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Iminium cations as intermediates in the hydrodenitrogenation of alkylamines over sulfided NiMo/γ-Al_2O_3

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Abstract

The mechanism of the hydrodenitrogenation of the mixed dialkyl- and trialkylamines C_1–NH–C_6 and C_1–N$(C_6)_2$ was studied over sulfided NiMo/γ-Al_2O_3 at 280 °C and 3 MPa. C_1–NH–C_6 reacted by disproportionation to C_1–N$(C_6)_2$ as well as C_6–N$(C_1)_2$ and by substitution by H_2S to methylamine and hexanethiol as well as hexylamine and methanethiol. C_1–N$(C_6)_2$ reacted by substitution with H_2S to C_1–NH–C_6 and C_6–NH–C_6 and methane- and hexanethiol. The probability of breaking the C_1–N bond was only slightly smaller than of breaking the C_6–N bond in C_1–N$(C_6)_2$. In the reaction of an equimolar mixture of C_5–NH–C_5 and C_1–N$(C_6)_2$ both C_1–N$(C_5)_2$ and C_6–N$(C_5)_2$ were formed. The transfer of the methyl group in these reactions cannot be explained by imine and enamine intermediates, only iminium cation intermediates can explain all the products in the hydrodenitrogenation of monoalkyl-, dialkyl- and trialkylamines.

Keywords: Hydrodenitrogenation; HDN; Disproportionation; Substitution; Mechanism; NiMo/γ-Al_2O_3; Mixed alkylamines; Imine; Iminium ion

1. Introduction

Deep hydrodesulfurization (HDS) technology will be implemented in the coming years to reduce the sulfur level of fuel below 10 ppm, as required by environmental legislation. Nitrogen-containing compounds are harmful in deep HDS, as they inhibit the adsorption of sulfur-containing compounds [1–3] and, therefore, it is important to know how hydrotreating catalysts remove nitrogen-containing molecules.

It is generally accepted that the hydrogenation of the heterocyclic ring is the first step in the HDN of nitrogen-containing aromatic molecules [4]. The mechanism of the second step, the breaking of the aliphatic C–N bond, has been debated for two decades [5–15]. Recent work by Zhao et al. [16–18] showed that it takes place by nucleophilic substitution with H_2S rather than by elimination over sulfided Mo, CoMo, and NiMo catalysts supported on alumina. Product selectivity measurements at short weight time revealed that alkanethiols were the primary products and that the alkenes and alkanes were secondary or even tertiary products. The fast decomposition of the alkanethiols leads to high concentrations of alkenes and alkanes at relatively short contact times and these molecules had therefore in the past been taken for primary products. Moreover, reactions of monoalkyl-, dialkyl- and trialkylamines revealed that the substitution of the amine group results either in an alkanethiol or in a dialkylamine, depending on the concentration of H_2S and alkylamine [16]. Alkanethiol is the main product at higher H_2S partial pressure and dialkylamine at lower partial pressure of H_2S. Monoalkyl- and dialkylamines react by substitution as well as disproportionation to thiols and dialkyl- and trialkylamines, while trialkylamines react only by substitution by H_2S leading to a dialkylamine and alkanethiol. The denitrogenated products, alkenes and alkane, are formed as secondary products from the alkanethiol.

HDN studies on the chiral 2-(*S*)-butylamine demonstrated that the substitution of an amine group to an alkanethiol or a dialkylamine is not a classic organic substitution involving Walden inversion but a multi-step process involving an imine [19]. This multi-step mechanism involves first the dehydrogenation of the amine to an imine. Thereafter, addition of H_2S or another amine molecule to the imine takes place and, after ammonia or amine elimination and hydrogenation, a thiol or a dialkylamine is formed. Imine formation is not possible in trialkylamines. The formation of an imine from an amine requires a hydrogen atom on both N and α-C atoms as in mono- and dialkylamines. However, if the alkyl group of a

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trialkylamine contains a β-hydrogen atom, an enamine can be formed and this would allow reaction with H_2S to a dialkylamine and alkanethiol as well. This would mean that longer alkyl groups, but not methyl groups, could be removed from trialkylamines. To investigate whether imines and enamines play a role as intermediates in the removal of nitrogen atoms from alkylamines, we studied the HDN reactions of the dialkylamine C_1–NH–C_6 and the trialkylamine C_1–N(C_6)$_2$ which both possess a C_1 as well as a C_6 group attached to the N atom.

2. Experimental

The NiMo/γ-Al_2O_3 catalyst used in the reactions of the alkylamines contained 8 wt% Mo and 3 wt% Ni and was prepared by a two-step pore-volume impregnation of γ-Al_2O_3; the details of the catalyst preparation have been reported before [16]. The catalyst was sulfided in situ in a continuous-flow fixed bed reactor 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 MPa and the liquid reactant was fed to the reactor by means of a high-pressure syringe pump (ISCO 500D). The feed consisted of 5 kPa amine, 10 kPa H_2S, 185 kPa octane (solvent), 20 kPa heptane (internal standard for GC analysis), and 2.78 MPa H_2. The experiments were carried out at 280 °C. To study the influence of weight time (the ratio between the catalyst weight and the total molar flow fed to the reactor) on product distribution, the weight time was changed by varying the flow rates of the liquid and the gaseous reactants with respect to the amine, while keeping their ratio constant. The reaction products were analyzed by off-line gas chromatography with a flame ionization detector (FID) and a pulsed flame photometric detector (PFPD). Mass spectrometry was used to identify the reaction products [16]. All products and reactants could be analyzed and quantified, with the exception of the C_1 products C_1–SH and C_1–NH_2. They could be detected but not quantified because their volatility was too high compared with the other products and a combined on-line and off-line analysis did not result in a good mass balance. After each series of HDN experiments, the original feed was re-entered to verify whether the activity of the catalyst had remained constant. Before the initiation of a new experiment, the whole reactor was cleaned by purging with only the solvent (octane) and a H_2S/H_2 gas mixture for 12 h at the reaction temperature. The samples were tested for the absence of any impurity in the reactor by GC-MS.

Similar to Zhao et al. [16–18], we will use the selectivities of the products in the HDN reaction of the alkylamines as a function of weight time to determine the reaction mechanism. Selectivities make it easy to distinguish between primary and higher order products, because primary products have a non-zero selectivity at $\tau = 0$, while secondary or tertiary products have a zero selectivity. Also, the selectivity of primary products decreases with τ while that of secondary and tertiary products increases with τ. The selectivity S_i of a product i was defined as S_i (%) = $100N_iP_i(\Sigma N_iP_i)$, with P_i being the number of molecules converted to product i and N_i the number of carbon atoms in product molecule i. In a bimolecular reaction involving pentyl- and hexylamines, selectivities based on the C_5-group as well as the C_6-group were calculated. With this selectivity definition, the mass balance of the C atoms is preserved. For instance, in the reaction

$$2C_5{-}NH{-}C_6 \rightarrow C_5{-}N(C_6)_2 + C_5{-}NH_2$$

the C_5 selectivity of C_5–N(C_6)$_2$ is 50%, while the C_6 selectivity is 100%. In a reaction of dialkylamine with a trialkylamine, for example

$$C_5{-}NH{-}C_5 + C_1{-}N(C_6)_2 \rightarrow C_6{-}N(C_5)_2 + C_1{-}NH{-}C_6$$

the C_6 selectivity of C_6–N(C_5)$_2$ is 50% and that of C_1–NH–C_6 is 50%. The C_5 selectivity of C_6–N(C_5)$_2$ is 100% while that of C_1–NH–C_6 is 0%. The conversion was determined from the amount of unreacted reactant.

3. Results

3.1. HDN of C_6–NH–C_6

Dihexylamine (5 kPa) reacted fast over sulfided NiMo/γ-Al_2O_3; at 280 °C and 3 MPa, in the presence of 10 kPa H_2S, the conversion was 87% at 9.5 g min/mol (Fig. 1). The main products of the reaction were trihexylamine, hexylamine, hexanethiol, hexane and hexenes. The selectivities of trihexylamine, hexylamine and hexanethiol were non-zero at $\tau = 0$ g min/mol, meaning that these molecules are primary products (Fig. 1). Trihexylamine and hexylamine can form as primary products by disproportionation of dihexylamine

$$2C_6{-}NH{-}C_6 \rightarrow (C_6)_3N + C_6{-}NH_2 \quad (1)$$

The fast decrease of the trihexylamine selectivity with τ must be due to the reaction

$$H_2S + (C_6)_3N \rightarrow C_6{-}NH{-}C_6 + C_6{-}SH \quad (2)$$

which is known to be fast over sulfided NiMo/γ-Al_2O_3 [16]. The primary character of hexanethiol is due to the reaction

$$H_2S + C_6{-}NH{-}C_6 \rightarrow C_6{-}SH + C_6{-}NH_2 \quad (3)$$

Eqs. (1) and (3) both produce hexylamine as a primary product. The increase in hexylamine selectivity with increasing weight time (Fig. 1) may indicate that Eq. (1) dominates at low τ (selectivity 25%) and Eq. (3) at high τ (selectivity 50%).

All three hexenes and hexane behaved as secondary products, as their selectivities extrapolated to zero at $\tau = 0$ g min/mol and increased with increasing weight time. Hexene can form from hexanethiol by the elimination reaction

$$C_6{-}SH \rightarrow C_6{}^{=} + H_2S \quad (4)$$

The selectivity of 1-hexene is initially higher than that of 2-hexene and 3-hexene and goes through a maximum (Fig. 1), indicating that 1-hexene is the product of hexanethiol and that 2-hexene and 3-hexene are formed by subsequent isomerization from 1-hexene. Hexane can form as a secondary product by the hydrogenolysis of hexanethiol

$$C_6{-}SH + H_2 \rightarrow C_6 + H_2S \quad (5)$$

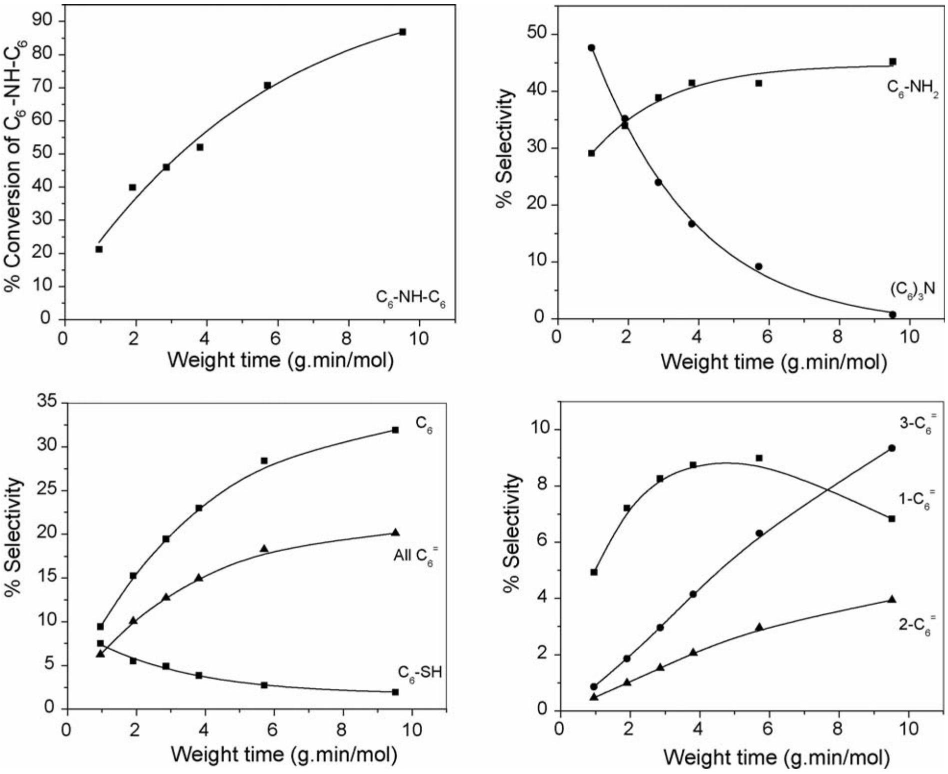


Fig. 1. Conversion and product selectivities (based on the C_6 mass balance) in the HDN of C_6–NH–C_6.

and as a tertiary product by the hydrogenation of hexenes

$$C_6{}^{=} + H_2 \rightarrow C_6 \qquad (6)$$

Thus, dihexylamine reacts primarily by disproportionation to trihexylamine and hexylamine and by substitution by H_2S to hexylamine and hexanethiol. The denitrogenated products are formed as secondary products by elimination and hydrogenolysis of the hexanethiol at higher weight times. These results, obtained at 280 °C, are in good agreement with previous results of Zhao et al. obtained at 300 °C [16]. The conversion of C_6–NH–C_6 at 300 °C [16] was two to three times higher than at 280 °C (Fig. 1). The selectivity of trihexylamine was much higher at 280 than at 300 °C due to the lower rate of the reaction of trihexylamine to hexanethiol and dihexylamine (Eq. (2)). The selectivities of hexene and hexane were lower at 280 °C due to the lower rates of C–N and C–S bond cleavage.

3.2. HDN of C_1–NH–C_6

C_1–NH–C_6 reacted slower than C_6–NH–C_6, its conversion was 58% at $\tau = 9.5$ g min/mol (Fig. 2). This is probably due to the lower adsorption constant of C_1–NH–C_6, because of a lower molecular weight. The main products were C_1–N(C_6)$_2$, C_6–N(C_1)$_2$, C_6–NH–C_6, hexylamine, hexanethiol, hexane, hexenes, and C_1-products (C_1–NH_2 and C_1–SH). The selectivities of C_1–N(C_6)$_2$, C_6–N(C_1)$_2$, hexylamine, and hexanethiol were non-zero at $\tau = 0$ g min/mol, which reveals that these molecules are primary products. The mixed trialkylamines C_1–N(C_6)$_2$ and C_6–N(C_1)$_2$ can form as primary products by disproportionation of the reactant

$$2C_1{-}NH{-}C_6 \rightarrow C_1{-}N(C_6)_2 + C_1{-}NH_2 \qquad (7)$$

$$2C_1{-}NH{-}C_6 \rightarrow C_6{-}N(C_1)_2 + C_6{-}NH_2 \qquad (8)$$

These reactions are the equivalents of the disproportionation reaction of an alkylamine with one type of alkyl group (Eq. (1)). From Fig. 2, we estimate initial selectivities of 50% for C_1–N(C_6)$_2$ and 16% for C_6–N(C_1)$_2$. Because of the mass-based definition of selectivity, this means that it is 1.5 times easier for the C_1–NH–C_6 molecule to react with the C_6 group of another C_1–NH–C_6 molecule (Eq. (7)) than with the C_1 group (Eq. (8)). As will be shown in Section 3.4, the trialkylamines C_1–N(C_6)$_2$ and C_6–N(C_1)$_2$ can react rapidly with H_2S to a dialkylamine and an alkanethiol, similar to Reaction (2). This explains the decrease in the selectivities of the trialkylamines with τ (Fig. 2). Hexylamine and hexanethiol are formed as primary products by substitution with H_2S

$$C_1{-}NH{-}C_6 + H_2S \rightarrow C_6{-}NH_2 + C_1{-}SH \qquad (9)$$

$$C_1{-}NH{-}C_6 + H_2S \rightarrow C_1{-}NH_2 + C_6{-}SH \qquad (10)$$

Hence, hexylamine can form by Eqs. (8) and (9). Hexenes and hexane behaved as secondary products and are formed from hexanethiol by Eqs. (4)–(6).

The selectivity of C_6–NH–C_6 increased with decreasing weight time and reached a maximum at $\tau = 1$, suggesting that dihexylamine is a primary product as well. The only way to form it from the reactant C_1–NH–C_6 would be by the reaction

$$2C_1{-}NH{-}C_6 \rightarrow C_6{-}NH{-}C_6 + C_1{-}NH{-}C_1 \qquad (11)$$

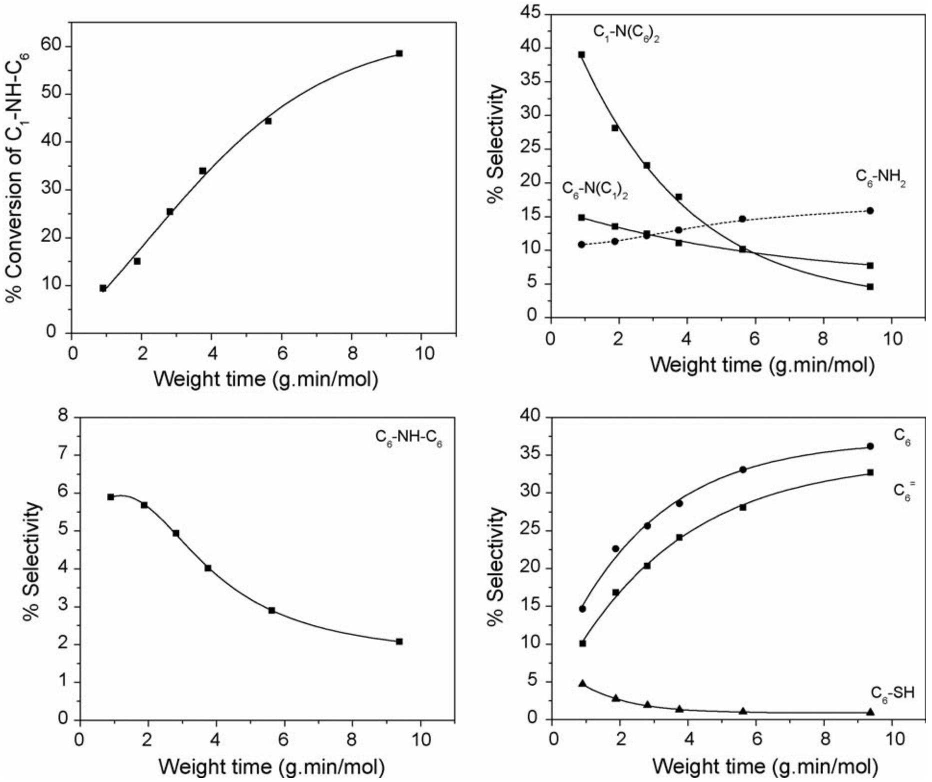


Fig. 2. Conversion and product selectivities (based on the C_6 mass balance) in the HDN of C_1–NH–C_6.

This reaction is not a disproportionation reaction, because in a disproportionation reaction an alkyl group and a hydrogen atom are exchanged. In Eq. (11), on the other hand, two alkyl groups are exchanged. Eq. (11) might be considered as a metathesis reaction, which is well known for metals and metal complexes [20] but unknown for metal sulfides. C_6–NH–C_6 can also be formed by secondary reactions. For instance, the disproportionation reaction of the C_1–NH–C_6 reactant with the product C_6–NH_2 gives C_6–NH–C_6 and C_1–NH_2. Also the reaction of the C_1–N$(C_6)_2$ product with H_2S to C_6–NH–C_6 and C_1–SH and with the reactant C_1–NH–C_6 to C_6–N$(C_1)_2$ and C_6–NH–C_6 can give C_6–NH–C_6. Secondary reactions do not seem to agree with the selectivity profile of C_6–NH–C_6 (Fig. 2). However, since no measurements could be made at very high space velocities, only results are available for $\tau > 1$ g min/mol. The two results obtained at the lowest possible weight times, $\tau = 1$ and 2 g min/mol, can be interpreted to demonstrate that the selectivity extrapolates to a non-zero value at $\tau = 0$ g min/mol but it is also possible that the selectivity goes through a maximum at low τ and decreases to zero at $\tau = 0$. The primary or secondary nature of dihexylamine in the HDN of C_1–NH–C_6 will be discussed further in Section 3.3, where the simultaneous reaction of C_5–NH_2 and C_1–NH–C_6 is described.

Similarly as dihexylamine, the mixed dialkylamine C_1–NH–C_6 reacts primarily by disproportionation and substitution. The denitrogenated products are formed as secondary products by elimination and hydrogenolysis of the hexanethiol at higher weight times.

3.3. Simultaneous reaction of C_1–NH–C_6 and C_5–NH_2

As noticed in the preceding section, alkylamines are primary products in the HDN reaction of (mixed) dialkylamines over sulfided NiMo/γ-Al_2O_3. In order to understand the role of an alkylamine during the HDN of a dialkylamine, we performed a simultaneous reaction over sulfided NiMo/γ-Al_2O_3 at 280 °C, 3 MPa, and 10 kPa H_2S. To distinguish the products, the reaction was carried out using C_5–NH_2 instead of C_6–NH_2. The partial pressures of C_1–NH–C_6 and C_5–NH_2 were 5 kPa each.

The conversion of C_5–NH_2 was 10% at $\tau = 10$ g min/mol (Fig. 3). The conversion of C_1–NH–C_6 was 48% at $\tau = 10$ g min/mol (Fig. 4), which is lower than the 58% at $\tau = 9.5$ g min/mol in the absence of C_5–NH_2 (Fig. 2). The lower conversion of C_1–NH–C_6 is due to the higher total amine concentration in the simultaneous reaction (10 instead of 5 kPa), and indicates that the reaction rate has a negative order in the amine concentration. The major products of the simultaneous reaction were: C_1–N$(C_6)_2$, C_6–N$(C_1)_2$, C_1–N$(C_5)C_6$, C_1–N$(C_5)_2$, C_5–NH–C_5, C_5–NH–C_6, C_6–NH–C_6, C_1–NH–C_5, C_6–NH_2, C_6–SH, C_5–SH, hexenes, hexane, pentenes, pentane (Figs. 3 and 4), and C_1-products (C_1–NH_2 and C_1–SH). To understand the mechanistic aspects of the simultaneous reaction, we calculated the selectivities of the products based on the C_5 (Fig. 3) as well as C_6 groups (Fig. 4).

The selectivities of the trialkylamines C_1–N$(C_6)_2$, C_6–N$(C_1)_2$, and C_1–N$(C_5)C_6$, the dialkylamines C_5–NH–C_5, C_1–NH–C_5, and C_5–NH–C_6, the monoalkylamine C_6–NH_2, and the alkanethiols C_6–SH and C_5–SH had a non-zero value at $\tau = 0$, indicating that they are primary products. The selectivity of

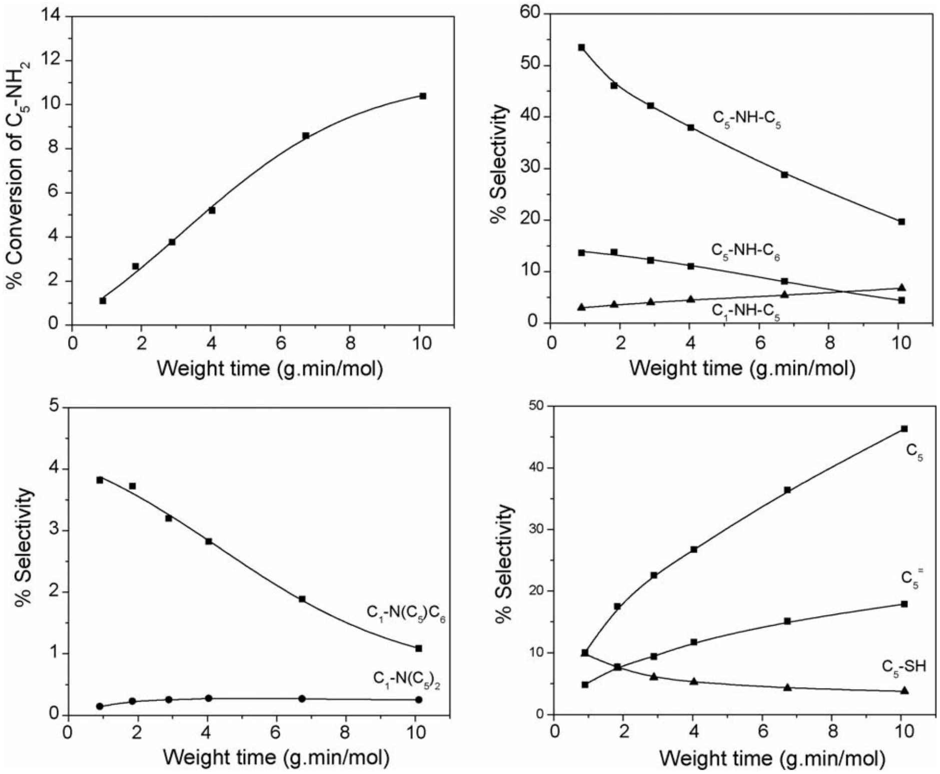


Fig. 3. Conversion and product selectivities (based on the C_5 mass balance) in the simultaneous reaction of 5 kPa $C_5–NH_2$ and 5 kPa $C_1–NH–C_6$.

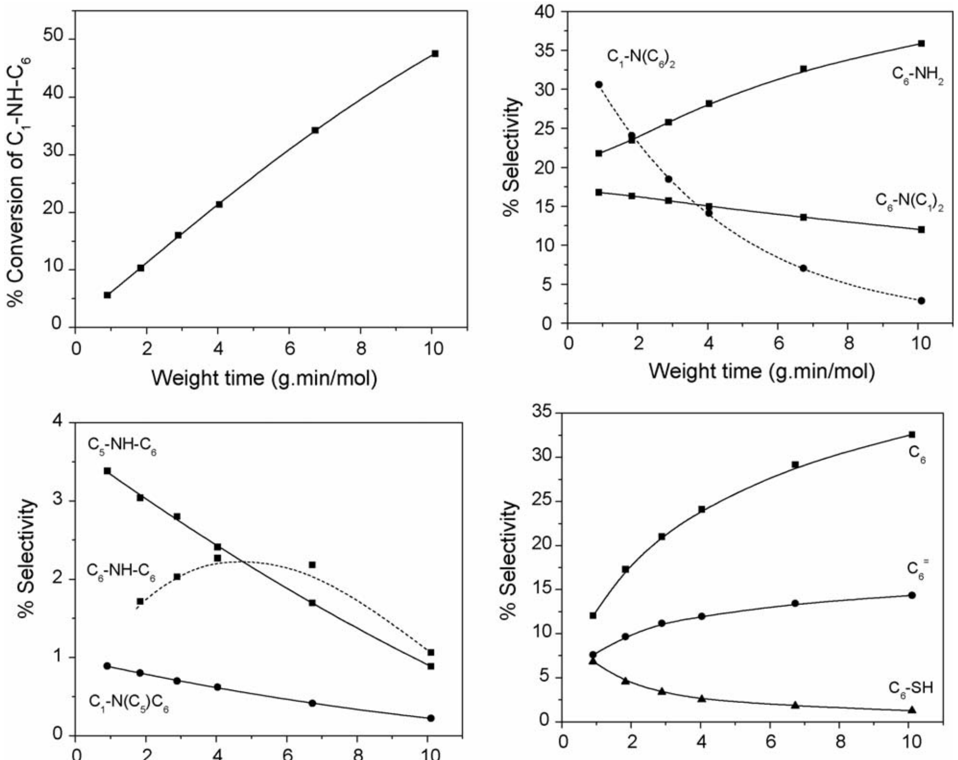


Fig. 4. Conversion and product selectivities (based on the C_6 mass balance) in the simultaneous reaction of 5 kPa $C_5–NH_2$ and 5 kPa $C_1–NH–C_6$.

C_6–NH–C_6 showed a maximum and most probably approaches zero at $\tau = 1$ g min/mol, showing that it is a secondary or even a tertiary product. The selectivities of C_1–N$(C_5)_2$, pentenes, pentane, hexenes, and hexane behaved as secondary products since their selectivities extrapolated to zero values at $\tau = 0$.

In the simultaneous reaction of C_1–NH–C_6 and C_5–NH_2 the main primary products are formed by reactions of the pure compounds. Thus, C_5–NH–C_5 and C_5–SH are formed by disproportionation of two pentylamine molecules and by substitution of pentylamine by H_2S, respectively, as in the reaction of pentylamine alone [18].

$$2C_5-NH_2 \rightarrow C_5-NH-C_5 + NH_3 \quad (12)$$

$$C_5-NH_2 + H_2S \rightarrow C_5-SH + NH_3 \quad (13)$$

The primary products C_1–N$(C_6)_2$ and C_6–N$(C_1)_2$ are produced by disproportionation of two C_1–NH–C_6 molecules, as shown in Section 3.2 (Eqs. (7) and (8)). The secondary products pentenes, pentane, hexenes, and hexane are formed from the respective alkanethiols by elimination and hydrogenolysis reactions and by hydrogenation of the alkenes (cf. Eqs. (4)–(6)).

The mixed trialkylamine C_1–N$(C_5)(C_6)$ and dialkylamines C_5–NH–C_6 and C_1–NH–C_5 behaved as primary products as well and can only have been formed by cross reactions of C_1–NH–C_6 with C_5–NH_2. They were formed in much smaller quantities as the products of the pure amines.

$$C_1-NH-C_6 + C_5-NH_2 \rightarrow C_1-N(C_5)C_6 + NH_3 \quad (14)$$

$$C_5-NH_2 + C_1-NH-C_6 \rightarrow C_5-NH-C_6 + C_1-NH_2 \quad (15)$$

$$C_5-NH_2 + C_1-NH-C_6 \rightarrow C_1-NH-C_5 + C_6-NH_2 \quad (16)$$

From the initial selectivities we estimate the ratios of the initial rates of Eqs. (7), (8) and (14)–(16) to be 19:17:1:3.5:0.5, respectively. Although the initial concentrations of C_1–NH–C_6 and C_5–NH_2 were equal, the reactions of two different alkylamines (Eqs. (14)–(16)) were much slower than the reactions of two equal dialkylamine molecules (Eqs. (7) and (8)). This can either be due to a slower rate of the reaction between an alkylamine and a dialkylamine than between two dialkylamine molecules, or to domain formation at the catalyst surface. If amine molecules prefer to adsorb near similar amines, then the chance of a reaction between different amines is small.

In the reaction of C_1–NH–C_6 (Section 3.2) it was not possible to decide whether dihexylamine was formed by a primary or secondary reaction, because it was not clear if the dihexylamine selectivity levelled off at low τ, or went through a maximum and extrapolated to zero at $\tau = 0$ (Fig. 2). In the simultaneous reaction of C_1–NH–C_6 and C_5–NH_2, on the other hand, there is a clear maximum in the dihexylamine selectivity and at low τ the selectivity tends to zero (Fig. 4). This indicates that it is not necessary to invoke a metathesis reaction (Eq. (11)) to explain the formation of C_6–NH–C_6. The maximum in the selectivity profile of dihexylamine in the simultaneous reaction (Fig. 4) suggests that the selectivity profile of dihexylamine in the reaction of pure C_1–NH–C_6 (Fig. 2) should also be considered to contain a maximum. The position of the maximum shifts to higher weight time in the presence of C_5–NH_2 (cf. Figs. 2 and 4).

3.4. HDN of C_1–N$(C_6)_2$

The conversion of the trialkylamine C_1–N$(C_6)_2$ (5 kPa) was 75% at $\tau = 9.5$ g min/mol (Fig. 5) and the products were C_6–NH–C_6, C_1–NH–C_6, C_6–NH_2, C_6–SH $(C_6)_3$N, C_6–N$(C_1)_2$, hexenes, hexane, and C_1-products. The selectivities of C_1–NH–C_6, and C_6–NH–C_6, C_6–SH extrapolate to a non-zero value at $\tau = 0$ and decrease with increasing weight time, indicating that they are primary products. This is explained by the substitution reactions

$$C_1-N(C_6)_2 + H_2S \rightarrow C_6-NH-C_6 + C_1-SH \quad (17)$$

$$C_1-N(C_6)_2 + H_2S \rightarrow C_1-NH-C_6 + C_6-SH \quad (18)$$

These reactions are equivalent to Eq. (2). From the extrapolated initial selectivities, we calculate that Eq. (18) is 2.6 times faster than Eq. (17). Because of the two hexyl and one methyl group in the reactant, this means that it is 30% easier to remove the C_6 group than a C_1 group from C_1–N$(C_6)_2$.

C_6–NH_2 $(C_6)_3$N, and C_6–N$(C_1)_2$ behaved as secondary products, as shown by the zero selectivity at $\tau = 0$ and increasing selectivity with increasing τ. $(C_6)_3$N and C_6–N$(C_1)_2$ can be formed by cross disproportionations of the primary dialkylamine products C_6–NH–C_6 and C_1–NH–C_6 with the reactant C_1–N$(C_6)_2$, respectively. The secondary products hexenes and hexane are formed from hexanethiol by Eqs. (4)–(6).

These results of the mixed trialkylamine are in good agreement with the HDN study of trihexylamine by Zhao et al. [16]. Thus, C_1–N$(C_6)_2$ reacted only by substitution with H_2S to dialkylamines and thiols because disproportionation is impossible for trialkylamines. However, the disproportionation of dialkylamines gives trialkylamines back as secondary products.

3.5. Simultaneous reaction of C_5–NH–C_5 and C_1–N$(C_6)_2$

The conversions of 5 kPa C_5–NH–C_5 and 5 kPa C_1–N$(C_6)_2$ in their simultaneous reaction were 51% (Fig. 6) and 59% (Fig. 7) at $\tau = 10$ g min/mol, respectively. The conversion of C_5–NH–C_5 was lower than that of C_6–NH–C_6 alone (Fig. 1), while the conversion of C_1–N$(C_6)_2$ was also lower than when reacted alone (Fig. 5). This is an indication of negative order and is caused by the strong adsorption of the amines on the catalyst surface. The products of the simultaneous reaction were $(C_5)_3$N, C_6–N$(C_5)_2$, C_1–N$(C_5)_2$, C_6–N$(C_1)_2$, C_5–N$(C_6)_2$, C_1–N$(C_5)C_6$, $(C_6)_3$N, C_1–NH–C_6, C_6–NH–C_6, C_5–NH–C_6, C_1–NH–C_5, C_6–SH, C_5–SH, C_6–NH_2, C_5–NH_2, hexenes, hexane, pentenes, pentane, and C_1–NH_2. The selectivities of all the products were calculated based on the C_5 (Fig. 6) and C_6 (Fig. 7) groups separately. The non-zero selectivities for $(C_5)_3$N, C_1–N$(C_5)_2$, C_6–N$(C_5)_2$, C_5–NH_2, C_5–SH, C_1–NH–C_6, C_6–NH–C_6, and C_6–SH at $\tau = 0$ mean that all these molecules are primary products. The selectivities of the trialkylamines

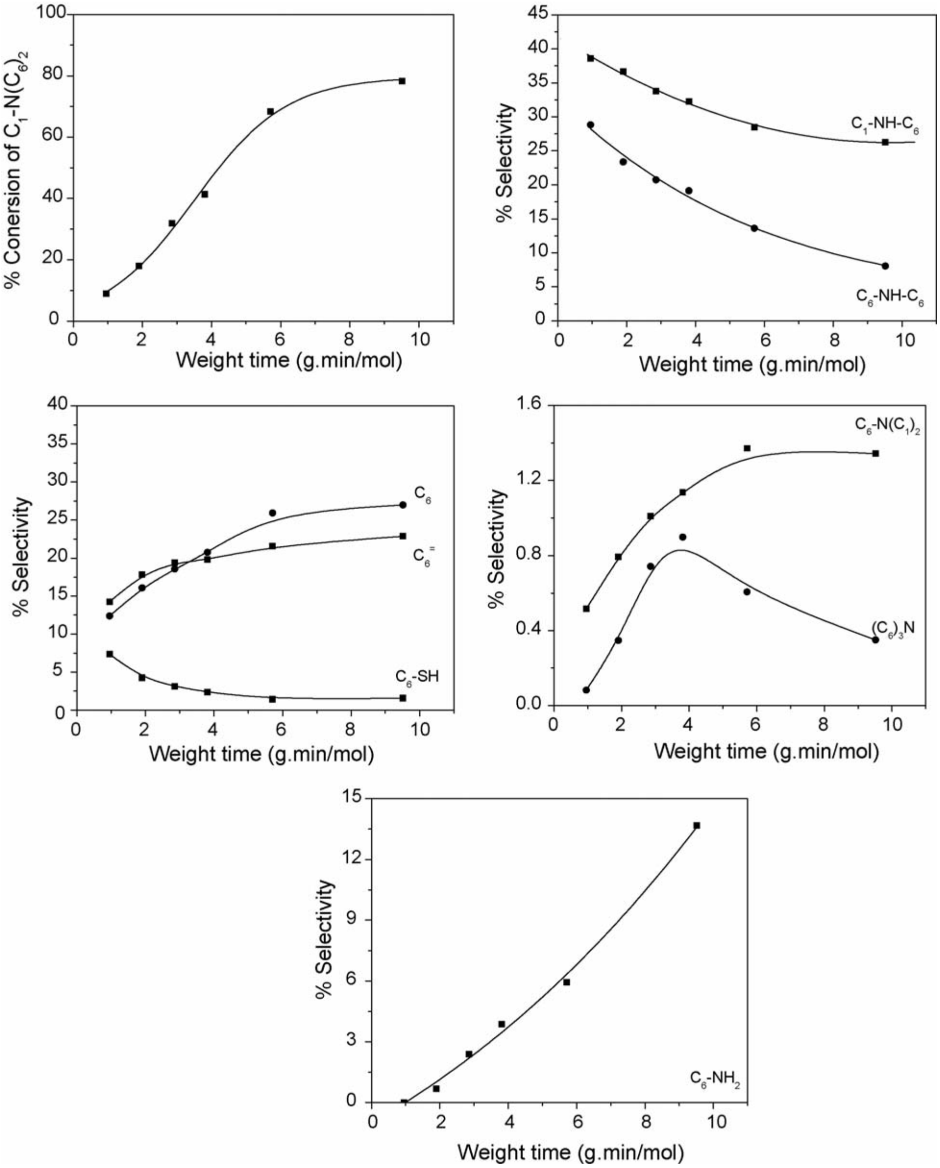


Fig. 5. Conversion and product selectivities (based on the C_6 mass balance) in the HDN of $C_1{-}N(C_6)_2$.

$C_5{-}N(C_6)_2$, $C_1{-}N(C_5)C_6$, $C_6{-}N(C_1)_2$, and $(C_6)_3N$, of the dialkylamines $C_1{-}NH{-}C_5$ and $C_5{-}NH{-}C_6$, of the alkylamine $C_6{-}NH_2$ and of the hydrocarbons $C_6^{=}$, C_6, $C_5^{=}$, and C_5 were low and extrapolated to zero values at $\tau = 0$ demonstrating that these molecules are secondary or even tertiary in nature.

The conversion of $C_5{-}NH{-}C_5$ is slightly lower than that of $C_1{-}N(C_6)_2$ in the simultaneous reaction. This might be due to the stronger adsorption of $C_1{-}N(C_6)_2$ as a consequence of higher molecular weight and or to a faster rate of reaction. As in the simultaneous reaction of $C_5{-}NH_2$ and $C_1{-}NH{-}C_6$, the majority of the products in the reaction of $C_5{-}NH{-}C_5$ and $C_1{-}N(C_6)_2$ comes from the reactions of the pure amines and not from the cross reaction between the two amines. $(C_5)_3N$, $C_5{-}SH$, and $C_5{-}NH_2$ are formed as primary products by disproportionation and substitution of the reactants (similar to Eqs. (1) and (3)). $C_1{-}N(C_6)_2$ reacted by substitution to $C_1{-}NH{-}C_6$, $C_6{-}NH{-}C_6$, and $C_6{-}SH$ as primary products (Eqs. (17) and (18)). Considering the statistical factor of 2 between C_6 and C_1 in $C_1{-}N(C_6)_2$, the chance to remove the C_6 group is 15% higher than to remove the C_1 group. This is slightly lower than the 30% higher chance of removing the C_6 group observed in the reaction of pure $C_1{-}N(C_6)_2$ (Section 3.4).

The trialkylamines $C_6{-}N(C_5)_2$ and $C_1{-}N(C_5)_2$ are formed as primary products by cross-disproportionation of the reactants

$$C_5{-}NH{-}C_5 + C_1{-}N(C_6)_2 \rightarrow C_6{-}N(C_5)_2 + C_1{-}NH{-}C_6 \tag{19}$$

$$C_5{-}NH{-}C_5 + C_1{-}N(C_6)_2 \rightarrow C_1{-}N(C_5)_2 + C_6{-}NH{-}C_6 \tag{20}$$

Considering the statistical factor of 2 between C_6 and C_1 in $C_1{-}N(C_6)_2$, the chance that $C_5{-}NH{-}C_5$ reacts with the C_1 group of $C_1{-}N(C_6)_2$ is about 5 times larger than that it reacts with the C_6 group.

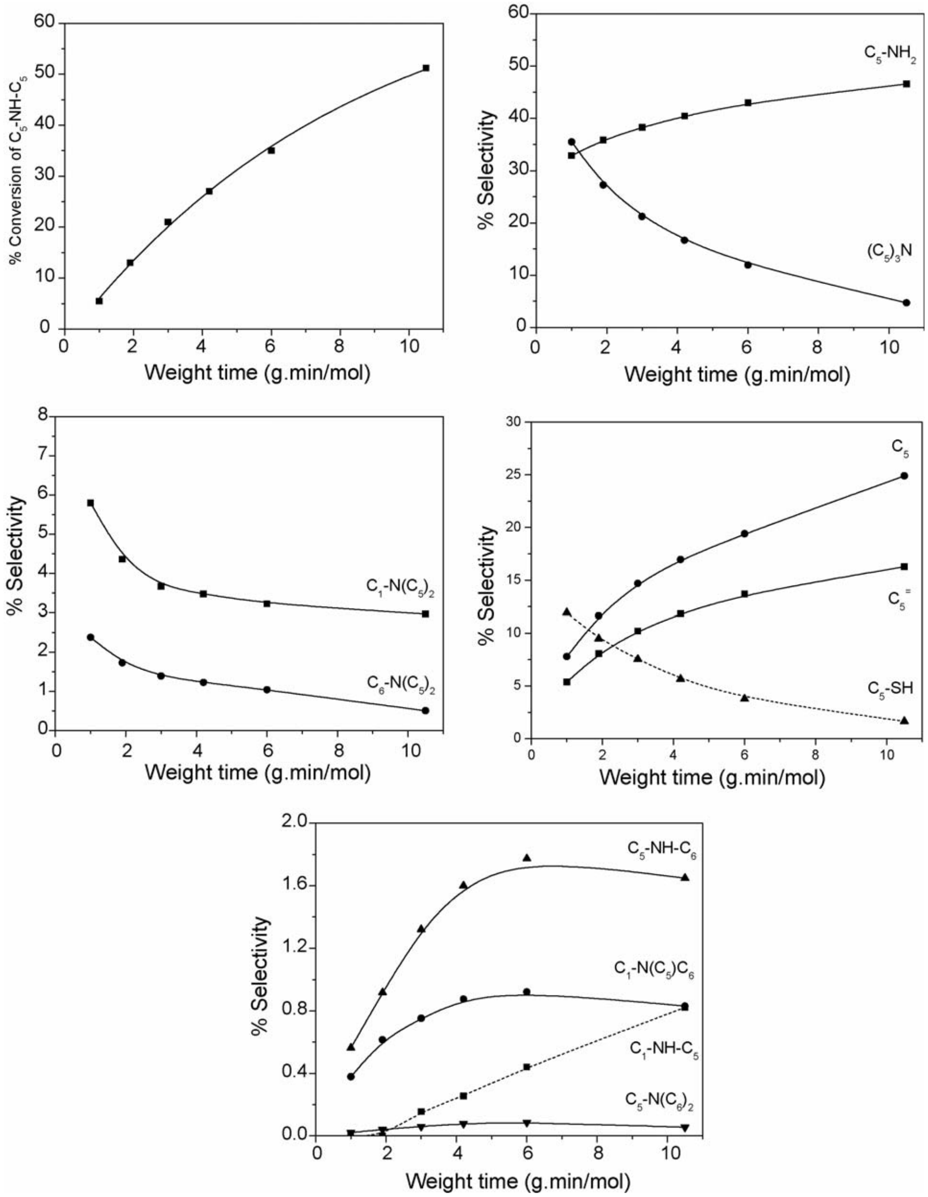


Fig. 6. Conversion and product selectivities (based on the C_5 mass balance) in the simultaneous reaction of 5 kPa C_5–NH–C_5 and 5 kPa C_1–N$(C_6)_2$.

The secondary products pentenes, pentane, hexenes, and hexane are formed from the respective alkanethiols by elimination and hydrogenolysis reactions (cf. Eqs. (4) and (5)). The alkanes can also form from the hydrogenation of the alkenes as tertiary product, as in Eq. (6).

3.6. HDN of *N,N,N^1,N^1-tetramethyldiaminomethane*

N,N,N^1,*N*^{1}-tetramethyldiaminomethane (5 kPa) was totally converted over sulfided NiMo/γ-Al_2O_3 at 3 MPa and 280 °C, in the presence of 10 kPa H_2S, at all weight times. Therefore, the reaction temperature was lowered, but the reaction turned out to be so fast that non-complete conversion could only be achieved below 150 °C. The main products at $\tau = 2.5$ g min/mol were dimethylamine, trimethylamine, methylamine, methanethiol, and dimethylsulfide. Dimethylamine and trimethylamine can be formed by substitution and hydrogenolysis

$$(C_1)_2N-CH_2-N(C_1)_2 + H_2S \rightarrow (C_1)_2N-CH_2-SH + C_1-NH-C_1 \quad (21)$$

$$(C_1)_2N-CH_2-SH + H_2 \rightarrow (C_1)_3N + H_2S \quad (22)$$

Substitution of C_1–NH–C_1 and $(C_1)_3N$ with H_2S then forms methylamine and methanethiol

$$C_1-NH-C_1 + H_2S \rightarrow C_1-NH_2 + C_1-SH \quad (23)$$

$$(C_1)_3N + H_2S \rightarrow C_1-NH-C_1 + C_1-SH \quad (24)$$

Dimethylsulfide arises from the condensation of two methanethiol molecules

$$2C_1-SH \rightarrow C_1-S-C_1 + H_2S \quad (25)$$

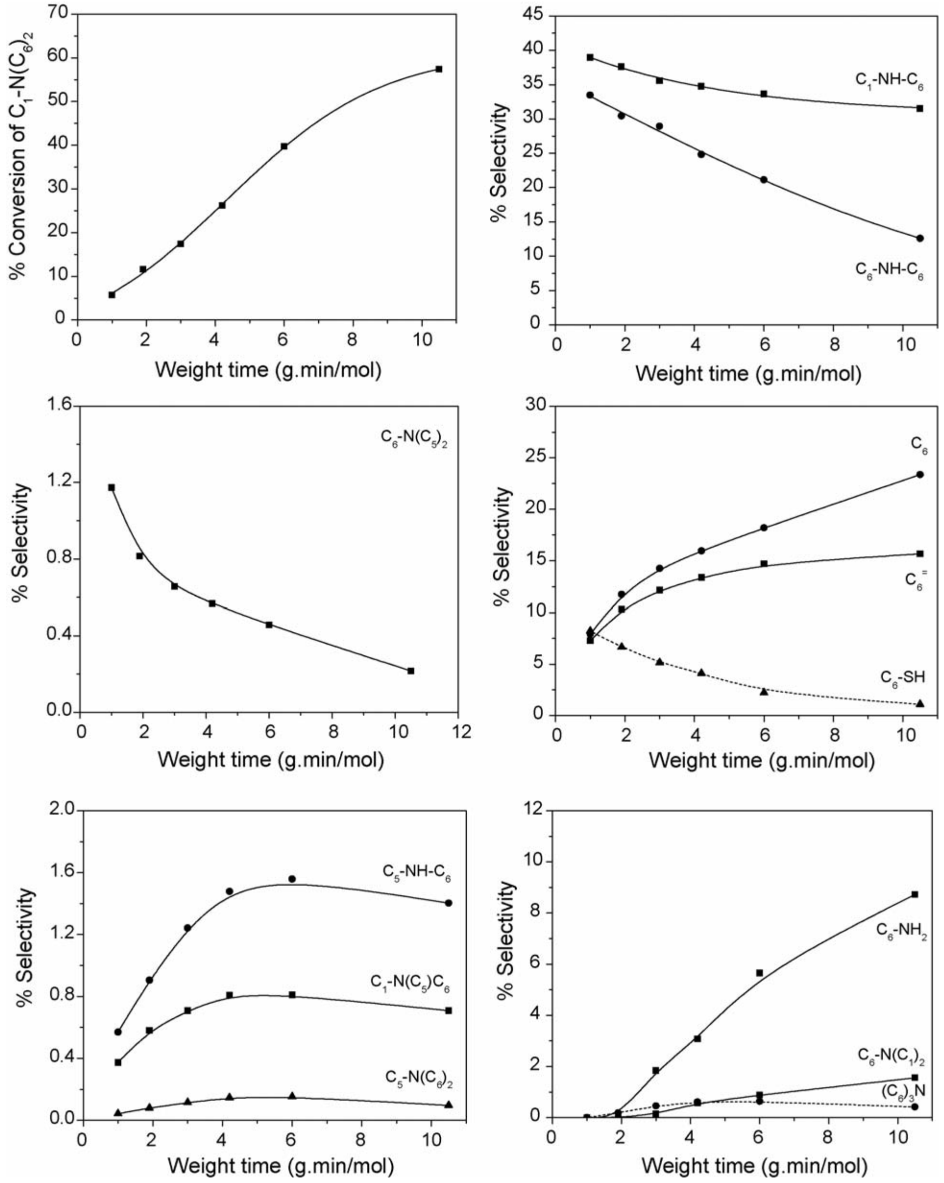
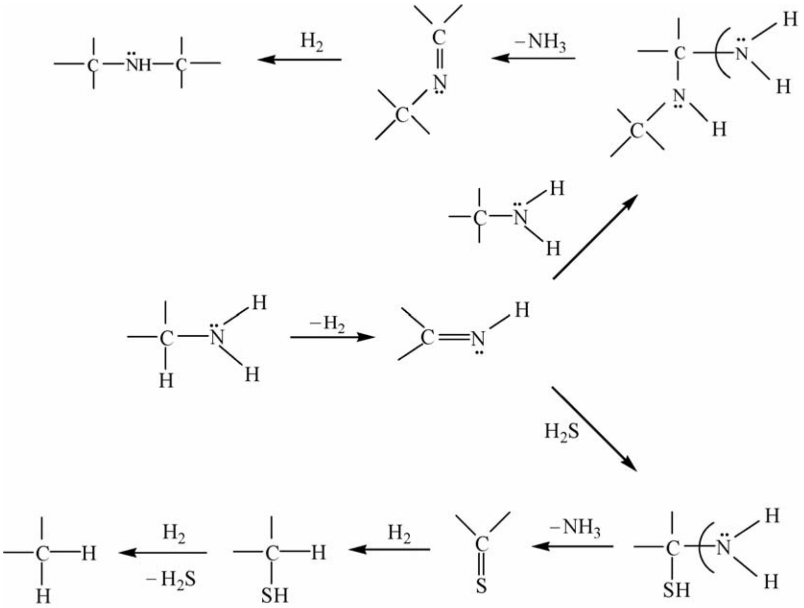


Fig. 7. Conversion and product selectivities (based on the C_6 mass balance) in the simultaneous reaction of 5 kPa C_5–NH–C_5 and 5 kPa C_1–N(C_6)$_2$.

Because a reaction catalyzed by the acid sites of the alumina support might be responsible for the decomposition of *N*,*N*,*N*^{1},*N*^{1}-tetramethyldiaminomethane over sulfided NiMo/γ-Al_2O_3, we also performed the reaction over γ-Al_2O_3. The conversion was much lower than over NiMo/γ-Al_2O_3, however, increasing from 15% at 200 °C to 34% at 300 °C. This demonstrates that it is the metal sulfide surface and not the support surface which is responsible for the fast decomposition of the geminal diamine.

4. Discussion

Our results show that mixed monoalkyl- and dialkylamines undergo substitution and disproportionation reactions, just as alkylamines with one and the same alkyl group do [16]. Trialkylamines only undergo a substitution reaction by H_2S leading to a thiol and a dialkylamine. The substitution and disproportionation of monoalkylamines go through an imine intermediate [19]. An imine is formed by dehydrogenation of an amine (Scheme 1). Then addition of H_2S or an amine to the imine takes place and a thiol or a dialkylamine is formed after ammonia elimination and hydrogenation, respectively (Scheme 1). Imines have been observed in the HDN of alkylamines over metal sulfide catalysts [17] and in reactions of alkylamines over an iridium hydride pincer complex [21]. Furthermore, transition-metal ions are known to promote the oxidation of amines to imines [22]. While the fraction of 1-alkylimines in equilibrium with the corresponding 1-alkylamines (with a primary α-carbon atom) is low, the fraction of dialkylimines and of 2-alkylimines (with a secondary α-carbon atom) can be substantial. The formation of imines would be in accordance with DFT calculations, which demonstrated that the edges of MoS_2 and Co and Ni-promoted MoS_2 have metallic properties. The DFT calculations predict that the band gap in bulk MoS_2

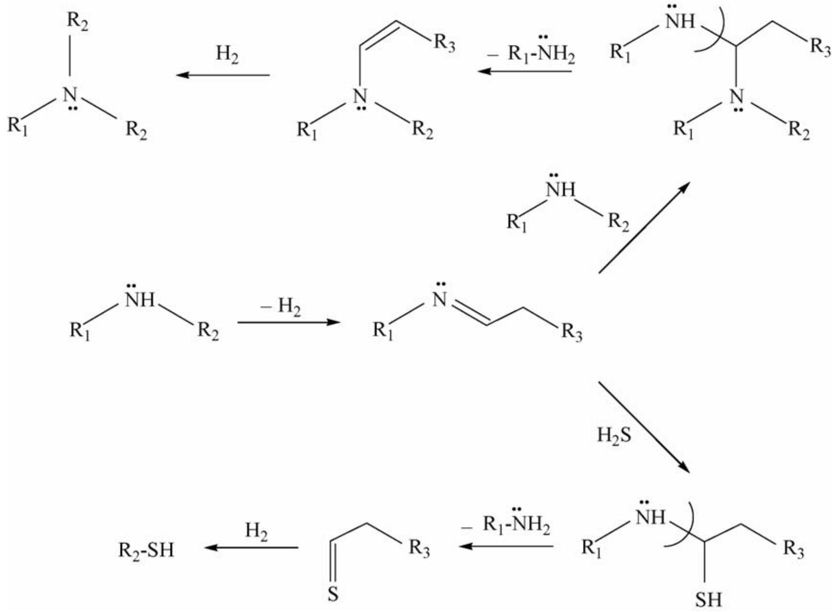


Scheme 1. Substitution of an alkylamine by H_2S and another alkylamine through an imine intermediate.

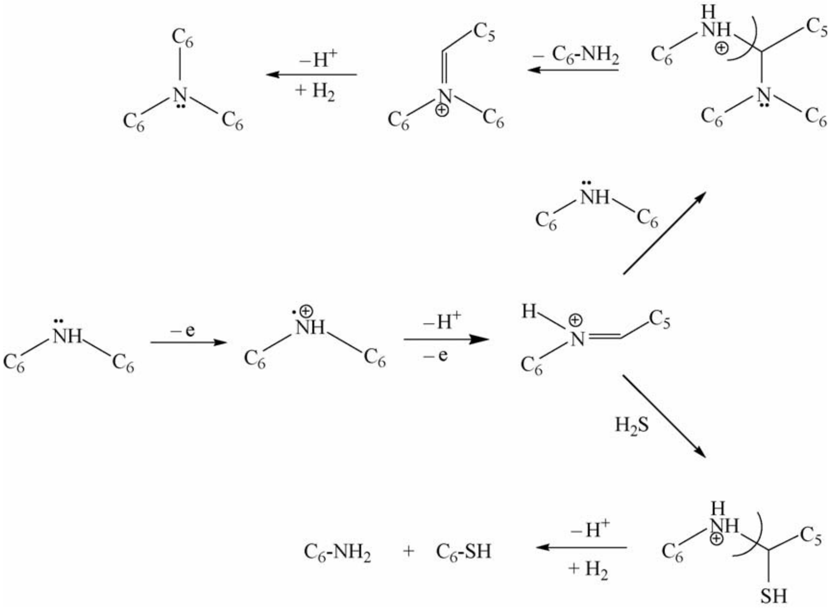
disappears at the edge surface as a result of the reduced coordination of the surface Mo and S atoms [23–25]. STM studies of MoS_2 crystallites on a gold support confirmed this prediction by showing a high electron density on the metal atoms at the MoS_2 edges [26].

In the HDN of dialkylamines not only an imine intermediate but also an enamine intermediate has to be invoked (Scheme 2). The elimination of the R_1-NH_2 amine from the aminal (geminal diamine) intermediate cannot occur by β-H elimination from the N atom, because this N atom does not contain a hydrogen atom. Elimination is, however, possible by β-H elimination from a carbon atom in the R_2 alkyl group, giving an enamine intermediate. This would mean that trialkylamines can only be formed from dialkylamines if β-H atoms are available in the alkyl groups. In other words, the transfer of an alkyl group from one amine to the other would only be possible for alkyl groups with two or more carbon atoms (cf. Scheme 2). In reverse, trialkylamines would only be able to react with H_2S to a dialkylamine and an alkanethiol if the alkanethiol has at least two carbon atoms.

Our results demonstrate, however, that alkyl transfer is also possible when the alkyl group is a methyl group. Thus, in the reaction of C_1–NH–C_6 not only hexyl transfer to give C_1–$N(C_6)_2$ but also methyl transfer to give C_6–$N(C_1)_2$ occurred and



Scheme 2. Substitution of a dialkylamine by H_2S and an amine to a thiol and a trialkylamine through imine and enamine intermediates.

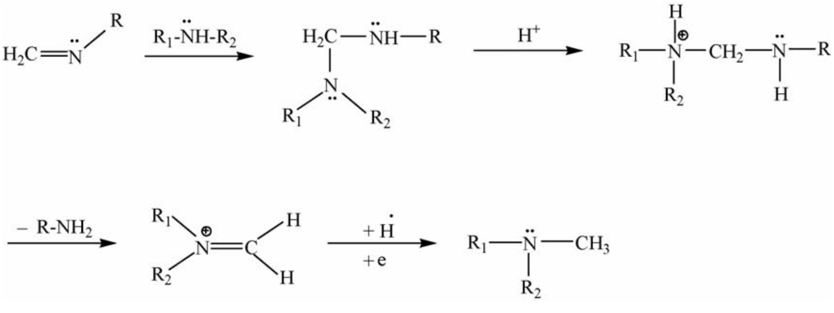


Scheme 3. Substitution of dihexylamine by H_2S and dihexylamine to hexanethiol and trihexylamine through iminium-cation intermediates.

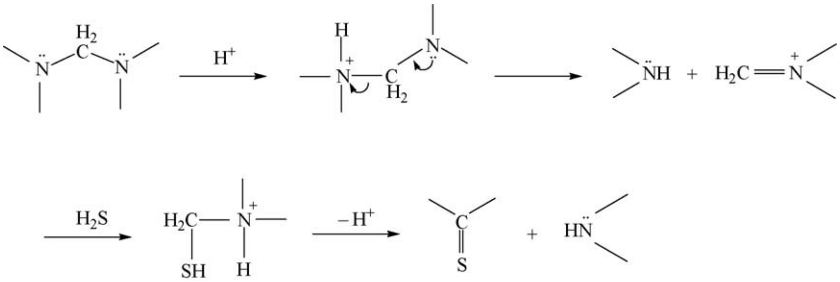
the hexyl transfer was only 50% faster than the methyl transfer (Section 3.2). C_1–N(C_6)$_2$ not only reacted to C_1–NH–C_6 but also to C_6–NH–C_6, the hexyl transfer being only 15–30% faster than the methyl transfer (Sections 3.4 and 3.5). Furthermore, C_5–NH–C_5 reacted 5 times faster with C_1–N(C_6)$_2$ by methyl transfer to C_1–N(C_5)$_2$ than by hexyl transfer to C_6–N(C_5)$_2$ (Section 3.5). Methyl transfer is thus at least as likely as alkyl transfer.

Since enamines cannot act as intermediates in methyl transfer reactions, the reactions of dialkyl- and trialkylamines have to be explained by other intermediates. They can be explained by iminium-cation intermediates. If the lone pair on the N atom and the H atom of the α-C atom undergo double oxidation and proton abstraction, then an imine cation is formed (Scheme 3). Addition of H_2S or an amine molecule to the iminium cation can take place and, after ammonia or amine elimination and hydrogenation, a thiol or a dialkylamine can be formed. Iminium cations are well known as intermediates in organic radical reactions [27,28]. On a heterogeneous catalyst, they can be formed when the surface contains reduction–oxidation centers as well as protons, as is the case for metal sulfides where the metal ions may undergo redox reactions and the H atoms of surface SH groups may act as protons. The formation of an imine from an amine requires a hydrogen atom on the α-C atom as well as on the N atom, while the formation of an enamine requires hydrogen atoms on the α-C and β-C atoms. The formation of an iminium ion, on the other hand, only requires a hydrogen atom on the α-C atom. Iminium cations thus even allow C_1 groups to be transferred in reactions between alkylamines. In the reaction of dialkylamines to tertiary amines, an aminal can be formed, followed by elimination of an amine. The resulting iminium cation can add an electron and an H atom and give $R_1R_2NCH_3$ (Scheme 4). This explains that not only C_1–N(C_6)$_2$ is formed from C_1–NH–C_6 but also C_6–N(C_1)$_2$.

The probability to transfer an alkyl group from one amine to the other will depend on the stability of the intermediate iminium cation. In the HDN of C_1–NH–C_6, the ratio C_1–N(C_6)$_2$/C_6–N(C_1)$_2$ was initially equal to 1.5 when pure C_1–NH–C_6 reacts and equal to 1.1 in the reaction of an equimolar mixture of C_1–NH–C_6 and C_5–NH_2, thus exchange of the C_6 group of C_1–NH–C_6 is more likely than of the C_1 group. This is probably caused by the higher stability of the intermediate hexylidene-*N*-methyliminium cation C_5H_{11}–CH=$N^+H(CH_3)$ than of the methylidene-*N*-hexyliminium cation CH_2=$N^+H(C_6H_{13})$, because iminium ions (like alkenes) are more stable the more they are substituted by



Scheme 4. Reaction of a dialkylamine and an imine to an aminal and elimination of an amine from the aminal through an iminium-cation intermediate.



Scheme 5. Decomposition of *N*,*N*,*N*^{1},*N*^{1}-tetramethyldiaminomethane.

alkyl groups. In addition, the hexylidene-*N*-methyliminium cation is stabilized by tautomerization to the enamine cation $(C_4H_9)CH{=}CH–N^+H_2(CH_3)$. The higher stability of the intermediate iminium cation $C_5H_{11}–CH{=}N^+H(CH_3)$ than of $CH_2{=}N^+H(C_6H_{13})$ may also be responsible for the higher proportion of the cross-disproportionation product $C_5–NH–C_6$ than of $C_1–NH–C_5$, respectively, in the simultaneous reaction of $C_1–NH–C_6$ and $C_5–NH_2$. Also the 15–30% higher chance to remove the C_6 group than the C_1 group from $C_1–N(C_6)_2$ can be explained by the stability of the intermediate cations, because the more highly substituted $C_5H_{11}–CH{=}N^+(CH_3)(C_6H_{13})$ cation is more stable than the $CH_2{=}N^+(C_6H_{13})_2$ cation.

The HDN reaction of *N*,*N*,*N*^{1},*N*^{1}-tetramethyldiaminomethane to dimethylamine, trimethylamine, methylamine, methanethiol, and dimethylsulfide (Scheme 5) demonstrated that the N–C–N bond can easily be broken, as shown in Scheme 4. The structure of *N*,*N*,*N*^{1},*N*^{1}-tetramethyldiaminomethane is very similar to that of the aminal (gem diamine) intermediate proposed in Scheme 4. The observation of reaction products, already at 130 °C, clearly demonstrates that the proposed N–C–N intermediates in the HDN reaction are very reactive.

5. Conclusions

Disproportionation of dialkylamines to trialkylamines and substitution of the alkylamines by H_2S are the primary reaction steps in the hydrodenitrogenation of mixed dialkyl- and trialkylamines over sulfided $NiMo/\gamma\text{-}Al_2O_3$. The probability for breaking the $C_6–N$ bond is only slightly higher than for the $C_1–N$ bond in the disproportionation reaction of two $C_1–NH–C_6$ molecules to $C_1–N(C_6)_2$ and $C_6–N(C_1)_2$ and in the reaction of $C_1–N(C_6)_2$ to $C_1–NH–C_6$ and $C_6–NH–C_6$, respectively. In all dialkyl- and trialkylamine reactions, alkenes, and alkanes are secondary products formed from elimination and hydrogenolysis of the alkanethiols that are formed as primary products by substitution of the amines by H_2S. For alkylamines and dialkylamines, the substitution by amine and H_2S may occur via imine intermediates. For trialkylamines, the intermediate has to be an enamine or an iminium cation and the transfer of a methyl group can only be explained by an iminium cation. The lone pair on the N atom and the H atom react by double oxidation and proton abstraction to an imine cation. Thereafter, the addition of H_2S or an amine molecule to the imine cation takes place and, after ammonia or amine elimination and hydrogenation, a thiol or a dialkylamine is formed. An iminium-ion intermediate can form not only in the presence but also in the absence of hydrogen on the N atom. Therefore, a single mechanism involving an iminium ion intermediate can explain all the products involved in the HDN, not only of trialkylamines but also of monoalkyl- and dialkylamines.

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