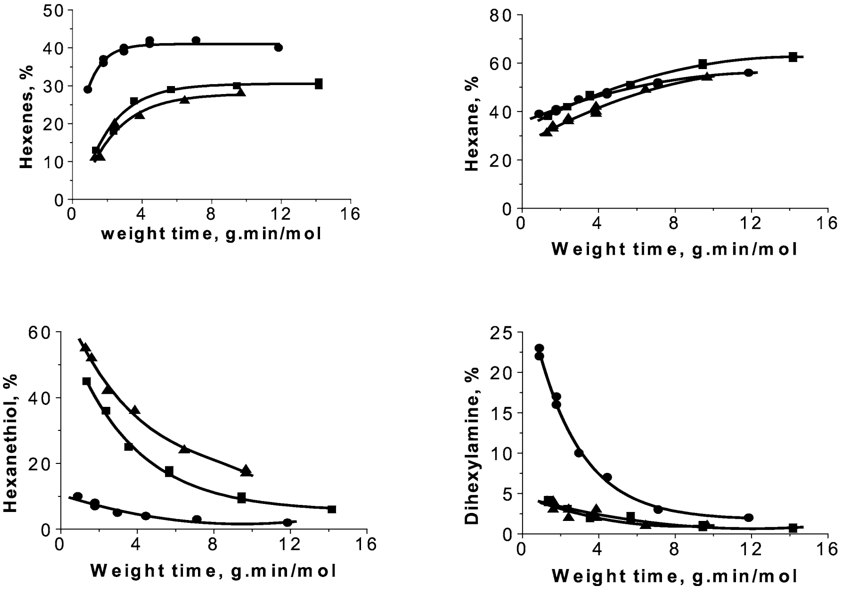


Fig. 9. Product selectivities in the HDN of 5 kPa hexylamine at 300 °C, 3 MPa, and 10 kPa H_2S (●), 50 kPa H_2S (■), and 100 kPa H_2S (▲).

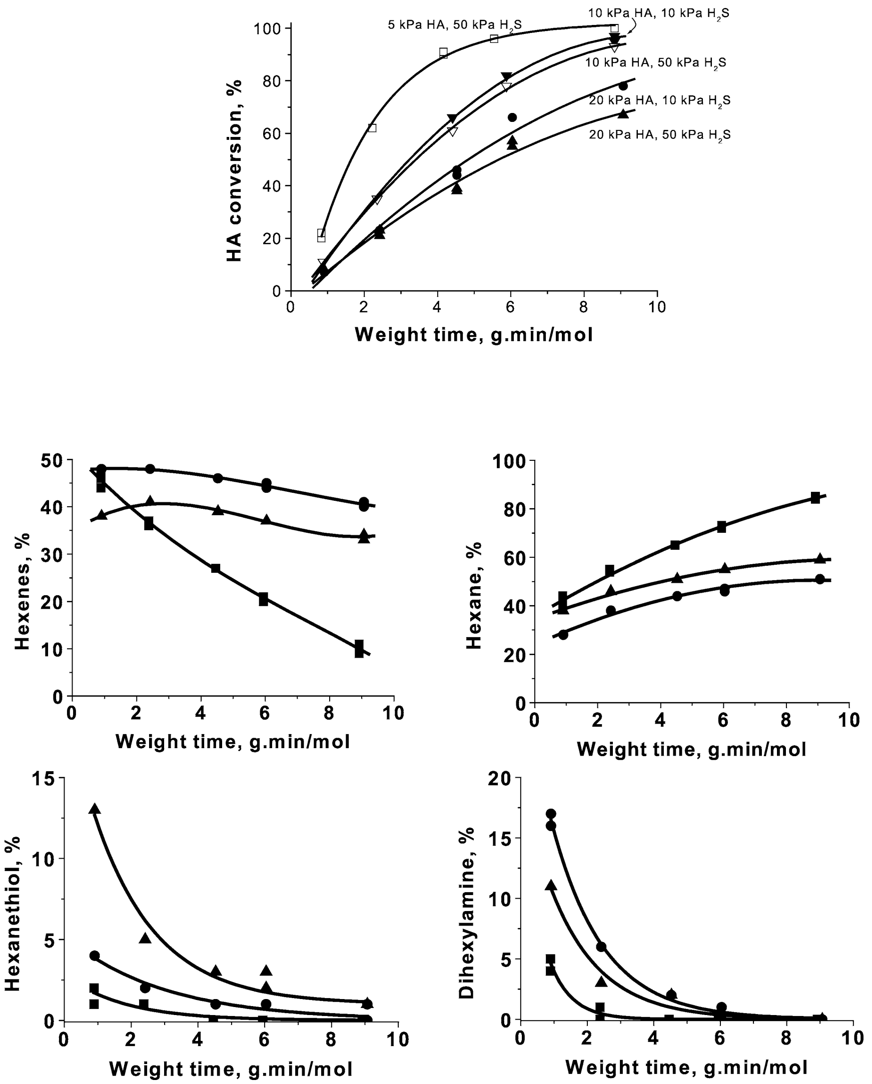


Fig. 10. Conversion and product selectivities in the HDN of 5, 10, and 20 kPa hexylamine (HA) at 340 °C and 3 MPa, in the presence of 5 kPa pentanethiol, and 10 and 50 kPa H_2S. ■, 5 kPa HA and 10 kPa H_2S; ●, 20 kPa HA and 10 kPa H_2S; ▲, 20 kPa HA and 50 kPa H_2S.

decreased strongly (Fig. 9). The weight time dependencies of the products show that dihexylamine and hexanethiol are primary products, that 1-hexene behaves like a secondary product, and that hexane might be formed as a primary as well as a secondary product.

To obtain a greater amount of product, and thus increase the accuracy of the selectivity measurements at short weight time, the reaction temperature was increased to 340 °C. Fig. 10 shows the conversion of hexylamine at 340 °C and 3 MPa in the presence of 10 or 50 kPa H_2S and 5 kPa pentanethiol. Because of the fast HDS reaction, this means that the actual H_2S pressure amounted to 15 or 55 kPa. The hexylamine conversion decreased strongly when its partial pressure was increased from 5 to 20 kPa and the dihexylamine selectivity increased (Fig. 10). Their nonzero initial selectivities show that dihexylamine and hexanethiol are primary products, while hexane and hexene behave like primary products. With increasing H_2S pressure, the dihexylamine and hexene selectivities decreased, while the hexanethiol selectivity increased sharply. The selectivity of hexane did not change much with H_2S pressure.

The alkenes/alkane ratio in the HDN of hexylamine and HDS of pentanethiol increased when increasing the temperature from 300 to 340 °C (cf. Figs. 4 and 11). The hexenes/hexane ratio was equal to the pentenes/pentane ratio resulting from the HDS of pentanethiol at two different H_2S and hexylamine partial pressures (Fig. 11). Both ratios decreased with increasing weight time, due to the hydrogenation of the alkene to the alkane. The decrease was less steep at higher hexylamine as well as H_2S partial pressure because of the slower hydrogenation of the alkene under those conditions.

3.3. *HDN of dihexylamine*

The conversion of dihexylamine (Fig. 12) was much faster than that of hexylamine (Fig. 6). At 320 °C, almost complete conversion was reached already at short contact

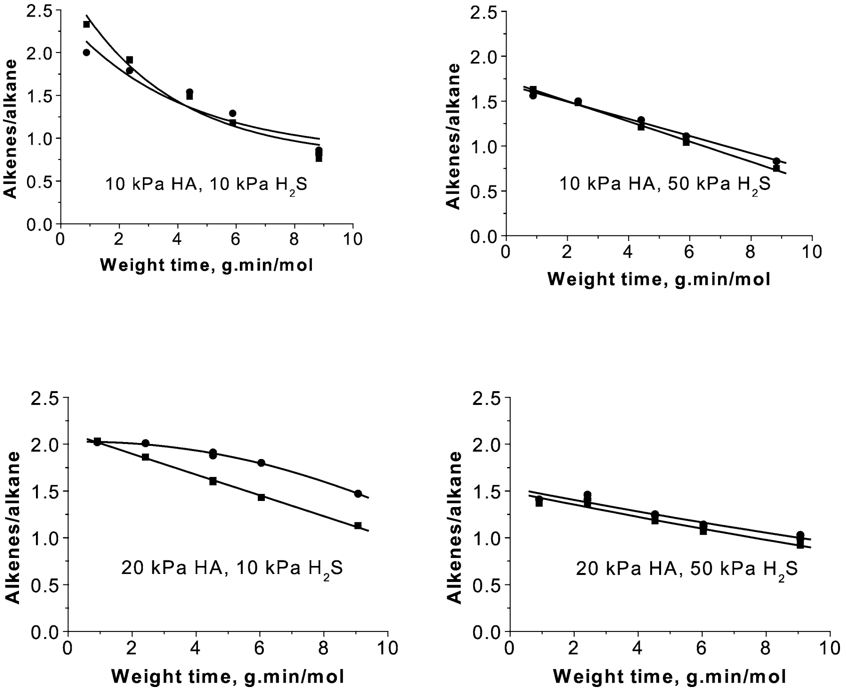


Fig. 11. Pentenes/pentane (■) and hexenes/hexane (●) ratios in the simultaneous HDS of 5 kPa pentanethiol and HDN of 10 and 20 kPa hexylamine (HA) at 340 °C and 3 MPa, and 10 and 50 kPa H_2S.

time. The conversion of dihexylamine hardly changed when the total pressure was increased from 3 to 5 MPa (not shown). Fig. 13 shows the product selectivities in the HDN of 5 kPa dihexylamine at 300 °C, 3 MPa, and 50 kPa H_2S. It is apparent from the selectivities at low weight time that hexylamine, hexanethiol, and trihexylamine behave like primary products and that hexene probably behaves like a secondary product. The hexane selectivity decreased with decreasing weight time, but it is not clear whether it extrapolates to zero. Therefore we cannot say whether hexane is a secondary or a primary as well as secondary product. The selectivities did not change significantly when the total pressure was increased from 3 to 5 MPa. The main difference was observed at low weight time, where the hexanethiol selectivity was lower and the hexane selectivity higher at 5 MPa. The selectivity patterns at short weight time were the same at both pressures, as were the conclusions about primary and secondary products.

When the dihexylamine partial pressure was increased from 5 to 20 kPa, while the other reaction conditions remained constant at 300 °C, 3 MPa, and 50 kPa H_2S, the conversion decreased substantially (Fig. 12). At the same time, the THA selectivity increased strongly, the thiol selectivity remained the same, but the hexylamine selectivity decreased at shorter weight time (cf. Figs. 13 and 14A). Trihexylamine, hexanethiol, and hexylamine are primary products.

While the conversion of dihexylamine decreased only slightly when increasing the H_2S pressure from 10 to 50 kPa (not shown), it influenced the product distribution substantially. With increasing partial pressure of H_2S, the hexanethiol selectivity increased strongly, the trihexylamine selectivity decreased sharply, the hexane and hexenes selectivities decreased, and the hexylamine selectivity remained the same (Fig. 13). The much higher rate of trihexylamine formation shows that disproportionation is favored by a low partial pressure of H_2S. At the high pressure of 20 kPa dihexylamine and low pressure of 10 kPa H_2S, the trihexylamine selectivity even reached 61% at short contact time, while the hexylamine selectivity was 26% and the sum of the thiol, hexene, and hexane selectivities was about 15% (Fig. 14B). Under these conditions, dihexylamine reacts predominantly by disproportionation. Extrapolation to zero weight time gave a hexylamine selectivity of 25%; thus, hexylamine is a primary product.

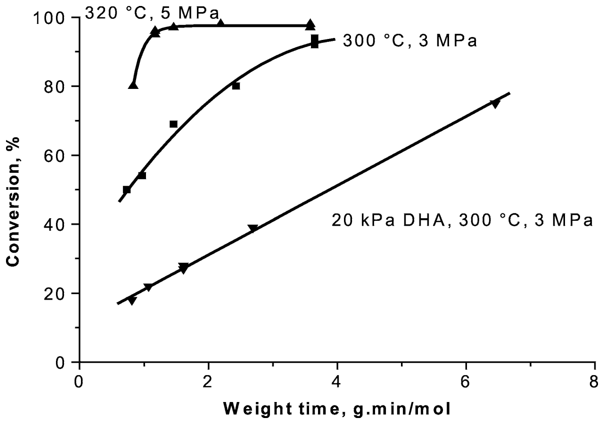


Fig. 12. Conversion of 5 or 20 kPa dihexylamine (DHA) at 300 or 320 °C, 3 or 5 MPa, and 50 kPa H_2S. ▲, 5 kPa DHA at 320 °C and 5 MPa; ■, 5 kPa DHA at 300 °C and 3 MPa; ▼, 20 kPa DHA at 300 °C and 3 MPa.

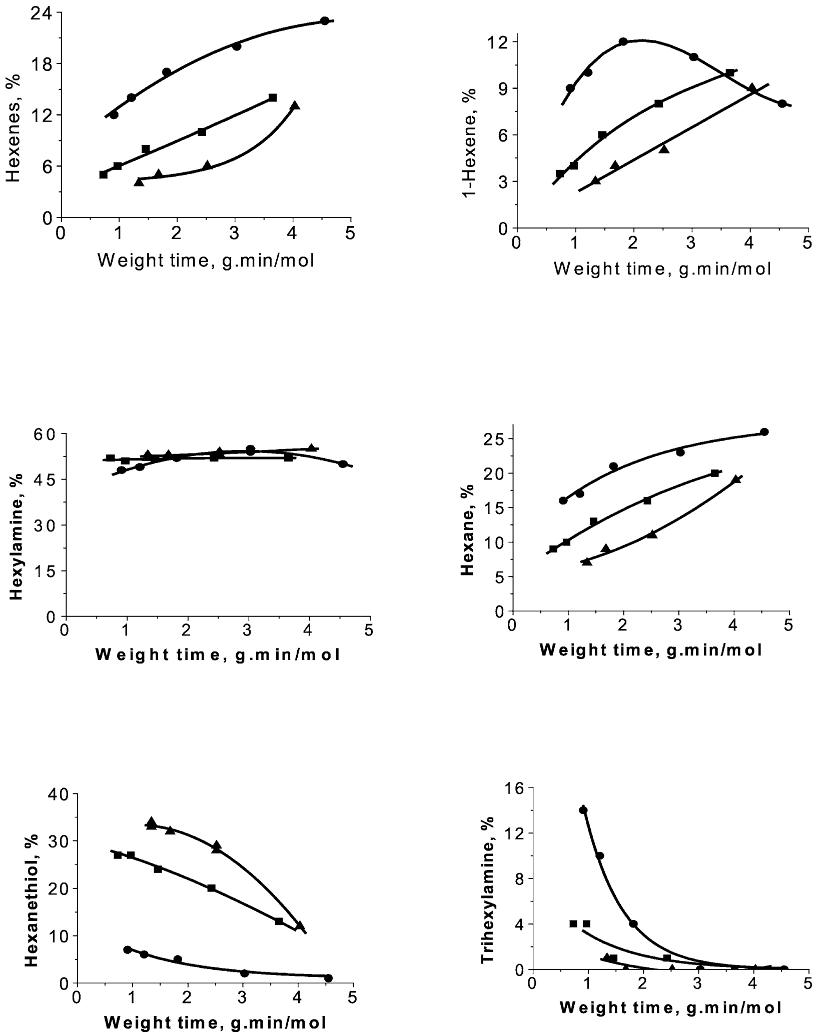


Fig. 13. Product selectivities in the HDN of 5 kPa dihexylamine at 300 °C, 3 MPa, and 10 kPa H_2S (●), 50 kPa H_2S (■), and 100 kPa H_2S (▲).

3.4. HDN of trihexylamine

The HDN conversion of trihexylamine at 300 °C and 5 MPa was very high; already at short weight time (0.9 $\mathrm{g\,min\,mol^{-1}}$) it reached 82% (not shown). The main products at $\tau = 0.9$ $\mathrm{g\,min\,mol^{-1}}$ were dihexylamine (43%), hexane (26%), and hexylamine (16%), while the 1-hexanethiol selectivity was 7% (Fig. 15). At 320 °C, the conversion of trihexylamine was even 92% at $\tau = 0.9$ $\mathrm{g\,min\,mol^{-1}}$, and at this temperature dihexylamine (28%), hexane (35%), and hexylamine (23%) were the main products. The time dependency of the products shows that dihexylamine and 1-hexanethiol are primary products, and that hexane, hexylamine, 2-hexene, and 3-hexene are secondary products, while 1-hexene behaves like a primary product (not shown).

The conversion of 5 kPa trihexylamine at $\tau = 0.9$ $\mathrm{g\,min\,mol^{-1}}$ and in the presence of 50 kPa H_2S decreased to 70% when the total pressure was decreased from 5 to 3 MPa (Fig. 16). Increasing the partial pressure of trihexylamine from 5 to 10 kPa at 3 MPa decreased the conversion even further to 50% (Fig. 16). Lowering the pressure from 5 to 3 MPa increased the selectivities of the primary products hexanethiol and dihexylamine and decreased those of the secondary products hexylamine and hexane (cf. Figs. 15 and 17). Fig. 17 shows the product distributions in the HDN of 5 kPa trihexylamine at 300 °C, 3 MPa, and 50 kPa H_2S. At short contact time, the main products were dihexylamine (63%) and 1-hexanethiol (20%), both being primary products. The initial selectivity of 1-hexene was less than 3%. Under these conditions, hexane and 1-hexene are clearly secondary products. At high weight time, the dihexylamine selectivity decreased substantially to less than 5%. The hexanethiol selectivity also decreased; only the hexylamine and hexane selectivities increased to 32 and 44%, respectively. The product selectivities at 5 and 10 kPa trihexylamine were the same at short contact time but changed less fast with weight time at 10 kPa than at 5 kPa trihexylamine (Fig. 17).

Whereas the conversion of hexylamine decreased slightly and that of dihexylamine decreased even less when the H_2S pressure was increased from 10 to 50 kPa, the conversion of trihexylamine increased (Fig. 16). At short contact time, the

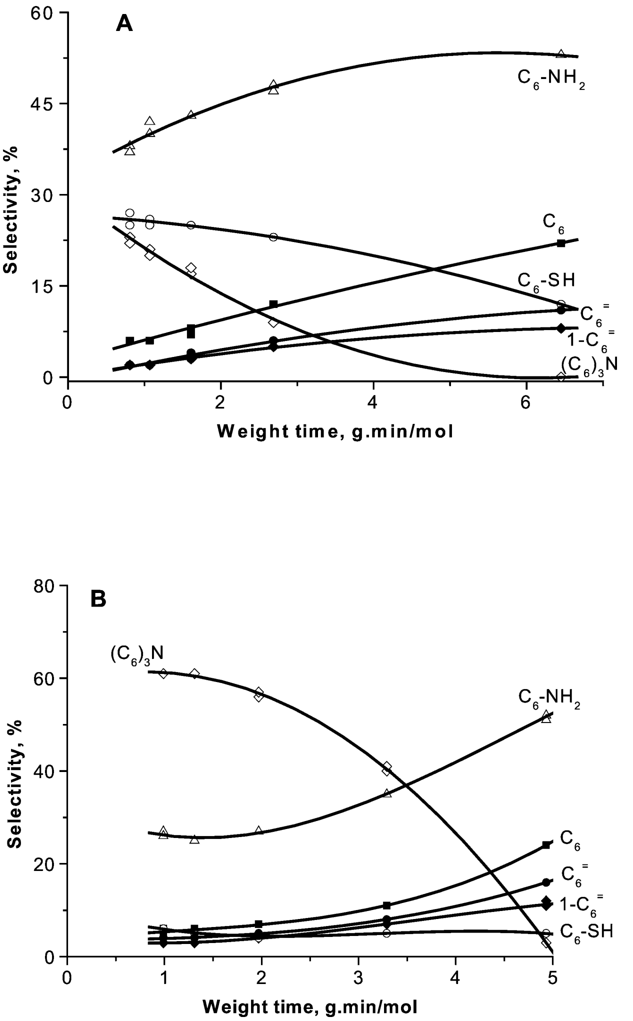


Fig. 14. Product selectivities in the HDN of 20 kPa dihexylamine at 300 °C, 3 MPa, and (A) 50 and (B) 10 kPa H_2S. △, hexylamine; ■, hexane; ●, hexenes; ○, hexanethiol; ◆, 1-hexene; ◇, trihexylamine.

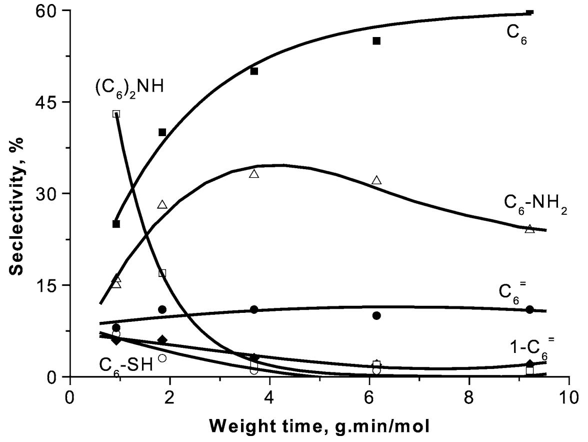


Fig. 15. Product selectivities in the HDN of 5 kPa trihexylamine at 300 °C, 5 MPa, and 50 kPa H_2S. □, dihexylamine; ■, hexane; △, hexylamine; ●, hexene; ◆, 1-hexene; ○, hexanethiol.

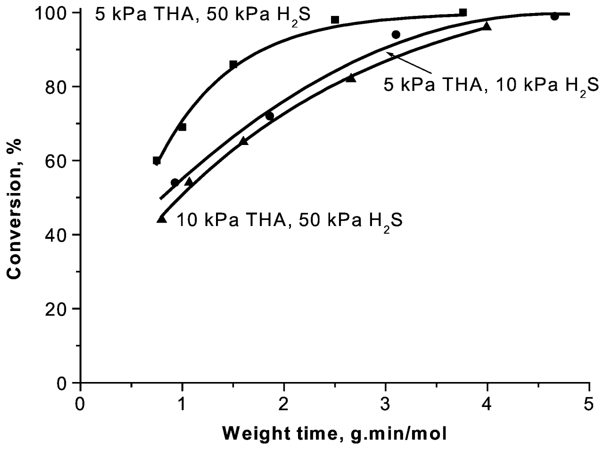


Fig. 16. Conversion in the HDN of 5 or 10 kPa trihexylamine (THA) at 300 °C and 3 MPa, in the presence of 10 or 50 kPa H_2S. ■, 5 kPa THA, 10 kPa H_2S; ●, 5 kPa THA, 50 kPa H_2S; ▲, 10 kPa THA, 50 kPa H_2S.

selectivities of dihexylamine and hexylamine were the same at both H_2S pressures, but the hexanethiol selectivity was much higher and the selectivities of hexane and 1-hexene lower at 50 kPa H_2S pressure (Fig. 17).

4. Discussion

To determine which mechanism is responsible for the HDN reaction of an n-alkylamine one can measure the product selectivities as a function of weight time (τ) and determine whether these extrapolate to a nonzero or zero value at $\tau = 0$. If a product such as 1-hexene has a zero selectivity at zero weight time, then it cannot be a primary product and elimination cannot play a role. If its selectivity is nonzero at $\tau = 0$, then 1-hexene might be a primary product, and elimination might be important. A zero selectivity at zero weight time does not automatically mean that a product is a secondary product, however, nor does a nonzero initial selectivity automatically mean that a product is primary. For instance, hexylamine may react slowly by substitution to hexanethiol, which then reacts fast to hexane and 1-hexene. The selectivities of hexane and 1-hexene may then extrapolate to a nonzero initial selectivity and these molecules may then appear to be primary products, although they are secondary. At the same time, the fast consecutive reaction of the real primary product hexanethiol will decrease its initial selectivity and the contribution of the substitution mechanism will be underestimated. With such potential pitfalls in mind, we will analyze the initial selectivities observed in the HDN of the hexylamines and try to determine the responsible mechanism(s). Since elimination is generally considered to be the main HDN mechanism [1,6,13,18], we will pay particular attention to the initial selectivity of hexene. Because isomerization of 1-hexene to 2- and 3-hexene is fast, we will use the initial selectivity of the sum of all hexenes, rather than that of 1-hexene, as a measure of the contribution of elimination.

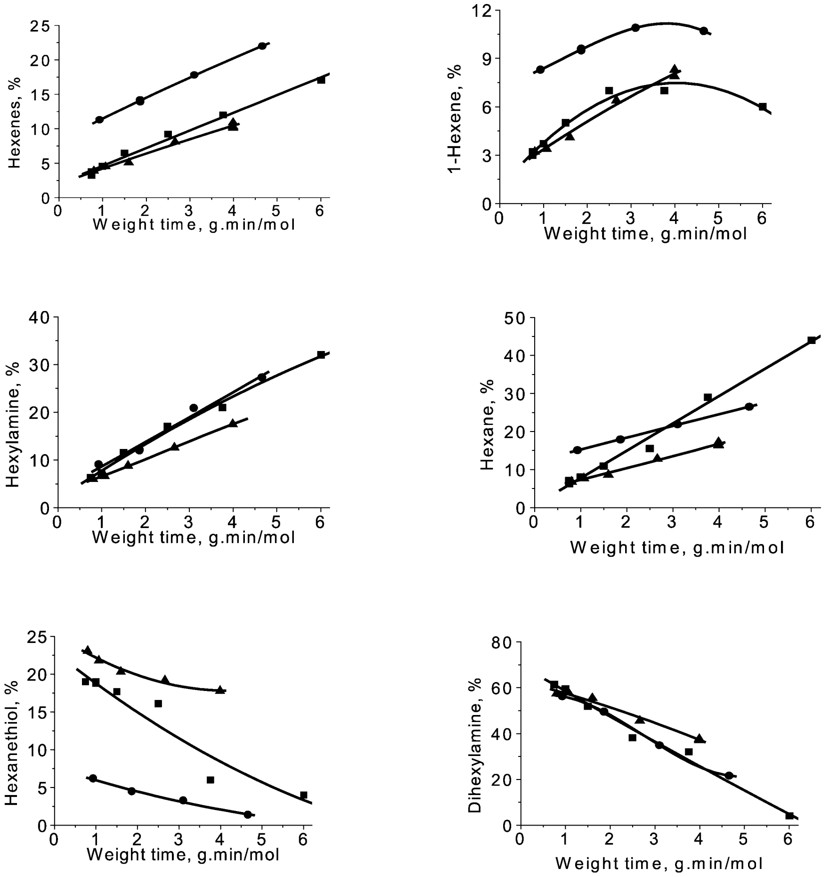


Fig. 17. Product selectivities in the HDN of 5 or 10 kPa trihexylamine (THA) at 300 °C, 3 MPa, and 10 and 50 kPa H_2S. ■, 5 kPa THA, 10 kPa H_2S; ●, 5 kPa THA, 50 kPa H_2S; ▲, 10 kPa THA, 50 kPa H_2S.

4.1. Hexylamine

Three reactions are possible in the HDN of n-hexylamine: elimination to 1-hexene, substitution to hexanethiol, and disproportionation to dihexylamine:

$$C_6H_{13}NH_2 \rightarrow C_6H_{12} + NH_3, \quad (1)$$

$$C_6H_{13}NH_2 + H_2S \rightarrow C_6H_{13}SH + NH_3, \quad (2)$$

$$2C_6H_{13}NH_2 \rightarrow (C_6H_{13})_2NH + NH_3. \quad (3)$$

At 300 °C, the hexanethiol selectivity increased and the disproportionation selectivity to dihexylamine decreased with increasing H_2S pressure (Fig. 9), because the higher H_2S pressure favors the substitution of the NH_2 group of hexylamine by H_2S over the substitution by another hexylamine molecule. The hexene selectivity was lower at high H_2S pressure and decreased strongly with decreasing weight time for all H_2S pressures. Unfortunately, measurements below $\tau = 0.8\ \mathrm{g\,min\,mol^{-1}}$ were not possible because the gas flow rate could not be increased further and using less than 50 mg catalyst led to channeling and to a decreased conversion and thus lower accuracy of the measurement. Therefore, the values to which the hexene selectivities extrapolate at $\tau = 0$ could not be determined with high precision. Nevertheless, the steep decrease of the hexene selectivity toward $\tau = 0$ indicates that the hexene selectivity is in any case smaller than 5% at 50 and 100 kPa H_2S and smaller than 20% at 10 kPa H_2S (Fig. 9).

$$C_6H_{13}SH \rightarrow C_6H_{12} + H_2S. \quad (4)$$

Under our conditions, the equilibrium of the decomposition of hexanethiol [reaction (4)] lies to the right [25]. This means that the hexene formed in the HDN of hexylamine will hardly react with H_2S. Also a disappearance of hexene by hydrogenation plays a minor role, as the hydrogenation of 1-pentene showed. It was strongly inhibited by hexylamine and the yield of pentane was only 5% at $\tau = 0.8\ \mathrm{g\,min\,mol^{-1}}$. This means that the observed hexene selectivities in the HDN of hexylamine are truly representative for the discussed HDN mechanisms.

The values of 5% for the hexene selectivity at 50 and 100 kPa H_2S and of 20% at 10 kPa H_2S at short weight time demonstrate that elimination is not the major mechanism in the HDN of hexylamine. These values are even upper limits to the contribution of elimination to the HDN of hexylamine [Eq. (1)]. The reason is that 1-hexene cannot only be formed by direct elimination of hexylamine [Eq. (1)], but also by substitution of hexylamine followed by elimination of the resulting thiol to 1-hexene [Eqs. (2) and (4)]. The pentenes/pentane ratio from the HDS of pentanethiol and the hexenes/hexane ratio from the HDN of hexylamine, measured simultaneously in the same reaction mixture, are about the same (Fig. 4). This similarity of the alkene/alkane branching ratio shows that substitution is the predominant route for nitrogen removal from hexylamine and that the contribution of elimination is even less than 5% at 50–100 kPa H_2S and 20% at 10 kPa H_2S. This also explains why, in the HDN of hexylamine, the selectivity of hexene is higher at low H_2S pressure. Namely, the HDS of pentanethiol demonstrated that the pentanethiol conversion increased strongly with decreasing H_2S pressure (Fig. 2).

At 340 °C, hexene and hexane behaved as primary products (Fig. 10), but the hexenes/hexane ratio was very similar to the pentenes/pentane ratio measured in the simultaneous HDS of pentanethiol (Fig. 11). Both ratios were not only very similar but also reacted in the same way on changes in the H_2S and hexylamine partial pressures. This shows that also at 340 °C the main reaction of hexylamine is substitution by H_2S to form hexanethiol. At the higher temperature of 340 °C, the subsequent decomposition of hexanethiol becomes so fast that hexene and hexane appear to be primary products.

Hexane is a product in the HDN of all three hexylamines. It is supposed to be formed from hexanethiol,

$$C_6H_{13}SH + H_2 \rightarrow C_6H_{14} + H_2S. \qquad (5)$$

The mechanism of this reaction is unclear. It might be a real hydrogenolysis reaction as on a metal surface or as reported in the homogeneous reaction of aliphatic and aromatic thiols with the $Cp'_2Mo_2Co_2S_3(CO)_4$ cluster (Cp' stands for pentamethylcyclopentadienyl) [26]. Another possibility would be that the alkene formed by elimination from the alkanethiol [Eq. (4)] is hydrogenated before desorbing from the catalyst surface. Both mechanisms explain the observed lower hexene/hexane ratio at higher H_2 pressure (total pressure), lower temperature, and higher H_2S and hexylamine pressure. The increase of the hexane selectivity with increasing τ (Figs. 9 and 10) is due to increased hexanethiol decomposition [Eq. (5)] as well as hydrogenation of hexene. These two factors oppose each other in the production of hexene, and explain the maximum in the hexenes/hexane ratio at 300 °C (Fig. 4).

4.2. Dihexylamine

Like hexylamine, dihexylamine can react in three ways: by elimination to hexylamine and 1-hexene, by substitution to hexylamine and 1-hexanethiol, and by disproportionation to hexylamine and trihexylamine:

$$(C_6H_{13})_2NH \rightarrow C_6H_{12} + C_6H_{13}NH_2, \qquad (6)$$

$$(C_6H_{13})_2NH + H_2S \rightarrow C_6H_{13}SH + C_6H_{13}NH_2, \qquad (7)$$

$$2(C_6H_{13})_2NH \rightarrow (C_6H_{13})_3N + C_6H_{13}NH_2. \qquad (8)$$

Furthermore, because of the much higher reactivity of trihexylamine than of hexylamine and dihexylamine, trihexylamine can react back to dihexylamine and 1-hexene or 1-hexanethiol:

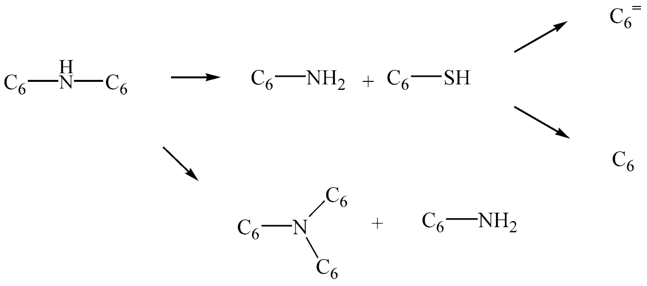
$$(C_6H_{13})_3N \rightarrow C_6H_{12} + (C_6H_{13})_2NH, \qquad (9)$$

$$(C_6H_{13})_3N + H_2S \rightarrow C_6H_{13}SH + (C_6H_{13})_2NH. \qquad (10)$$

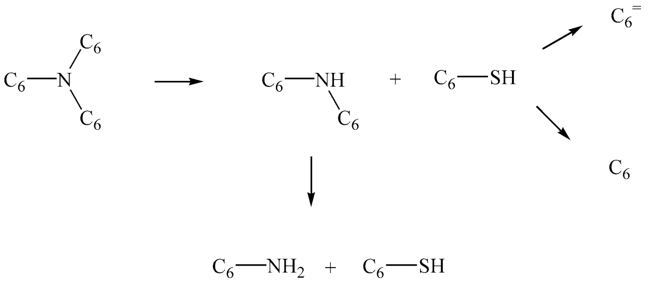
At 320 °C and 5 MPa we observed only a trace amount of trihexylamine, which means that, under these conditions, either disproportionation hardly took place or that trihexylamine reacted away faster than it was formed. The product selectivity suggests that 1-hexene is a primary product, which would mean that 1-hexene is formed by elimination of dihexylamine. At 300 °C and 5 MPa (not shown) and 3 MPa, however, 1-hexene behaves more like a secondary product. The maximum hexene selectivities at $\tau = 0$ are 3% at 50 and 100 kPa H_2S and 8% at 10 kPa H_2S (Fig. 13). Because of the stoichiometry of Eq. (6) this means that the maximum relative contributions of elimination to the HDN of dihexylamine are 6 and 16%, respectively. As in the case of hexylamine, these percentages overestimate the contribution of elimination substantially, because the hexene/hexane ratio in the HDN of dihexylamine was not much different from that of the HDS of hexanethiol. This means that reaction (7) followed by reaction (4) is the main pathway for the formation of hexene.

Trihexylamine behaved as a primary product, meaning that dihexylamine quickly forms trihexylamine by disproportionation. At 320 °C less trihexylamine was observed as at 300 °C, probably because trihexylamine quickly reacts to hexanethiol and dihexylamine by substitution. This would also explain why the conversion of dihexylamine and trihexylamine never reached 100%, neither at 320 °C nor at high weight time. This can be explained by reformation of these molecules by a disproportionation reaction of two molecules of hexylamine to dihexylamine, or two molecules of dihexylamine to trihexylamine, or of one molecule of dihexylamine and one molecule of hexylamine to trihexylamine.

The trihexylamine selectivity in the HDN of dihexylamine increased with increasing partial pressure of dihexylamine, while the hexanethiol selectivity stayed almost the same, and the hexylamine selectivity became much lower (cf. Figs. 13 and 14). At first glance this seems strange; if the thiol selectivity stays the same, one would expect that the hexylamine selectivity is also the same [Eq. (7)]. We can only explain the increased trihexylamine selectivity and decreased hexylamine selectivity by assuming that the hexylamine obtained from the decomposition of dihexylamine reacts with dihexylamine to form trihexylamine. Although the trihexylamine selectivity increased and trihexylamine has a much higher reactivity, fewer active centers are available for trihexylamine to decompose at high partial pressure of dihexylamine. This also explains why the conversion of dihexylamine decreased at higher partial pressure of dihexylamine. We therefore suggest that at 300 °C, 3 MPa, and 50 kPa H_2S dihexylamine reacts by substitution by H_2S to hexylamine and 1-hexanethiol and by disproportionation to



Scheme 1. HDN network of dihexylamine.



Scheme 2. HDN network of trihexylamine.

trihexylamine and hexylamine (Scheme 1). 1-Hexene and hexane are subsequently formed from 1-hexanethiol. An analysis of the mass balance supports the conclusion that mainly substitution and disproportionation and hardly any elimination occurred in the HDN of dihexylamine.

Cattenot et al. studied the HDN of n-pentylamine over unsupported MoS_2 at 275 °C and atmospheric pressure [15]. They observed dipentylamine and pentanethiol as primary products and pentenes as secondary products. From the initially larger amount of dipentylamine, they concluded that the majority of the pentenes formed from dipentylamine and only a fraction from pentanethiol. Under our conditions (300–320 °C, 3 MPa, $NiMo/Al_2O_3$), however, dihexylamine mainly reacted by substitution with another amine molecule and with H_2S, and hexanethiol was the main source of hexene.

4.3. *Trihexylamine*

Trihexylamine can only react by elimination to dihexylamine and 1-hexene and by nucleophilic substitution by H_2S to dihexylamine and 1-hexanethiol [Eqs. (9) and (10)]. As shown in Section 3.2, dihexylamine will react further to hexylamine, hexanethiol, hexane, and 1-hexene. At higher temperatures, the scission of the C–N bond of dihexylamine becomes faster, and thus the selectivity of dihexylamine in the HDN of the trihexylamine is much lower at 320 than at 300 °C and substantially more hexylamine and hexane are formed at 320 °C. At lower total pressure, the C–N cleavage rate of trihexylamine is lower and the selectivity of dihexylamine increases. High selectivities to dihexylamine and hexanethiol and a low selectivity to hexenes were obtained at short weight time (Fig. 17). The dihexylamine selectivity extrapolates to 67% at $\tau = 0$ (Fig. 17), as is expected for both elimination and nucleophilic substitution [Eqs. (9) and (10)]. Note that the selectivity is defined so as to preserve the carbon mass balance, which is the hexyl balance in this case. The hexene selectivity extrapolates to 2% at $\tau = 0$ at 50 kPa H_2S and to 8% at 10 kPa H_2S (Fig. 17). With a maximum selectivity of 33.3% for hexene [Eq. (9)], this means that the relative contribution of elimination to the HDN of trihexylamine is 6 and 24%, respectively. As in the case of n-hexylamine and dihexylamine, these percentages overestimate the contribution of elimination substantially, because the hexene/hexane ratio in the HDN of trihexylamine was not much different from that of the HDS of hexanethiol. This means that reaction (10) followed by reaction (4) is the main pathway for the formation of hexene. The reason that the hexene selectivity was higher at the lower H_2S pressure of 10 kPa is due to the higher reactivity of alkanethiol to alkene under these conditions. Assuming that the reactivity of hexanethiol is similar to that of pentanethiol, we expect less hexanethiol and more 1-hexene in the HDN of trihexylamine at lower H_2S pressure. This means that elimination of 1-hexene from trihexylamine to form dihexylamine plays a minor role at all H_2S pressures. The qualitative conclusion about the dominant role of nucleophilic substitution was substantiated by the mass balance of the amounts of the products from the HDN of trihexylamine (Scheme 2).

Substitution explains the higher conversion of trihexylamine at higher H_2S pressure and the higher selectivity to hexanethiol and lower selectivity to hexane and hexene. At a higher H_2S pressure there will be more SH groups at the surface and trihexylamine will react faster with SH to dihexylamine and hexanethiol. At the same time, the hexanethiol decomposition will be more inhibited because there are fewer vacancies on which hexanethiol can adsorb; this causes an increase in the hexanethiol selectivity and a decrease in the hexane plus hexene selectivity. The increased number of SH groups at the catalyst surface not only increases the formation of dihexylamine from trihexylamine, but also the further (substitution) reaction of dihexylamine to hexylamine and hexanethiol. As a consequence, the H_2S pressure does not have a significant influence on the dihexylamine selectivity at short weight time.

4.4. *General discussion*

The conversion of the hexylamines increased with increasing basicity of the amine in the gas phase in the order hexylamine < dihexylamine < trihexylamine. The conversion of all three hexylamines increased with increasing total pressure (higher H_2 pressure). Since the primary reactions of the hexylamines (be it elimination, nucleophilic substitution, or disproportionation) are chemically independent of hydrogen, the positive influence of hydrogen must be due to a secondary effect. Most probably it is caused by the number of vacancies on the catalyst surface, which is generated by the H_2S/H_2 ratio and, at constant H_2S pressure, increases with the H_2 pressure. On the other hand, when increasing the H_2S pressure at constant total pressure, the conversion of the hexylamines did not show a strong decrease. While it decreased slightly for hexylamine and dihexylamine, it even increased with the H_2S pressure for trihexylamine. This may be due to two competing factors. On the one hand, H_2S decreases the number of vacancies on the catalyst surface and, thus, the reaction rate. On the other hand, more sulfur on the catalyst surface increases the nucleophilic substitution by H_2S, which was demonstrated to be the main HDN reaction. These two factors are almost equal for hexylamine and dihexylamine, but the second factor is more important in the case of trihexylamine. This might be due to a strong adsorption of trihexylamine and even the replacement of H_2S from the catalyst surface.

An additional explanation for the increased activity of trihexylamine and slightly decreased activities of hexylamine and dihexylamine at increasing H_2S pressure could be that only the latter two molecules can undergo disproportionation. At low H_2S pressure, disproportionation determines the conversion of hexylamine and dihexylamine but not that of trihexylamine. At increasing H_2S pressure, nucleophilic substitution increases in importance for all three molecules, while the contribution of disproportionation to the conversion decreases. This would explain why the conversion of trihexylamine continuously increased with increasing H_2S pressure, while the contributions of disproportionation and nucleophilic substitution are influenced in opposite ways by H_2S.

Our results clearly demonstrate that nucleophilic substitution is the dominant HDN mechanism for unbranched alkylamines, dialkylamines, and trialkylamines. For the first two molecules the substitution can occur by an amine as well as by H_2S, while for the trialkylamine only substitution by H_2S is possible. Portefaix et al. showed that more β-H atoms led to a higher HDN conversion of piperidines [6,13]. We showed, however, that the higher conversion of 2-methylpiperidine was not due to HDN but to dehydrogenation to 2-methylpyridine [14]. In fact, 2-methylpiperidine preferentially underwent ring opening to 2-aminohexane by C–N bond cleavage of the α-carbon atom that did not carry the methyl group. Thus, the extra three β-H atoms on this methyl group did not increase the HDN conversion. To prove that this has nothing to do with the type of H atoms (on primary or secondary carbon atoms), we performed an HDN experiment with 2-ethylpiperidine. Also for this molecule, with two extra β-H atoms on a secondary carbon atom, ring opening occurred mainly on the less sterically hindered side of the piperidine ring. We take this as evidence that, also for piperidine-like molecules, HDN occurs by nucleophilic substitution rather than by elimination, as is also the case for dihexylamine, which is a secondary amine like piperidine.

A remaining question is how the nucleophilic substitution of alkylamines takes place at the catalyst surface. Hydroxyl and amine groups are very poor leaving groups in nucleophilic substitution [27,28]. Protonation of the amine group or complexing with a Lewis acid group gives a better leaving group and this might be the main role of the catalyst surface. The nucleophile that attacks the α-carbon atom can either be an alkylamine, or an SH^- or S^{2-} group at the catalyst surface. Laine suggested that a metal-assisted nucleophilic substitution might occur via a metal alkyl or alkylidene intermediate [10]. Another mechanism could be a sequence of dehydrogenation, addition, elimination, and hydrogenation reactions, which is an established method for replacing a hydroxyl or amine group. For instance, the conversion of an amine into an alcohol takes place via

$$\begin{aligned}\mathrm{R{-}CH_2{-}NH_2} &\overset{-\mathrm{H_2}}{\rightarrow} \mathrm{R{-}CH{=}NH} \overset{\mathrm{H_2O}}{\rightarrow} \mathrm{R{-}CHOH{-}NH_2}\\ &\overset{-\mathrm{NH_3}}{\rightarrow} \mathrm{R{-}CH{=}O} \overset{\mathrm{H_2}}{\rightarrow} \mathrm{R{-}CH_2{-}OH}.\end{aligned}$$

Similarly, an alkylamine can be transformed into an alkanethiol. In that case, one obtains a reaction sequence that has the same overall stoichiometry as the nucleophilic substitution reaction of an alkylamine and H_2S, giving an alkanethiol and NH_3. All four reactions in the sequence are known to take place on metals. For instance, copper is the metal of choice in the reaction sequence from alcohol to amine [29]. If such reactions take place on copper, they may also take place on metal sulfides. The dehydrogenation of amines to nitriles has been reported by Cattenot et al. in the HDN of pentylamine at low pressure (0.1 MPa) [15]. In the present work we never observed nitriles, but did observe imines in low concentration. This may be due to the higher H_2 pressure used in our work than in that of Portefaix et al. Further work must clarify which mechanism is responsible for the HDN of alkylamines. For the moment, we can only conclude that, in the HDN of linear alkylamines, elimination plays a minor role and that a reaction with the stoichiometry of nucleophilic substitution can explain all observations.

5. Conclusions

Our results show that the removal of the nitrogen atom from alkylamines occurs mainly by a nucleophilic substitution of the alkylamine to an alkanethiol, which subsequently reacts to an alkene or alkane and H_2S. This makes sense from the point of view of organic chemistry. The aliphatic C–N bond is strong and the amine group is thus a bad leaving group. Also, an SH^- group is too weak a base to remove the hydrogen atom from the β-carbon atom. As a consequence, Hofmann elimination of an alkylamine to an alkene and ammonia is an unlikely reaction. Nucleophilic substitution, on the other hand, may very well occur with an SH^- group, because it is a strong nucleophile [15,27]. Even the NHR group can act as a nucleophile. At the same time, the α-carbon atom in a n-alkylamine is easily accessible for the nucleophile. Thus, nucleophilic substitution of the NH_2 group of an amine by an SH group, leading to an alkanethiol, as well as by an NHR group (leading to disproportionation) occurred readily. The much higher reaction rates of dihexylamine and trihexylamine than the hexylamine might, on the one hand, be caused by their higher number of carbon atoms and, thus, higher adsorption constants and, on the other hand, by their higher basicities. The nucleophilic substitution is aided by protonation of the nitrogen atom by a Brønsted acid or by interaction of the nitrogen atom with a Lewis acid in order to create a better leaving group [27]. The Ni atom at the catalyst surface may act as the Lewis acid site.

The reaction sequence dehydrogenation–H_2S addition–NH_3 elimination–hydrogenation may explain the HDN of hexylamines equally well. This reaction scheme has the same overall stoichiometry as nucleophilic substitution and therefore reacts in the same way on temperature, pressure, and other parameters. Also the metal-assisted nucleophilic substitution proposed by Laine [10] explains our results.

The reason that elimination has long been held to be the dominant nitrogen-removal reaction is due to the fact that relatively large amounts of alkenes are observed in HDN at longer weight time. Our results show that, at least for *n*-alkylamines, these large amounts of alkenes are caused by the elimination reaction of alkanethiols and not by the elimination of alkylamines. It is the fast reaction of alkanethiols that obscures the true origin of the alkenes. Only when measuring at short reaction time can one identify the true origin of the alkene.

References

[1] N. Nelson, R.B. Levy, J. Catal. 58 (1979) 485.
[2] C.N. Satterfield, M. Modell, J.A. Wilkens, Ind. Eng. Chem. Proc. Des. Dev. 19 (1980) 154.
[3] R. Ramachandran, F.E. Massoth, Chem. Eng. Commun. 18 (1982) 239.
[4] R.T. Hanlon, Energy & Fuels 1 (1987) 424.
[5] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[6] J.L. Portefaix, M. Cattenot, M. Guerriche, J. Thivolle-Cazat, M. Breysse, Catal. Today 10 (1991) 473.
[7] L. Vivier, V. Dominguez, G. Perot, S. Kasztelan, J. Mol. Catal. 67 (1991) 267.
[8] U.S. Ozkan, S. Ni, L. Zhang, E. Moctezuma, Energy & Fuels 8 (1994) 249.
[9] R. Prins, Adv. Catal. 46 (2001) 399.
[10] R.M. Laine, Catal. Rev.-Sci. Eng. 25 (1983) 459.
[11] M. Zdrazil, J. Catal. 141 (1993) 316.
[12] S. Rajagopal, R. Miranda, J. Catal. 141 (1993) 318.
[13] J.L. Portefaix, M. Cattenot, M. Guerriche, M. Breysse, Catal. Lett. 9 (1991) 127.
[14] M. Egorova, Y. Zhao, P. Kulula, R. Prins, J. Catal. 206 (2002) 263.
[15] M. Cattenot, J.L. Portefaix, J. Afonso, M. Breysse, M. Lacroix, G. Perot, J. Catal. 173 (1998) 366.
[16] M. Breysse, J. Afonso, M. Lacroix, J.L. Portefaix, M. Vrinat, Bull. Soc. Chim. Belg. 100 (1991) 923.
[17] J.H. Lee, C.E. Hamrin, B.H. Davis, Appl. Catal. A 111 (1994) 11.
[18] P. Clark, X. Wang, P. Deck, S.T. Oyama, J. Catal. 210 (2002) 116.
[19] F. Rota, R. Prins, J. Catal. 202 (2001) 195.
[20] M. Fikry Ebeid, J. Pasek, Coll. Czech. Chem. Commun. 35 (1970) 2166.
[21] P. Hogen, J. Pasek, Coll. Czech. Chem. Commun. 39 (1974) 3696.
[22] R. Pille, G. Froment, Stud. Surf. Sci. Catal. 106 (1997) 403.
[23] S. Eijsbouts, C. Sudhakar, V.H.J. de Beer, R. Prins, J. Catal. 127 (1991) 605.
[24] H. Schulz, M. Schon, N.M. Rahman, Stud. Surf. Sci. Catal. 27 (1986) 201.
[25] J.G. Speight, The Desulfurization of Heavy Oils and Residua, Dekker, New York, 2000.
[26] M.D. Curtis, S.H. Druker, J. Am. Chem. Soc. 119 (1997) 1027.
[27] R. Bruckner, Advanced Organic Chemistry, Academic Press, San Diego, CA, 2002.
[28] J. Clayden, N. Greeves, S. Warren, P. Wothers, Organic Chemistry, Oxford Univ. Press, London, 2001.
[29] T. Mallat, A. Baiker, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol 5, Wiley–VCH, New York, p. 2334.