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Mechanisms of the hydrodenitrogenation of alkylamines with secondary and tertiary α-carbon atoms on sulfided $NiMo/Al_2O_3$

Y. Zhao and R. Prins *

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

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Abstract

The hydrodenitrogenation (HDN) of alkylamines with secondary and tertiary α-carbon atoms (2-pentylamine, 3-methyl-2-butylamine, 3,3-dimethyl-2-butylamine, 2-methylcyclohexylamine, 2-methyl-2-butylamine) and benzylamine and the hydrodesulfurization (HDS) of corresponding alkanethiols were studied over sulfided $NiMo/Al_2O_3$. Alkanethiols and dialkylamines were primary products in the HDN of the amines with secondary α-carbon atoms, formed by substitution of the amine group by H_2S or an alkylamine. Alkanes and alkenes were secondary products, formed from elimination and hydrogenolysis of the alkanethiols, as confirmed by the similar alkenes/alkane ratios in the HDN of the alkylamines and HDS of the corresponding alkanethiols. 2-Methyl-2-butylamine and benzylamine reacted much faster than the amines with secondary α-carbon atoms. Methylbutenes and methylbutane were the primary products of 2-methyl-2-butylamine, and toluene was the primary product of benzylamine. This and the different methylbutenes/methylbutane ratios in the HDN of 2-methyl-2-butylamine and HDS of 2-methyl-2-butanethiol indicate that 2-methyl-2-butylamine, with a tertiary α-carbon atom, and the activated benzylamine react by means of an E1 mechanism.

Keywords: 2-Pentylamine; 3-Methyl-2-butylamine; 3,3-Dimethyl-2-butylamine; 2-Methyl-2-butylamine; 2-Methylcyclohexylamine; Benzylamine; HDN; Hydrotreating catalysts

1. Introduction

Nitrogen atoms are removed from hetero-aromatic compounds by hydrogenation of the aromatic ring, which contains the nitrogen atom, and breaking of the resulting aliphatic C–N bonds to form a hydrocarbon molecule and ammonia [1–5]. Hydrogenation is not required for the removal of a sulfur atom from an aromatic ring that contains a sulfur atom, as in (di)benzothiophene, because the relatively weak C–S bond can be broken by hydrogenolysis [6,7]. The presence of a large amount of alkenes and a minor amount of alkanes in the reaction product of HDN suggests that aliphatic C–N bond breaking occurs mainly by elimination of NH_3 [1,3]. Nucleophilic substitution of the alkylamine by H_2S, followed by C–S bond hydrogenolysis, explains the presence of alkanes [1,4]. Cattenot et al. showed, however, that in the HDN of the linear n-pentylamine over unsupported MoS_2 at 275 °C and atmospheric pressure the formation of pentenes was negligible at short weight time and that the major product was dipentylamine [8]. At higher weight times pentenes and pentanethiol were observed and the production of the pentenes was ascribed mainly to the elimination of pentylamine from the dipentylamine and, in part, to the elimination of H_2S from pentanethiol. We showed that, over a sulfided $NiMo/Al_2O_3$ catalyst at 300 to 340 °C and elevated pressure (3 MPa), n-hexylamine, di-n-hexylamine, and tri-n-hexylamine react predominantly by nucleophilic substitution of the amines by H_2S and not by elimination of NH_3 [9]. The resulting hexanethiol reacts very fast to hexenes as well as to hexane. The very low selectivity of the hexenes at low weight time demonstrates that the hexenes are secondary not primary products in the HDN of n-hexylamines. As a consequence, the hexene/hexane ratio in the HDN product mixture is determined by the HDS reaction, as demonstrated by the similar alkenes/alkane ratios in the simultaneous HDN of hexylamine and HDS of pentanethiol [9].

The nucleophilic substitution by a good nucleophile such as SH^- is aided by the accessibility of the α-carbon atom in

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

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linear alkylamines. The accessibility of the α-carbon atom decreases with substitution and, at the same time, the number of β-hydrogen atoms increases. Thus, amines with secondary and tertiary α-carbon atoms may react differently as linear alkylamines [8]. Therefore, we report the results of the organic part of our mechanistic investigation of the removal of ammonia from such alkylamines in this work. In future work we will report on the inorganic aspects, the catalytic sites, and the mode(s) of adsorption.

2. Experimental

HDN and HDS experiments were carried out in a microflow reactor with an $NiMo/Al_2O_3$ catalyst prepared by sequential pore-volume impregnation of γ-Al_2O_3, as described elsewhere [9,10]. The catalyst was sulfided in situ and used immediately, without exposing it to nitrogen or air. The total pressure in the HDN and HDS experiments was 3 MPa and the partial pressure of the alkylamines was 5 kPa. A higher alkylamine pressure would not lead to a greater amount of the product (which would be more easily detectable at very low weight time) as long as the reaction has an order above zero. At 5 kPa alkylamine the order of the HDN reactions at 300 °C was about 0.5 in the alkylamine pressure. The HDS of alkanethiols was studied, because they are intermediates in the HDN of alkylamines. They were studied at 5 kPa, always in the presence of 5 kPa hexylamine. Although the presence of the alkylamine substantially decreased the rates of the HDS reactions of the alkanethiols, the rates of HDS were still much faster than the rates of HDN of the alkylamines. The experiments were carried out at 270, 300, and 340 °C with a partial pressure of H_2S of 10 or 100 kPa. When the partial pressure of the reactant, was charged, 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}) ($1\ (g\,min)/mol = 0.68 \times 10^{-3}\ (g\,h)/l$). 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 accuracy in the measured conversion was 2% (relative).

2-Pentylamine (Lancaster), 2-pentanethiol (Aldrich), 3-methyl-2-butylamine (Aldrich, 98%), 3-methyl-2-butanethiol (ABCR, 100%), 3,3-dimethyl-2-butylamine (ABCR, 100%), 2-methylcyclohexylamine (Fluka), 2-methyl-2-butylamine (Aldrich, 98%), 2-methyl-2-butanethiol (TCI, Japan, 99%), benzylamine (Fluka, purum), α-toluenethiol (Fluka, purum), and cyclohexane (Fluka, puriss.) were all used as purchased in the HDN tests. 2-Methyl-3-pentylamine was synthesized from 2-methylpentanone-3 by reaction with hydroxylamine and reduction of the resulting oxime with $LiAlH_4$ in ether. The product was purified by destillation. The gases used were hydrogen (PanGas 4.0) and a mixture of 10% H_2S in H_2 (Messer Griesheim 3.0).

3. Results

3.1. 2-Pentylamine and 2-pentanethiol

The conversion of 2-pentylamine at 300 °C in the presence of 10 kPa H_2S was 12% at $\tau = 0.9\ (g\,min)/mol$ and 53% at 8.9 (g min)/mol (Fig. 1). The conversion increased slightly when the H_2S pressure was increased from 10 to 100 kPa but increased considerably with an increase in temperature from 300 to 340 °C. The products were 2-pentanethiol, di-(2-pentyl)amine, 1-pentene, 2-pentene, and pentane (Fig. 2). The selectivity of 2-pentanethiol increased with decreasing weight time, showing that 2-pentanethiol is a primary product (of the nucleophilic substitution of 2-pentylamine with H_2S). Di-(2-pentyl)amine, the disproportionation product of two molecules of 2-pentylamine, behaved as a primary product as well. The selectivity of 2-pentanethiol increased and that of di-(2-pentyl)amine decreased with increasing H_2S pressure.

The selectivity of the pentenes (i.e., the sum of the two pentene isomers) as a function of weight time was different at 300 °C than at 340 °C. At 300 °C the selectivity extrapolates to zero with decreasing weight time, which indicates that pentenes are a secondary product. On the other hand, at 340 °C the pentenes behaved like a primary product because

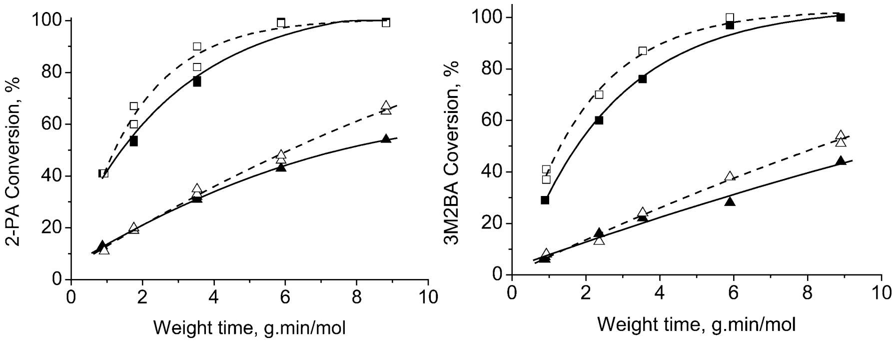


Fig. 1. Conversions of 2-pentylamine (2-PA) and 3-methyl-2-butylamine (3M2BA) at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

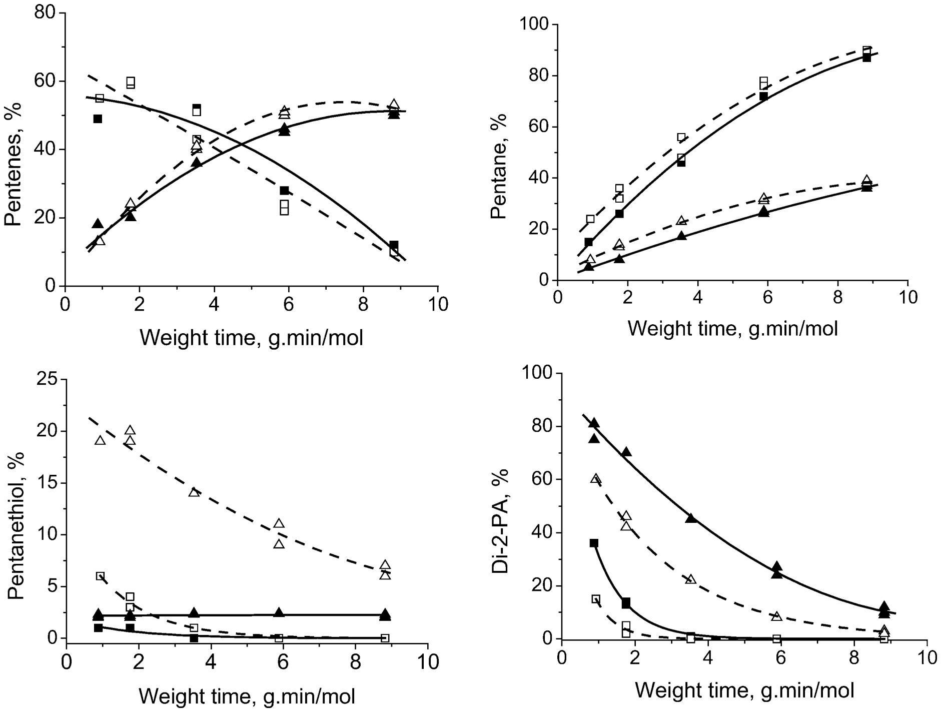


Fig. 2. Product selectivities in the HDN of 2-pentylamine (2-PA) at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

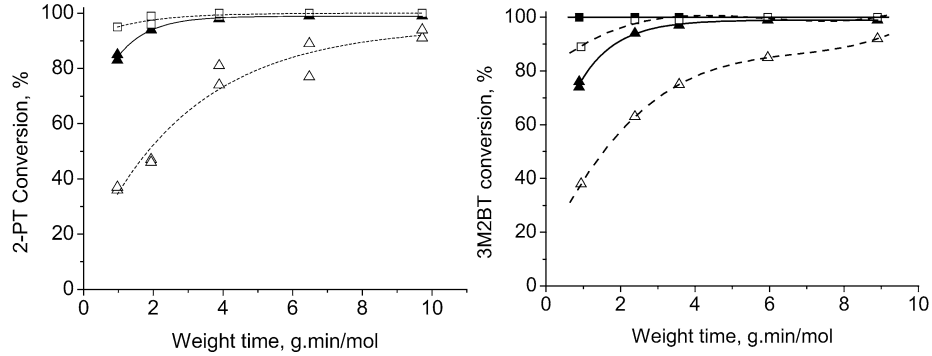


Fig. 3. Conversions in the HDS of 2-pentanethiol (2-PT) and 3-methyl-2-butanethiol (3M2BT) in the presence of hexylamine at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

their selectivity extrapolates to a nonzero value at $\tau = 0$. At both temperatures, the selectivity of pentane decreased with decreasing weight time to a value close to zero.

The conversion of 2-pentanethiol in the presence of 10 kPa H_2S and 5 kPa hexylamine was much larger than that of the corresponding 2-pentylamine. Thus, at $\tau = 0.9$ (g min)/mol the conversion of the thiol was 83% at 300 °C and 95% at 340 °C (Fig. 3), while that of the amine was 12% at 300 °C and 42% at 340 °C (Fig. 1). The conversion of 2-pentanethiol decreased strongly when the H_2S pressure was increased from 10 to 100 kPa. The main products at 300 °C and 10 kPa H_2S were 1-pentene (21%), 2-pentene (52%), and pentane (27%) at $\tau = 0.9$ (g min)/mol (not shown). All three molecules were primary products. The selectivity of 1-pentene decreased and that of pentane increased with weight time, while the selectivities of *cis*- and *trans*-2-pentene were constant. This difference between the pentenes must be due to the easier hydrogenation of the terminal 1-pentene. The pentenes/pentane ratio, obtained from the HDS of 2-pentanethiol, was similar to that obtained in the HDN of 2-pentylamine (Fig. 4).

3.2. *3-Methyl-2-butylamine and 3-methyl-2-butanethiol*

The conversion of 3-methyl-2-butylamine was slightly lower than that of 2-pentylamine (Fig. 1). It increased weakly with increasing H_2S pressure and increased substantially with increasing temperature. The main products were 3-methyl-2-butanethiol, di-(3-methyl-2-butyl)amine, 2-methyl-2-butene, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methylbutane. The selectivities of 3-methyl-2-butanethiol and di-(3-methyl-2-butyl)amine increased with

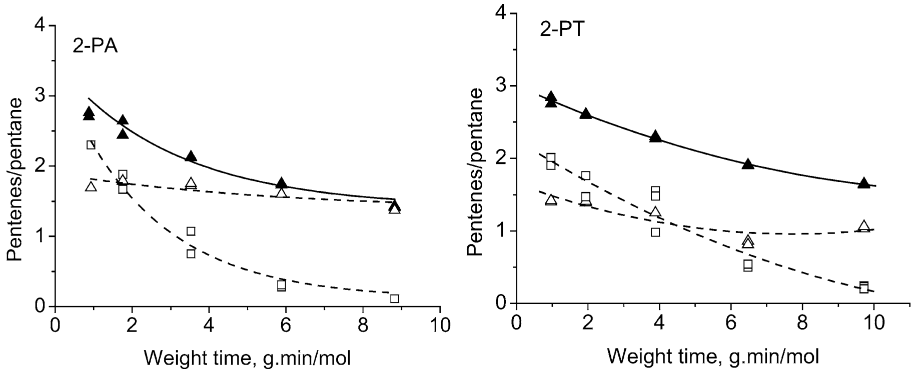


Fig. 4. Pentenes/pentane ratio in the HDN of 2-pentylamine (2-PA) and HDS of 2-pentanethiol (2-PT) in the presence of hexylamine at 300 °C (▲ and △) and 340 °C (□), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

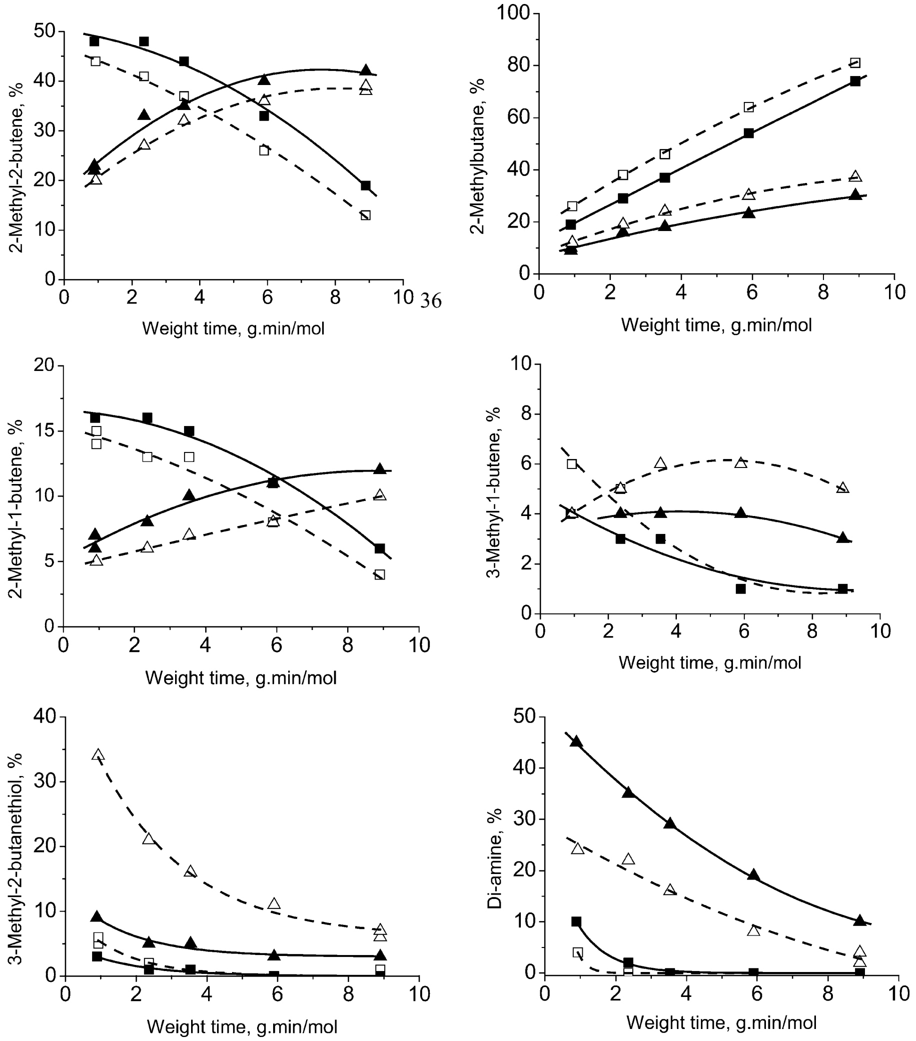


Fig. 5. Product selectivities in the HDN of 3-methyl-2-butylamine at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

decreasing weight time (Fig. 5). This shows that they are primary products of the nucleophilic substitution of 3-methyl-2-butylamine with H_2S and with another molecule of 3-methyl-2-butylamine, respectively. As expected for a molecule with two chiral atoms (3-methyl-2-butylamine has one chiral atom), the gas chromatogram of di-(3-methyl-2-butyl)amine showed two peaks of equal intensity and only a small difference in retention time; the correspond-

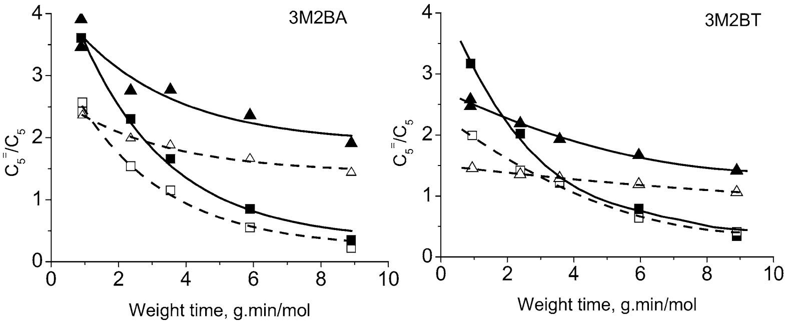


Fig. 6. Methylbutenes/methylbutane ratio in the HDN of 3-methyl-2-butylamine (3M2BA) and HDS of 3-methyl-2-butanethiol (3M2BT) in the presence of hexylamine at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

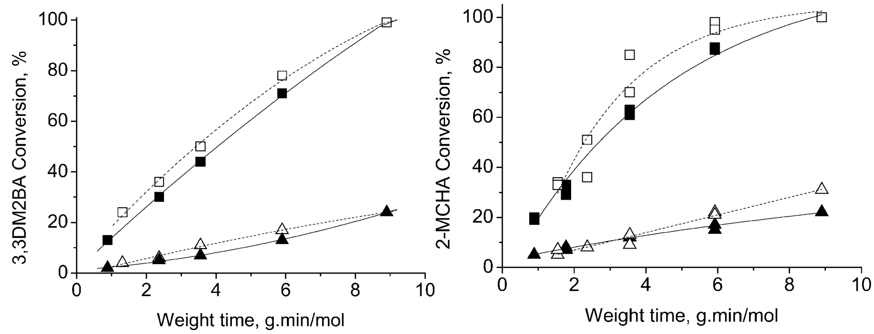


Fig. 7. Conversions of 3,3-dimethyl-2-butylamine (3,3DMBA) and 2-methylcyclohexylamine (2-MCHA) at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

ing products had equal mass spectra. One GC peak is due to the (*R*,*R*) and (*S*,*S*) isomers, the other to the meso (*R*,*S*) isomer. The selectivity of di-(3-methyl-2-butyl)amine decreased with increasing H_2S pressure, while the reverse was true for the selectivity of 3-methyl-2-butanethiol.

As in the HDN of its isomer 2-pentylamine (Section 3.1), the selectivities of the alkene products in the HDN of 3-methyl-2-butylamine differed at 300 and 340 °C. At 300 °C the methylbutene selectivities were low at $\tau = 0$ and increased with weight time, while at 340 °C and $\tau = 0$ they were higher and decreased with weight time. At both temperatures, all three methylbutenes behaved as primary products (Fig. 5) as the selectivities extrapolated to nonzero with decreasing weight time to zero.

The conversion of 3-methyl-2-butanethiol in the presence of 10 kPa H_2S and 5 kPa hexylamine was much larger than that of the corresponding 3-methyl-2-butylamine: The conversion of the thiol was 74% at $\tau = 0.9$ (g min)/mol at 300 °C and 100% at 340 °C (Fig. 3), while that of the corresponding amine was 7% at 300 °C and 29% at 340 °C (Fig. 1). The main products at 300 °C and 10 kPa H_2S were 3-methyl-1-butene (17%), 2-methyl-2-butene (49%), and 2-methylbutane (29%) at $\tau = 0.9$ (g min)/mol, while the selectivity of 2-methyl-1-butene was 5% (not shown). The methylbutenes/methylbutane ratio obtained from the HDS of 3-methyl-2-butanethiol in the presence of hexylamine was slightly lower than that obtained from the HDN of 3-methyl-2-butylamine at low weight time but was similar at high weight time (Fig. 6).

To determine whether a methyl-shift rearrangement occurred during the HDN of 3-methyl-2-butylamine, the HDN of 2-methyl-3-pentylamine was measured. The selectivity of the rearrangement products 3-methyl-2-pentene and 3-methylpentane was below 1%. The main products (di-(2-methyl-3-pentyl)amine, 2-methyl-1-pentene, 2-methyl-2-pentene, 2-methyl-3-pentene, 2-methylpentane, and 2-methyl-3-pentanethiol) corresponded to those in the HDN of 3-methyl-2-butylamine and were present in similar amounts (Fig. 5). In addition, a constant selectivity of 2% was observed for 2-methyl-4-pentene.

3.3. *3,3-Dimethyl-2-butylamine*

The conversion of 3,3-dimethyl-2-butylamine was even lower than that of 3-methyl-2-butylamine: only 2% at 300 °C and 10 kPa H_2S at $\tau = 0.9$ (g min)/mol but 24% at $\tau = 8.9$ (g min)/mol. The conversion increased strongly with increasing temperature and increased slightly with increasing H_2S pressure (Fig. 7). 3,3-Dimethyl-2-butanethiol formed and behaved as a primary product, because its selectivity increased with decreasing weight time (Fig. 8). We did not observe a disproportionation product, probably because of the combined steric hindrance of the tertiary butyl and methyl groups attached to the same carbon atom as the NH_2 group.

In addition to the normal products (3,3-dimethyl-1-butene and 2,2-dimethylbutane), rearranged products (2,3-dimethylbutane, 2,3-dimethyl-2-butene, and 2,3-dimethyl-1-butene) also formed. The sum of the selectivities of these

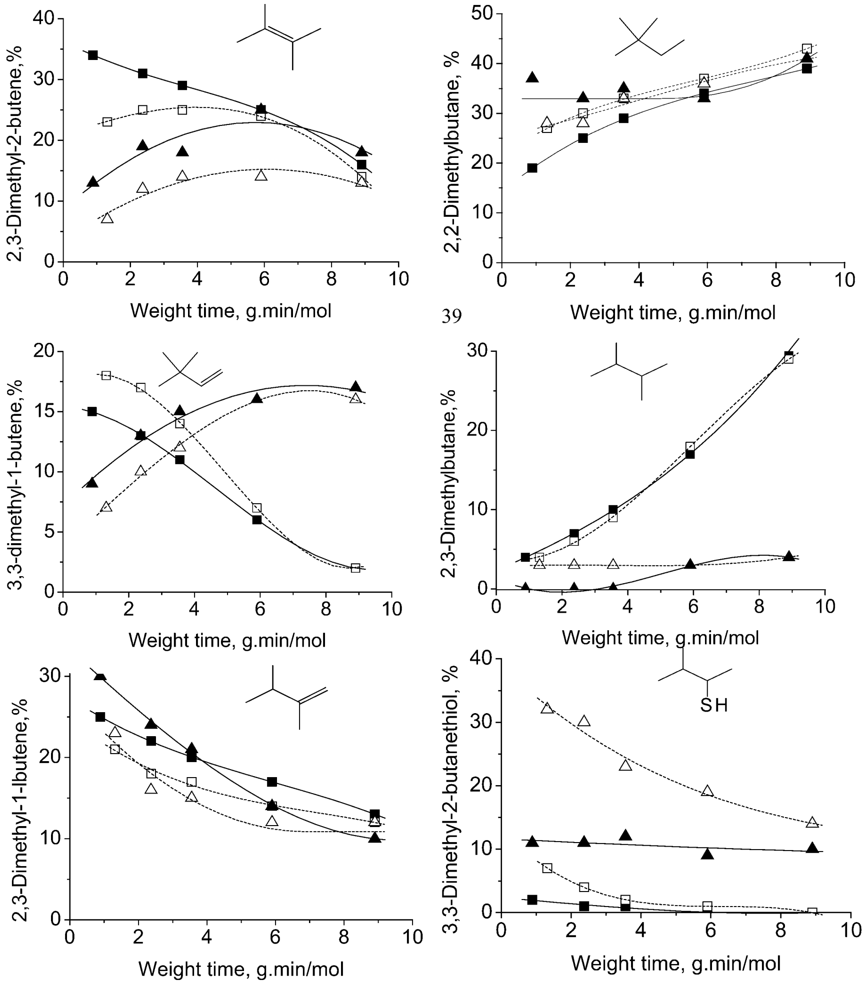


Fig. 8. Product selectivities in the HDN of 3,3-dimethyl-2-butylamine at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

rearranged products was 43% at 300 °C and 63% at 340 °C and 10 kPa H_2S at $\tau = 0.9$ (g min)/mol. As in the case of 2-pentylamine and 3-methyl-2-butylamine, the selectivity of 3,3-dimethyl-1-butene in the HDN of 3,3-dimethyl-2-butylamine as a function of weight time was different at 300 °C than at 340 °C. At 300 °C the 3,3-dimethyl-1-butene selectivity went through a maximum, while at 340 °C it decreased continuously with increasing weight time.

3.4. 2-Methylcyclohexylamine

2-Methylcyclohexylamine has the same molecular structure as 3-methyl-2-butylamine, with the amine group attached to a secondary α-carbon atom and a methyl group on the neighboring β-carbon atom. The conversion of 2-methylcyclohexylamine was lower than that of 3-methyl-2-butylamine, both at 300 °C and at 340 °C, and H_2S had a positive influence on the conversion of both amines (cf. Figs. 1 and 7). The selectivities of the methylcyclohexenes, methylcyclohexane, 2-methylcyclohexanethiol, and di-(2-methylcyclohexyl)amine products (Fig. 9) were similar to those of the respective alkenes, alkane, alkanethiol, and dialkylamine products in the HDN of 3-methyl-2-butylamine, respectively (Fig. 5).

3.5. 2-Methyl-2-butylamine and 2-methyl-2-butanethiol

The HDN of 2-methyl-2-butylamine occurred fast; the conversion was already 7% at 270 °C and 10 kPa H_2S at low weight time (0.9 (g min)/mol) and reached 90% at $\tau = 8.9$ (g min)/mol (Fig. 10). The main products were 2-methyl-2-butene, 2-methyl-1-butene, and 2-methylbutane (Fig. 11). The nonzero selectivities of these products at $\tau = 0$ showed that they behaved as primary products. The selectivity of 2-methyl-1-butene decreased and that of 2-methylbutane increased with increasing weight time due to isomerization and hydrogenation. A separate experiment of 2-methyl-1-butene in the presence of hexylamine at 270 °C, 3 MPa, and 10 kPa H_2S showed 30% conversion to 2-methyl-2-butene and 10% conversion to 2-methylbutane at $\tau = 10$ (g min)/mol. The selectivity of 3-methyl-1-butene, the isomerization product of 2-methyl-2-butene, was less than 1% over the whole range of weight times. A small amount of 2-methyl-2-butanethiol was observed

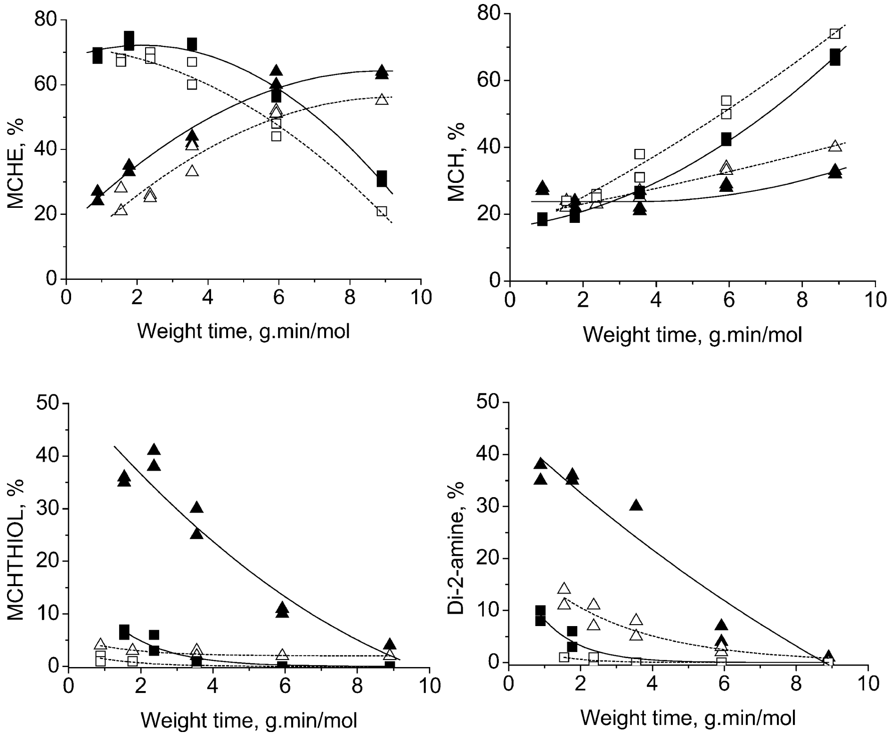


Fig. 9. Product selectivities of methylcyclohexenes (MCHE), methylcyclohexane (MCH), 2-methylcyclohexanethiol (MCHTHIOL), and di(2-methylcyclohexyl)amine (Di-2-amine) in the HDN of 2-methylcyclohexylamine at 300 °C (▲ and △) and 340 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

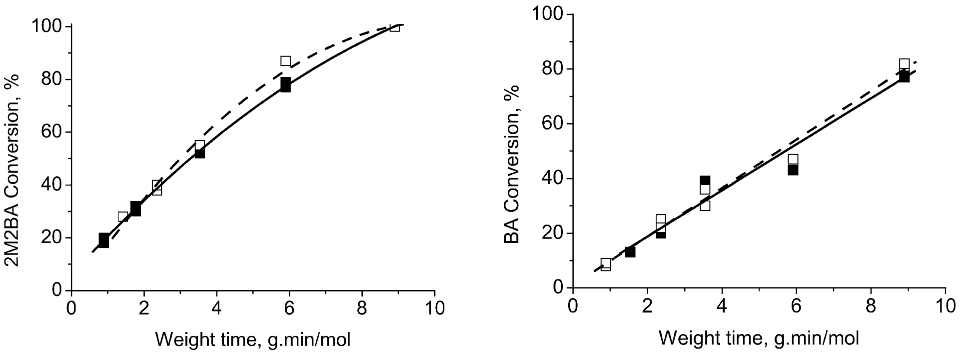


Fig. 10. Conversions in the HDN of 2-methyl-2-butylamine (2M2BA) and benzylamine (BA) at 270 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

that increased with increasing H_2S pressure. Its selectivity was 1.5% at $\tau = 0.9$ (g min)/mol and 100 kPa H_2S. Increasing the H_2S pressure from 10 to 100 kPa hardly influenced the conversion and product selectivities of 2-methyl-2-butylamine.

The conversion of 2-methyl-2-butanethiol at 270 °C in the presence of 10 kPa H_2S and 5 kPa hexylamine was much larger than that of the equivalent amine: It was already 66% at $\tau = 0.9$ (g min)/mol (Fig. 12), while the conversion of the corresponding amine was only 20% (Fig. 10). The conversion of 2-methyl-2-butanethiol decreased with increasing H_2S pressure. The main products at $\tau = 0.9$ (g min)/mol were 2-methyl-1-butene (35%), 2-methyl-2-butene (39%), and methylbutane (25%) (not shown). The methylbutenes/methylbutane ratio, obtained in the HDS of 2-methyl-2-butanethiol, was 3 at 270 °C and 10 kPa at $\tau = 0.9$ (g min)/mol, which is very different from the value of 16.5 obtained in the HDN of 2-methyl-2-butylamine under the same conditions (Fig. 13).

The conversion of benzylamine was lower than that of 2-methyl-2-butylamine at 270 °C (32% for benzylamine and 52% for 2-methyl-2-butylamine at $\tau = 3.4$ (g min)/mol) and was not influenced by the H_2S pressure (Fig. 10). The main product at 10 kPa H_2S was toluene (> 99%); only traces of α-toluenethiol (benzyl mercaptan), methylcyclohexene, and methylcyclohexane formed. At 100 kPa H_2S, the α-toluenethiol selectivity was 3% at low weight time and even smaller at high weight time. The conversion of

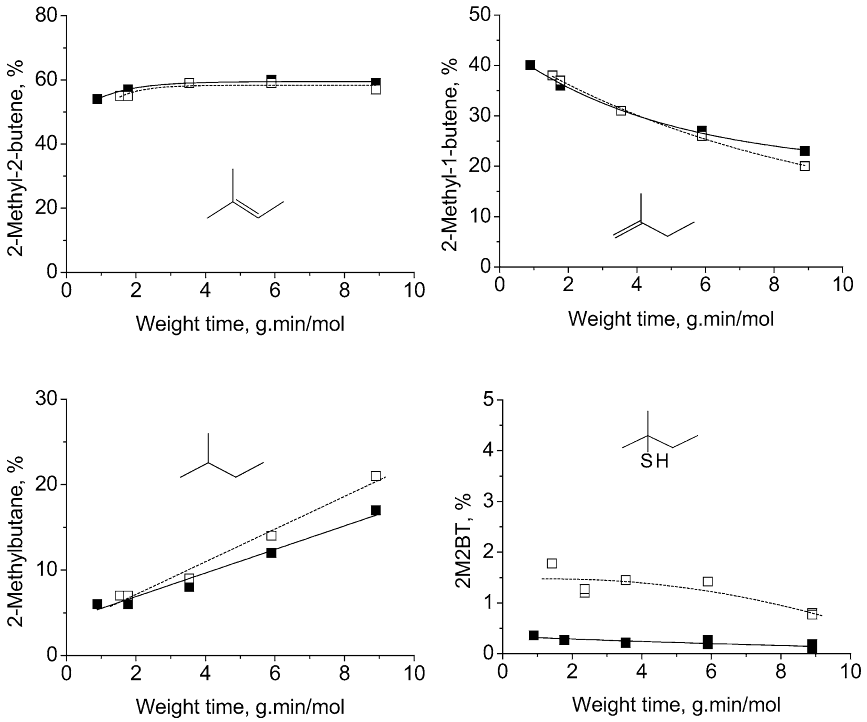


Fig. 11. Product selectivities in the HDN of 2-methyl-2-butylamine at 270 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

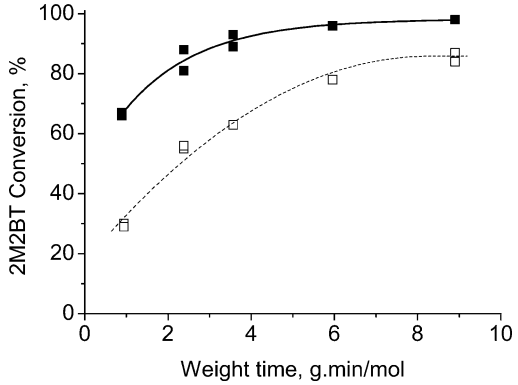


Fig. 12. Conversion in the HDS of 2-methyl-2-butanenethiol (2M2BT) in the presence of hexylamine at 270 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

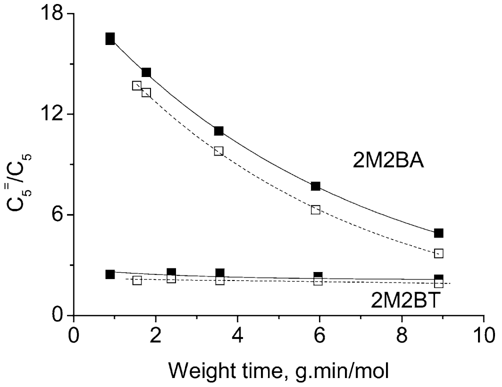


Fig. 13. Methylbutenes/methylbutane ratio in the HDN of 2-methyl-2-butylamine (2M2BA) and HDS of 2-methyl-2-butanethiol (2M2BT) in the presence of hexylamine at 270 °C (■ and □), and 10 kPa (drawn line) and 100 kPa H_2S (dashed line).

α-toluenethiol was 100% under all conditions at 270 °C, even at the lowest weight time, and toluene was the only product.

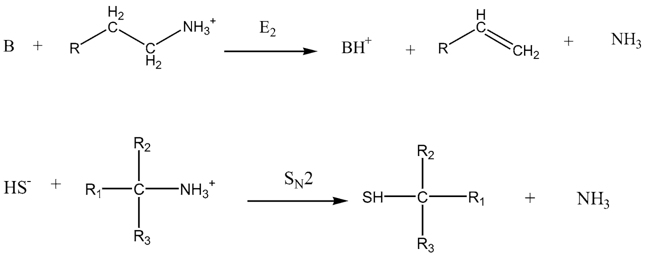
4. Discussion

4.1. HDN and HDS mechanisms

As shown above, the products of the HDN of alkylamines are dialkylamines, alkanethiols, alkenes, and alkanes, while alkenes and alkanes are the products of the HDS of alkanethiols. Dialkylamines and alkanethiols are formed by substitution of the NH_2 group in alkylamines by an alkylamine or H_2S, respectively. The alkenes can be formed by elimination of NH_3 from the alkylamines or of H_2S from the alkanethiols. The alkanes are formed by hydrogenolysis, which is the rupture of the C–N or C–S bond and simultaneous hydrogenation. Dialkylamines, alkanethiols, and alkenes can, in principle, form by acid–base catalysis as well as metal-like catalysis, while alkanes can only form by metal-catalyzed hydrogenolysis.

4.1.1. Acid–base mechanisms

In acid–base catalyzed elimination [1,3] and nucleophilic substitution [1,4] reactions of alkylamines, the amine group reacts first with a proton or a Lewis acid in order to create a better leaving group (in the subsequent schemes, only the reaction with a proton is indicated). Then a concerted bimolec-



Scheme 1. E2 and S_N2 reactions of an alkylamine to an alkene and alkanethiol.

ular reaction takes place in the E2 elimination as well as S_N2 nucleophilic substitution (Scheme 1), in which a base or nucleophile reacts with the protonated amine and ammonia is split off. In the E2 mechanism, the base subtracts a hydrogen atom from the β-carbon atom of the alkylamine. That is why this elimination can only occur when β-H atoms are present and why it was proposed that the HDN of alkylamines occurs faster when a greater number of β-H atoms is present [3]. In the S_N2 reaction, the base attacks the α-carbon atom of the alkylamine. In classic nucleophilic substitution this attack takes place from the backside of the molecule, at the side opposite to the leaving amine group, with inversion of the configuration at the α-carbon atom.

In the E1 elimination and S_N1 nucleophilic substitution mechanisms, ammonia splits off from the protonated amine in the rate-limiting step and forms a carbenium ion (Scheme 2). The carbenium ion quickly undergoes proton abstraction to form an alkene (E1), or it reacts with a nucleophile, such as H_2S or another alkylamine, to form an alkanethiol or dialkylamine, respectively (S_N1). E1 and S_N1 mechanisms are likely to occur only if relatively stable carbenium ions (such as a benzyl, allyl, or tertiary trialkyl carbenium ion) can be formed. Linear alkylamines will not react by E1 and S_N1 mechanisms, because they would lead to an unstable primary carbenium ion. Secondary alkylcarbenium ions are more stable than primary ions and may form from alkylamines with a secondary α-carbon atom. They will only form, however, if sufficiently strong acid sites are available and this is not the case on the surface of metal sulfides. On the other hand, HDN reactions are carried out at least 300 °C. Such temperatures, which are much higher than normally used for organic reactions, might increase the participation of carbenium ions [11].

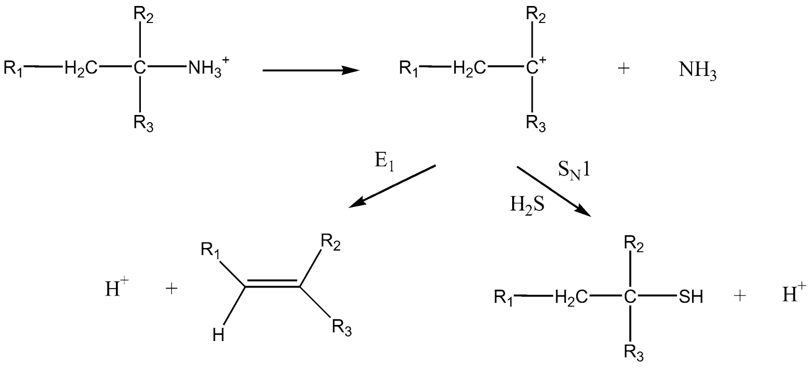
The E1 and E2 reactions of an alkylamine lead to an alkene and the S_N1 and S_N2 reactions to an alkanethiol or dialkylamine. The dialkylamine can undergo further nucleophilic substitution to give an alkanethiol. As this and other studies [9,12–15] have shown, alkanethiols react fast to alkenes and alkanes. Acid–base-catalyzed elimination explains the formation of an alkene from a thiol by an E1 or E2 reaction. In both cases, the reaction rate and, thus, the conversion might be positively influenced by the H_2S pressure. In the E1 reaction protonation of the SH group takes place before the rate-determining breaking of the C–S bond. As a consequence, the E1 reaction may be aided by H_2S. In the E2 reaction, a higher H_2S pressure increases the concentration of the S^{2-} or SH^- base at the catalyst surface. However, in the HDS reactions that we studied, H_2S had a strong negative influence on the conversion of all n-alkanethiols, be it primary, secondary, or tertiary alkanethiols (Table 1). This must be due to the fact that H_2S adsorbs rather strongly on the catalyst surface and inhibits the adsorption of the alkanethiol.

4.1.2. Metal-like mechanisms

Substitution and elimination of alkylamines can be catalyzed not only by acids and bases, but also by metals. Nucleophilic substitution can take place by a series of metal-catalyzed reactions: dehydrogenation of an amine to an imine, addition of H_2S, elimination of NH_3, and hydrogenation of the resulting thioaldehyde to a thiol (Eq. 1) [16]. Analogous reaction schemes for homogeneous catalysts have been proposed by Laine [17]:

$$R_1R_2CH\text{–}NH_2 \rightarrow R_1R_2C{=}NH \rightarrow R_1R_2C(SH)\text{–}NH_2,$$
$$R_1R_2C(SH)\text{–}NH_2 \rightarrow R_1R_2C{=}S \rightarrow R_1R_2CH\text{–}SH. \quad (1)$$

Furthermore, the elimination of NH_3 from an amine to form an alkene can be metal-catalyzed [2,5]. In a first step, C–N bond hydrogenolysis would take place. This is an easy reaction on metal catalysts [18]; on supported platinum, for example, it is already fast at around 150 °C [19]. The resulting alkyl fragment can lose a β-hydrogen atom and form an alkene, or it can add a hydrogen atom to form an alkane.



Scheme 2. E1 and S_N1 reactions of an alkylamine to an alkene and alkanethiol.

Both reactions are well known in Fischer–Tropsch catalysis by metals. The fast and reversible addition of the H atom to the alkene and rupture from the alkyl fragment explain the double-bond shift in the alkene. C–S bond breaking (hydrogenolysis) has also been demonstrated for the homogeneous $Cp^*_2Mo_2Co_2S_3(CO)_4$ cluster catalyst (Cp* stands for pentamethylcyclopentadienyl) [20].

4.2. HDN of amines with secondary α-carbon atoms

2-Pentanethiol and di-(2-pentyl)amine were primary products and pentane and pentenes were secondary products in the HDN of 2-pentylamine at 300 °C (cf. Fig. 2). The alkenes and alkane are formed from the corresponding alkanethiol, that is formed from the alkylamine

$$RNH_2 + H_2S \rightarrow RSH + NH_3 \tag{2}$$

and dialkylamine by substitution of the amine group by H_2S

$$RNHR + H_2S \rightarrow RSH + RNH_2. \tag{3}$$

The pentenes/pentane ratio in the HDN of 2-pentylamine was very similar to that obtained in the HDS of 2-pentanethiol in the presence of hexylamine (Fig. 4). This demonstrates that the branching ratio between alkenes and alkane is determined by the thiol and that the thiol is an intermediate between alkylamine and hydrocarbons.

At 340 °C, the pentenes behaved like a primary product (Fig. 2) due to the fast formation of pentenes from 2-pentanethiol (Fig. 3). The decrease in the selectivity of the alkenes and increase in the selectivity of the alkane with weight time at 340 °C (Fig. 2) is due to hydrogenation of the alkenes. At this elevated temperature the hydrogenation of the alkenes is relatively fast because of the high conversion (and thus decreased inhibition) of the alkylamine. The HDN of 2-pentylamine is, thus, similar to that of n-hexylamine [9]. This shows that amines with primary and secondary α-carbon atoms do not undergo elimination to alkenes or hydrogenolysis to an alkane.

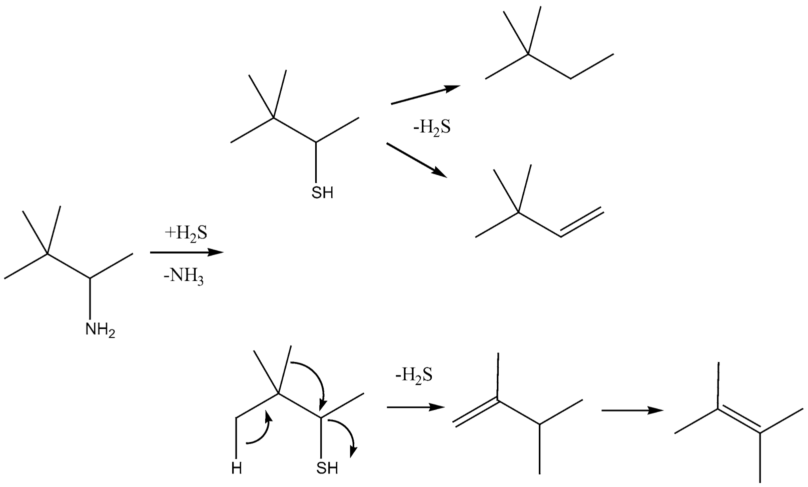
The reactions of 3-methyl-2-butylamine, 2-methylcyclohexylamine, and 3,3-dimethyl-2-butylamine showed many similarities (cf. Figs. 5, 8, 9). The conversions vary within a factor of 3 in the order 3-methyl-2-butylamine > 2-methylcyclohexylamine > 3,3-dimethyl-2-butylamine (Table 1). Alkanethiol and dialkylamine are primary products (nonzero selectivities at $\tau = 0$) and alkenes and alkane are primary as well as secondary products (increasing selectivity with τ). The initial alkene selectivities at 300 °C and 100 kPa H_2S were about 22% for 3-methyl-2-butylamine, 8% for 2-methylcyclohexylamine, and 34% for 3,3-dimethyl-2-butylamine. The nonzero selectivities of the alkenes at $\tau = 0$ are due either to direct elimination of NH_3 from the respective alkylamine or to a relatively slow reaction of the alkylamine to the corresponding alkanethiol followed by a fast reaction of this thiol to the alkenes. The latter seems more feasible, because it is hardly likely that 2-pentylamine does not undergo elimination, but that the introduction of a methyl group on the neighboring β-carbon atom induces such a change in the mechanism. The higher initial selectivities at 340 °C than at 300 °C are, thus, due to an even faster formation of alkenes from the alkanethiol and the decrease with weight time at 340 °C to a relatively fast hydrogenation of the alkenes. This agrees with the fact that the HDS rates of the alkanethiols decrease less than the conversions of the corresponding alkylamines as a result of methyl substitution (Table 1). Thus, the HDS of the intermediate is relatively faster for the methyl-substituted thiol than for the unsubstituted thiol and the final secondary products tend to behave like primary products.

Table 1
Conversions and effect of H_2S on conversion at time τ, and product selectivities at $\tau = 1$ (g min)/mol

Reactant	T (°C)	τ ((g min)/mol)	Conversion (%)	Effect H_2S	$C_n^{=}/C_n$	Selectivity (%)	
						RNHR	RSH
2M2BA	270	3	30	(+)	16.5	0	0
	300	1	46	(+)	16	0	0
2M2BT	270	1	65	−−	3.0		
BA	270	3	25	0	0	0	0
TT	270	1	100		0		
2PA	300	3	27	(+)	2.9	80	2
	340	3	75	+		35	1
2PT	300	1	83	−−	2.9		
	340	1	95				
3M2BA	300	3	18	+	3.5	45	9
	340	3	70	+	3.5	10	3
3M2BT	300	1	75	−−	2.5		
	340	1	100	−−	3.2		
2MCHA	300	3	10	(+)	1.0	38	4
	340	1	55	(+)	3.5	10	1
3,3DM2BA	300	3	5	+	1.5	0	10
	340	3	35	+	4.1	0	2
HA [9]	300	3	8	−	0.9	22	10
	320	3	24	(−)	1.3	20	7
HT	300	1	90	−−	2.0		
	320	1	100		2.0		
DHA [9]	300	1	55		0.8	14*	7
THA [9]	300	1	55	+	0.8	58	7

0, H_2S hardly influences conversion; (+), H_2S has a weak positive influence; +, H_2S has a positive influence; (−), H_2S has a weak negative influence; −, H_2S has a negative influence; −−, H_2S has a strong negative influence.

Furthermore, the alkenes/alkane ratio, obtained in the HDN of 3-methyl-2-butylamine, is about the same as that obtained in the HDS of the corresponding 3-methyl-2-butanethiol (Fig. 6) and similar to the alkenes/alkane ratio obtained in the HDN of 2-pentylamine (Fig. 4). These ratios of the alkylamines and alkanethiols with a secondary α-C atom are much lower than the ratio obtained for 2-methyl-2-butylamine, an alkylamine with a tertiary α-C atom (cf. Section 4.3). In Section 4.3 we will show that the latter alkylamine reacts by direct elimination of ammonia. The alkenes/alkane ratios thus confirm that the alkylamines with a secondary α-C atom do not react by elimination of ammonia.

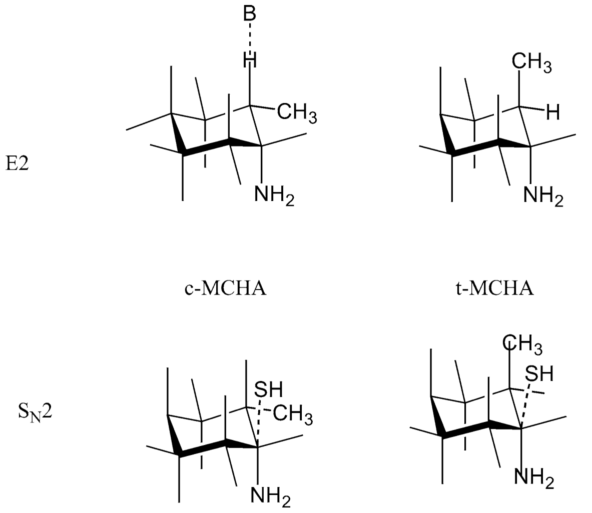


Scheme 3. Reaction network of 3,3-dimethyl-2-butylamine.

The amines with secondary α-carbon atoms reacted faster than the primary n-hexylamine [9] but much slower than 2-methyl-2-butylamine with a tertiary α-carbon atom and the activated benzylamine (Section 3.5). 2-Pentylamine and 3,3-dimethyl-2-butylamine, both with secondary α-carbon atoms, reacted four times faster at 300 °C than n-hexylamine and neopentylamine [21], both with primary α-carbon atoms, respectively (Table 1). This indicates that a pure S_N2 mechanism cannot be responsible for the reaction of 2-pentylamine and 3,3-dimethyl-2-butylamine. In a pure S_N2 mechanism the extra methyl group on the α-carbon atom would hinder the approach of a nucleophile, and the rate of reaction of the alkylamine with a secondary α-carbon atom would be lower than that of the corresponding alkylamine with a primary α-carbon atom [22]. The higher rates of the amines with secondary α-carbon atoms are probably due to a weakening of the C–N bond because of the higher ionic character of the C–N bond for a secondary carbon atom. The limit would be the dissociation of the amine group with the formation of a secondary carbenium ion. This extreme situation did not occur, however, for the amines in this study. In that case, an S_N1 or E1 reaction would have taken place and H_2S would not have influenced the reaction rate.

The Wagner–Meerwein-type rearrangement of the carbon skeleton in the reaction of 3,3-dimethyl-2-butylamine is ascribed to a nucleophilic substitution to 3,3-dimethyl-2-butanethiol, followed (partly) by γ elimination aided by the neighboring group effect of the methyl groups on the β-carbon atom (Scheme 3), analogous to reactions of branched alcohols [23]. As to be expected, the rearrangement in the reaction of 2-methyl-3-pentylamine was much less pronounced ($< 1\%$).

The HDN of cyclohexylamine and 2-methylcyclohexylamine and the HDS of the corresponding thiols were described recently [15,24]. These compounds also have secondary α-carbon atoms. The removal of ammonia from cyclohexylamine and 2-methylcyclohexylamine was mainly (60–70%) ascribed to an E2 elimination reaction to cyclohexene and methylcyclohexenes, respectively, because *cis*-2-methylcyclohexylamine (c-MCHA) reacted much faster to 1-methylcyclohexene than *trans*-2-methylcyclohexylamine (t-MCHA) [24]. Elimination is assumed to occur with the β-H atom in an antiperiplanar configuration relative to the axial NH_2 group. As the conformations in Scheme 4 show, the elimination of c-MCHA should then be faster than that of t-MCHA because of the presence of the hydrogen atom on the tertiary carbon atom in the antiposition to the amine group [24]. In t-MCHA the methyl group occupies this anti position and cannot be eliminated. It was overlooked, however, that nucleophilic substitution of the amine group by an SH group may also explain the faster reaction of c-MCHA. As in the antiperiplanar E2 elimination, S_N2 substitution can only occur when the leaving group is in the axial position (Scheme 4). In that case, the methyl group in the antiposition in t-MCHA hinders the approach of an SH nucleophile from the backside of the carbon atom bearing the amine group and, thus, the S_N2 reaction should also be faster



Scheme 4. E2 and S_N2 reactions of *cis*- and *trans*-2-methylcyclohexylamine.

for c-MCHA than for t-MCHA. Thus, our conclusion, that 2-methylcyclohexylamine reacts by substitution and not by elimination, does not contradict the experimental results described in Refs. [15,24].

4.3. HDN of 2-methyl-2-butylamine and benzylamine

2-Methyl-2-butylamine and benzylamine reacted much faster than the other amines studied. Whereas 2-pentylamine, 3-methyl-2-butylamine, 3,3-dimethyl-2-butylamine, and 2-methylcyclohexylamine (all with secondary α-carbon atoms) did not show appreciable conversion below 300 °C, 2-methyl-2-butylamine, with a tertiary α-carbon atom, already reached a conversion of 30% at $\tau = 3$ (g min)/mol at 270 °C. The product distribution was also different. For the most part, alkenes (2-methyl-1-butene and 2-methyl-2-butene) and an alkane (methylbutane), but no di-(2-methyl-2-butyl)amine, and only a trace of 2-methyl-2-butanethiol were observed. This behavior indicates that 2-methyl-2-butylamine, with a tertiary α-carbon atom, reacts by a different mechanism than the amines with secondary α-carbon atoms. Furthermore, because H_2S does not influence the reaction rate, the most likely mechanisms are E1 elimination and S_N1 nucleophilic substitution.

If 2-methyl-2-butylamine were to react by a classic organic E1 or S_N1 mechanism, then it would be protonated and would react by ammonia removal to the tertiary isopentyl carbenium ion (Scheme 2). In the E1 mechanism, this ion would then react further to 2-methyl-1-butene and 2-methyl-2-butene by proton removal and the formation of methylbutane would be unaccounted for. However, on the metal sulfide surface, the 2-methyl-2-butylamine adsorbs with the nitrogen lone pair on an Mo or Ni atom. After C–N bond breaking, the isopentyl carbenium ion will either move to a neighboring Mo or Ni atom or to a sulfur atom. If the carbenium ion binds to a metal atom, an electron transfer reaction may take place with the formation of the isopentyl radical. As in Fischer–Tropsch chemistry on a metal surface [2], this alkyl radical may react to an alkene by removal of a hydrogen atom, or it may add a hydrogen atom and become an alkane. If the carbenium ion binds to a sulfur atom, then adsorbed 2-methyl-2-butanethiol forms and the mechanism changes to the S_N1 type. 2-Methyl-2-butanethiol can react to 2-methylbutenes as well as to methylbutane.

The methylbutenes/methylbutane ratio of the products of the HDN of 2-methyl-2-butylamine was about five times larger than that obtained in the HDS of the corresponding 2-methyl-2-butanethiol (Fig. 13). This demonstrates that the methylbutenes/methylbutane ratio in the HDN is not determined by the thiol and that 2-methyl-2-butylamine reacts by an E1 rather than an S_N1 mechanism. In agreement with this conclusion, only 0.3% thiol was observed in the HDN of 2-methyl-2-butylamine in the presence of 10 kPa H_2S at $\tau = 1$ (g min)/mol; even in the presence of 100 kPa H_2S, the initial selectivity of the thiol was only 1.5% (Fig. 11). Fig. 12 demonstrates that 2-methyl-2-butanethiol reacts rather slowly in the presence of 100 kPa H_2S. Thus, if this thiol had been an intermediate in the HDN of 2-methyl-2-butylamine, then a quantity larger than 1.5% would have been observed.

Benzylamine cannot react by elimination, because it has no β-hydrogen atoms. The high reaction rate and lack of an effect of the H_2S pressure suggest that benzylamine does not react by an S_N2 but by an S_N1 reaction. Protonation of the amine group and the removal of ammonia would lead to the relatively stable benzyl carbenium ion. As indicated above for the isopentyl carbenium ion, the benzyl carbenium ion will move to a neighboring Mo or Ni atom or to a sulfur atom. If it binds to a metal atom, an electron-transfer reaction may take place with the formation of the benzyl radical, which can be hydrogenated to toluene. If the carbenium ion binds to a sulfur atom, adsorbed α-toluenethiol forms and may react to toluene.

5. Conclusions

Our former [9] and present results show that alkylamines with the NH_2 group attached to a primary or secondary carbon atom react by substitution of the NH_2 group by an SH or amine group to form an alkanethiol or a dialkylamine. After subsequent substitution by H_2S the dialkylamine also reacts to an alkanethiol. The alkanethiol finally reacts to an alkene or alkane and H_2S. Only an alkylamine with the NH_2 group attached to a tertiary or activated carbon atom reacts directly to an alkene or alkane. The C–N bonds of alkylamines with primary and secondary α-carbon atoms are too strong to be easily broken. For such alkylamines elimination is, therefore, too difficult and they react by other mechanisms. The stabilization of the tertiary or benzyl carbenium cation is necessary to weaken the C–N enough for elimination to take place.

The proposal by Portefaix et al. [3], that alkylamines react by elimination and that the number of β-H atoms determines their HDN rate, is thus incorrect. The fact that 2-methyl-2-butylamine reacts much faster than n-pentylamine has nothing to do with the four times larger number of β-H atoms but has everything to do with the fact that the NH_2 group of the former amine is attached to a tertiary α-C atom and the NH_2 group of the latter amine to a primary α-C atom. Even when elimination occurs, as for 2-methyl-2-butylamine, the selectivity for 2-methyl-2-butene is higher than that for 2-methyl-1-butene, although there are three times more β-H atoms on the terminal methyl groups than on the internal methylene group. We checked that this is not due to a fast isomerization of 2-methyl-1-butene to 2-methyl-2-butene. The higher selectivity for 2-methyl-2-butene is due to the fact that in an E1 mechanism the leaving group is gone before the proton. The product is thus determined by thermodynamic factors and Zaitsev's rule applies: the double bond goes preferentially to the most highly substituted carbon atom. We conclude therefore that the number of β-H atoms, as proposed by Portefaix et al., does not determine the HDN rate of the alkylamines. In alkylamines with primary and secondary α-C atoms the number of β-H atoms is of no importance, because substitution rather than E2 elimination takes place. In alkylamines with a tertiary α-C atom the reverse occurs: the hydrogen atom is preferentially removed from the β-C atom with the lowest number of β-H atoms!

Even though elimination of the NH_2 group from an alkylamine does not take place when it is attached to a primary or secondary carbon atom, removal of nitrogen does take place for such alkylamines. The substitution of the NH_2 group by H_2S leads to an alkanethiol and ammonia and, thus, to total denitrogenation. Substitution by an amine leads to a dialkylamine and ammonia and to 50% nitrogen removal. The rest of the nitrogen is removed in the subsequent substitution of the dialkylamine by H_2S to an alkanethiol and the original alkylamine. High partial pressures of H_2S and alkylamine increase the rate of transformation of alkylamine to alkanethiol and, thus, of denitrogenation. At the same time, however, the rate of sulfur removal from the alkanethiol decreases.

While we have pinpointed the types of reactions that alkylamines undergo, we have not answered the question as to how these reactions are catalyzed by the supported metal sulfide. Our future work will address the question of how the substitution of the NH_2 group by H_2S takes place on the surface of nickel- and cobalt-promoted and unpromoted MoS_2.

Acknowledgments

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References

[1] N. Nelson, R.B. Levy, J. Catal. 58 (1979) 485.

[2] H. Schulz, M. Schon, N.M. Rahman, Stud. Surf. Sci. Catal. 27 (1986) 201.

[3] J.L. Portefaix, M. Cattenot, M. Guerriche, J. Thivolle-Cazat, M. Breysse, Catal. Today 10 (1991) 473.

[4] L. Vivier, V. Dominguez, G. Perot, S. Kasztelan, J. Mol. Catal. 67 (1991) 267.

[5] R. Prins, Adv. Catal. 46 (2001) 399.

[6] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick, B.C. Gates, AIChE J. 24 (1978) 1015.

[7] J. Mijoin, G. Pérot, F. Bataille, J.L. Lemberton, M. Breysse, S. Kasztelan, Catal. Lett. 71 (2001) 139.

[8] M. Cattenot, J.L. Portefaix, J. Afonso, M. Breysse, M. Lacroix, G. Perot, J. Catal. 173 (1998) 366.

[9] Y. Zhao, P. Kukula, R. Prins, J. Catal., in press.

[10] M. Egorova, Y. Zhao, P. Kukula, R. Prins, J. Catal. 206 (2002) 263.

[11] H. Knözinger, A. Scheglila, J. Catal. 17 (1970) 252.

[12] P. Desikan, C.H. Amberg, Can. J. Chem. 42 (1964) 843.

[13] D.L. Sullivan, J.G. Ekerdt, J. Catal. 178 (1998) 226.

[14] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.

[15] F. Rota, R. Prins, J. Catal. 202 (2001) 195.

[16] R. Prins, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, Wiley–VCH, New York, 1997, p. 1916.

[17] R.M. Laine, Catal. Rev.-Sci. Eng. 25 (1983) 459.

[18] G. Meitzner, W.J. Mykytka, J.H. Sinfelt, J. Catal. 98 (1986) 513.

[19] Triyono, R. Kramer, Appl. Catal. A 100 (1993) 145.

[20] M.D. Curtis, S.H. Druker, J. Am. Chem. Soc. 119 (1997) 1027.

[21] Y. Zhao, J. Czyzniewska, R. Prins, Catal. Lett. 88 (2003) 155.

[22] J. Clayden, N. Greeves, S. Warren, P. Wothers, Organic Chemistry, Oxford Univ. Press, London, 2001.

[23] H. Pines, J. Manassen, Adv. Catal. 16 (1966) 49.

[24] F. Rota, V.S. Ranade, R. Prins, J. Catal. 200 (2001) 389.