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Investigation of the steric course of the C–N bond breaking in the hydrodenitrogenation of alkylamines

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Abstract

The steric course of the hydrodenitrogenation reactions of 2-(*R*)- and 2-(*S*)-butylamine to 2-butanethiol and di-*sec*-butylamine was studied at 3 MPa and 300 °C over sulfided NiMo/γ-Al_2O_3. After separation of the thiol from the dialkylamine and unreacted alkylamine, the chirality of the thiol and unreacted alkylamine was determined by analysis of the diastereomers formed by reaction with Moscher's acid chloride, (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride. The dialkylamine was analyzed by direct chiral chromatography without derivatization, using another type of chiral column. When 2-(*S*)-butylamine was used as reactant, the 2-butanethiol product was completely racemic, whereas the di-*sec*-butylamine consisted of 48% (*R*,*S*), 32% (*S*,*S*), and 20% (*R*,*R*) isomers and the 2-butylamine of 70% (*S*) and 30% (*R*) isomers. These results cannot be explained by a classic S_N2 substitution mechanism. Two similar mechanisms can explain all products and their configurations, as well as the racemization of the amine reactant. In one mechanism the amine first reacts by dehydrogenation to an imine, whereas in the other the amine first reacts by electron and proton transfer to an imine cation. Thereafter, the addition of H_2S or an amine molecule to the imine or to the imine cation occurs, and, after ammonia or amine elimination and hydrogenation, a thiol or a dialkylamine is formed.

Keywords: Hydrodenitrogenation; NiMo/γ-Al_2O_3; Substitution; Mechanism; Steric course; 2-Butylamine; Chiral separation

1. Introduction

Hydrodenitrogenation (HDN) and hydrodesulfurization reactions occur in the hydrotreating of oil fractions, one of the most important catalytic processes in the petroleum industry. In HDN, first the heterocyclic ring of a nitrogen-containing aromatic molecule is hydrogenated, and then the aliphatic C–N bond is cleaved [1–9]. Hofmann-type elimination and nucleophilic substitution have been proposed as mechanisms for the C–N bond cleavage and nitrogen removal [1,10–12]. Elimination of the NH_2 group and a β-hydrogen atom from an alkylamine leads to an alkene and ammonia, whereas nucleophilic substitution of the NH_2 group at the α-carbon atom by H_2S forms an alkanethiol and ammonia. Evidence for elimination as well as nucleophilic substitution has been presented in the literature [6,7,13–15]. Alkenes as well as alkanes, but only a small amount of thiols, have been observed in many HDN studies. The presence of alkenes and the higher conversion of alkylamines with a larger number of β-hydrogen atoms in HDN experiments at elevated pressure was considered proof that C–N bond cleavage in alkylamines occurs mainly by Hofmann elimination [6,13]. The presence of alkanes was explained by nucleophilic substitution by H_2S followed by C–S bond hydrogenolysis of the resulting thiols. Alkenes and dialkylamines were observed as primary products in the HDN of pentylamines on unsupported transition-metal sulfides at atmospheric pressure [15]. The alkenes were again considered proof of elimination, and the dialkylamines were considered proof of nucleophilic substitution. The fast formation of toluene from benzylamine, which does not have β-hydrogen atoms and thus cannot react by elimination, was ascribed to nucleophilic substitution of the amine group by H_2S or an SH group on the catalyst surface, followed by rapid hydrogenolysis of the intermediate thiol [7].

Recently we showed that alkylamines with the amine group attached to a primary or a secondary carbon atom and that

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have β-hydrogen atoms do not react by elimination at temperatures around 300 °C and pressures of 1–5 MPa, but rather react by nucleophilic substitution by H_2S [16–18]. By measuring at short contact times and analyzing the product selectivities, it was proved that alkanethiols are the primary products and that the alkenes and alkanes are 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 thus in the past these molecules were taken for primary products. In agreement with the conclusion that substitution and not elimination is the primary reaction of alkylamines, ring opening of 2-methylpiperidine occurred mainly on the CH_2–N side and not on the $CH(CH_3)$–N side, although the latter has 2.5 times more β-hydrogen atoms [19].

How the substitution of the amine group by H_2S occurs at the catalyst surface has not been studied. In analogy to reactions of amines catalyzed by transition-metal complexes, one might suppose that the catalyst weakens the C–N bond through bonding of the amine group to a metal atom on the catalyst surface. Ammonia removal by attack of H_2S at the α-carbon atom then becomes easier. In such a metal-ion catalyzed substitution reaction, Walden inversion of a chiral alkylamine molecule may occur, and a thiol will be formed with the opposite chiral configuration from the alkylamine at the α-carbon atom. In contrast, the substitution may also proceed in several steps through an imine intermediate. In that case, the amine is dehydrogenated to an imine, H_2S is added to the imine to form a thio-hemiaminal, which is deaminated, and the resulting thioketone is hydrogenated to the thiol [9]. The chirality of the amine is lost during the formation of an imine intermediate, and the thiol is racemic.

To determine the mechanism responsible for the HDN reaction, we studied substitution of the optically pure isomers of 2-butylamine by analysis of the stereochemistry of the formed products. We started with racemic 2-butylamine to determine the reaction conditions under which a substantial amount of thiol and dibutylamine is formed. Then HDN experiments with pure 2-(*R*)- and 2-(*S*)-butylamine were carried out, and the optical configurations of the resulting 2-butanethiol and di-*sec*-butylamine products, as well of the remaining nonconverted 2-butylamine, were determined. A preliminary report of our results has been published as priority communication [20]; here we describe the experiment and our results in more detail.

2. Experimental

2.1. Reaction conditions

The NiMo/γ-Al_2O_3 catalyst (8 wt% Mo and 3 wt% Ni) was prepared by a two-step pore-volume impregnation of γ-Al_2O_3 (Condea, pore volume 0.5 cm^3/g, specific surface area 230 m^2/g). The catalyst was crushed and sieved to a 230-mesh (<0.063-mm) particle size. Further details of the catalyst preparation have been reported previously [16]. 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 (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 MPa, and the liquid reactant was fed to the reactor through a high-pressure syringe pump (ISCO 500D). The partial pressures of octane and heptane [which were used as a solvent and an internal standard for gas chromatography (GC) analysis] were maintained at 185 and 20 kPa, respectively. The partial pressures of 2-butylamine and H_2S were 5 and 100 kPa respectively, whereas the pressure of H_2 was 2.69 MPa. The experiments were carried out at 300 °C. All chemicals (from Aldrich and Fluka) were used without further purification. The weight time, defined as the ratio between the catalyst weight and the total molar flow fed to the reactor [18], was varied by changing the flow rates of the liquid and the gaseous reactants while keeping their ratio constant. Before each new experiment, the reactor was cleaned by purging with the solvent (octane) and the H_2S/H_2 gas mixture for 12 h at reaction temperature, and samples were taken and analyzed by gas chromatography–mass spectroscopy (GC-MS) to check whether any impurities remained in the reactor.

The HDN reactions of the (*R*)- and (*S*)-isomers of 2-butylamine over NiMo/γ-Al_2O_3 were carried out at a weight time of 3.38 g min/mol (0.15 ml/min feed over 0.05 g catalyst) at 300 °C. Under these conditions, the yields of thiol and dibutylamine were sufficient to enable their analysis. 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 [16]. For instance, the selectivity of di-*sec*-butylamine is 100% in the reaction $2C_4H_9NH_2 \rightarrow (C_4H_9)_2NH + NH_3$, because all of the carbon atoms of the reactant (2-butylamine) react to the same product (di-*sec*-butylamine).

2.2. Product analysis

The HDN reaction products were analyzed by on-line GC on a Varian 3800 instrument equipped with a CP-Sil 8CB (50 m × 0.25 mm × 0.25 µm) capillary column. The following temperature program was used to separate the reaction products: initial temperature 35 °C kept constant for 15 min and then raised at rate of 5 °C/min to 160 °C and then at 30 °C/min to 280 °C, where it was maintained for 1 min. The helium pressure was 66 kPa, the split ratio was 30:1, and the injection, FID, and PFPD temperatures were 280, 280, and 220 °C, respectively. MS was used to identify the reaction products [16].

The chirality of the 2-butanethiol product and remaining 2-butylamine educt was determined from the conformations of the diastereomers formed by derivatization with Moscher's acid chloride, (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl-chloride. The diastereomers were prepared by adding 1–2 µL of Moscher's acid chloride to a vial with 2 or 3 drops of organic phase. The vial was closed and heated at 70 °C for 45 min. The derivatization procedure was first carried out with racemic 2-butanethiol, 2-(*R*)-butylamine, and 2-(*S*)-butylamine to characterize the formed diastereomers by their GC reten-

tion times and, in the case of the 2-butylamines, also by their mass spectrum. Then the analysis of the HDN product mixture was performed. This analysis was done on an Agilent GC-MS with a chiral β-DEX 120 capillary column (Supelco, 30 m × 0.25 mm × 0.30 µm. The initial temperature of 50 °C was kept constant for 5 min and then increased at a rate of 5 °C/min to 230 °C, where it was maintained for another 30 min. The helium pressure was 45 kPa, the helium flow rate was 1 ml/min, the split ratio was 20:1, and the injection, transfer line, and MSD temperatures were 260, 270, and 150 °C, respectively. MS of 2-butanethiol did not reveal any characteristic fragments, and thus we had to rely only on the retention time of the product obtained by the reaction with the standard compound. The retention times of the formed diastereomers were 32.17 min for 2-(*S*)-butylamine and 32.36 min for 2-(*R*)-butylamine. Two peaks at 31.88 and 32.08 min were from 2-butanethiol. Because no commercial samples of 2-(*R*)- or 2-(*S*)-butanethiol were available, we do not know which of these peaks belongs to 2-(*R*)- or 2-(*S*)-butanethiol.

The derivatization procedure was not as convenient in the case of di-*sec*-butylamine as in the case of the primary amine, because significant formation of various byproducts was observed. Therefore, we separated all isomers of di-*sec*-butylamine directly by chiral GC using another type of chiral column [CP-Chirasil-DEX CB (Varian); 25 m × 0.25 mm × 0.25 µm]. The following temperature program was used: 35 °C (5 min), 9 °C/min to 180 °C (5 min). The helium pressure was 100 kPa, the helium flow rate was 1.7 ml/min, the split ratio was 50:1, and the injector and detector temperatures were kept at 200 and 250 °C, respectively. The retention times were 11.00 min for (*R*,*R*)-di-*sec*-butylamine, 11.08 min for (*S*,*S*)-di-*sec*-butylamine, and 11.17 min for (*R*,*S*)-di-*sec*-butylamine.

3. Results

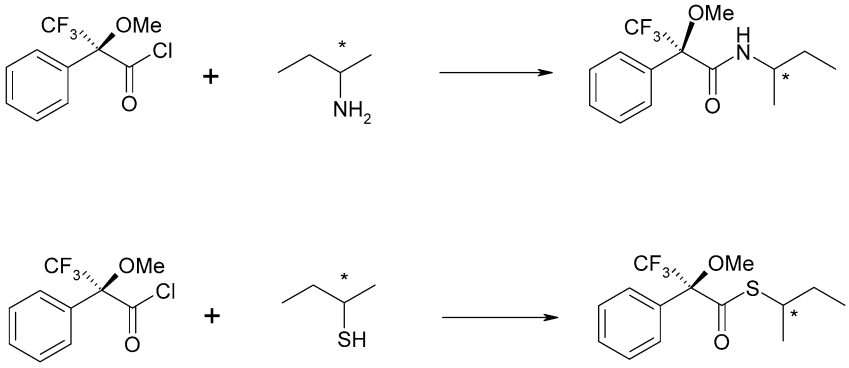
In accordance with our former work on 2-pentylamine [17], the HDN reaction of 2-butylamine over sulfided NiMo/γ-Al_2O_3 at 300 °C gave butane, 1-butene, *cis*-2-butene, *trans*-2-butene, 2-butanethiol, and di-*sec*-butylamine as products; their amounts were quantified using internal standards. The reaction conditions for the HDN of racemic 2-butylamine were optimized to obtain reasonable yields of 2-butanethiol and di-*sec*-butylamine. At 300 °C, 5 kPa 2-butylamine, 100 kPa H_2S, and a weight time of 3.4 g min/mol (i.e., 0.15 ml/min total feed over 0.05 g catalyst) sufficient product was obtained for qualitative analysis. Under these conditions, the product consisted of 29% butane and butenes, 33% 2-butanethiol, and 38% di-*sec*-butylamine at a conversion of 28%.

The products obtained from the reactions of the pure 2-(*R*)- and 2-(*S*)-butylamine enantiomers contained approximately the same amounts of reaction components as the product of the racemic 2-butylamine. First, the product samples were analyzed as obtained from the reaction, and then the amines were separated by extraction to increase their concentration before derivatization. A 2-ml sample of product was extracted with 2 ml of a 1-M HCl solution. The remaining organic layer, which contained the thiols, was separated and dried with Na_2SO_4, then subjected to reaction with Moscher's acid chloride, the chiral derivatization reagent (Scheme 1). The water phase, in which the amines were present as chloride salts, was made basic with a 2 M NaOH solution and extracted with 2 ml of octane. After separation from the water layer, the octane phase was dried and derivatized with Moscher's acid chloride in the same way as done for the organic phase that contained the thiols.

Fig. 1a shows the chromatogram of the diastereomers obtained from reaction of Moscher's acid chloride with the organic phase containing 2-butanethiol. The equal size of the two peaks demonstrates that the 2-butanethiol formed in the reaction of 2-(*S*)-butylamine was racemic. The same result was obtained when carrying out the reaction with 2-(*R*)-butylamine, demonstrating that the reaction was not stereoselective.

The chirality of the 2-butylamine that remained in the reaction product was analyzed in the same way as that of the 2-butanethiol product, by reaction with Moscher's salt (Scheme 1) and analysis of the resulting diastereomers. Fig. 1b shows that the optical purity of the remaining 2-(*S*)-butylamine decreased during the HDN reaction. We observed $(R)/((R) + (S)) = 0.3$ at the weight time of 3.4 g min/mol, meaning that 60% racemization had occurred. The same degree of racemization was obtained when starting with 2-(*R*)-butylamine (Fig. 1c).

Because the concentration of di-*sec*-butylamine in the reaction product was low, the solvent had to be partly evaporated before the analysis was conducted. Because the derivatization procedure proved complicated, we analyzed the isomers of di-*sec*-butylamine directly by chiral GC. The chromatogram of racemic di-*sec*-butylamine showed three isomers,



Scheme 1. Derivatization of 2-butylamine and 2-butanethiol with Moscher's acid chloride.

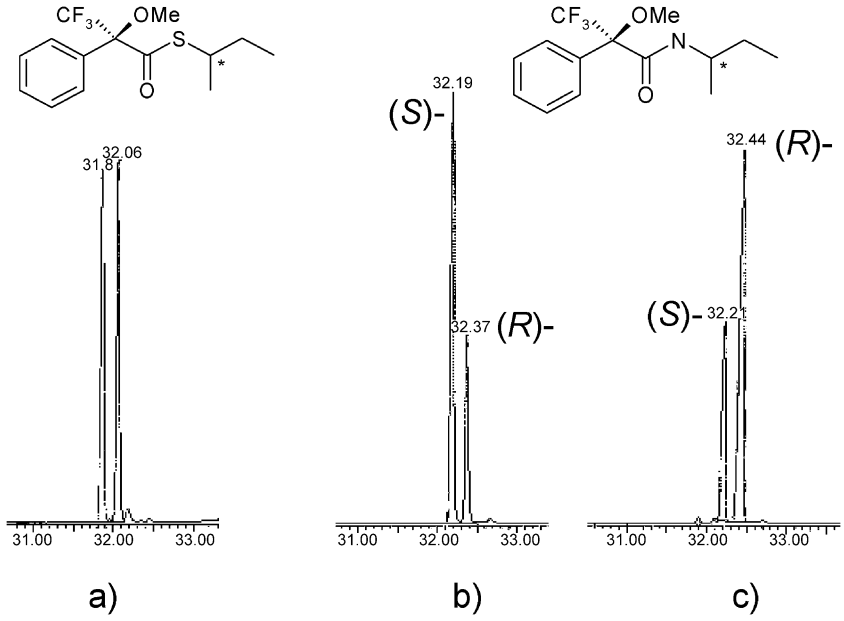


Fig. 1. Chromatograms of thiol and amine extracts from the HDN reaction of 2-(*S*)- and 2-(*R*)-butylamine after derivatization with Moscher's acid chloride: (a) thiol extract from the reaction of 2-(*S*)-butylamine; (b) and (c) amine extracts from the reaction of 2-(*S*)- and 2-(*R*)-butylamine, respectively.

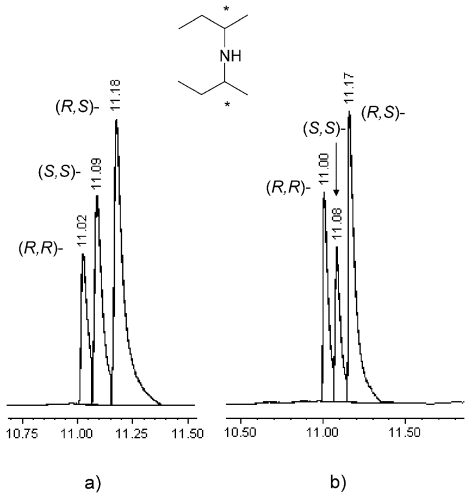


Fig. 2. Chiral separation of di-*sec*-butylamine isomers after the HDN reaction of 2-(*S*)-butylamine (a) and 2-(*R*)-butylamine (b).

Table 1
Stereoconfigurations of the 2-butanethiol and di-*sec*-butylamine products and of the reactant in the HDN of 2-(*S*)-butylamine* or 2-(*R*)-butylamine^{+}

2-Butanethiol$^{*,+}$	50% (*S*) + 50% (*R*) and vice versa
Di-*sec*-butylamine*	48% (*R*,*S*) + 32% (*S*,*S*) + 20% (*R*,*R*)
Di-*sec*-butylamine^{+}	50% (*R*,*S*) + 22% (*S*,*S*) + 28% (*R*,*R*)
2-Butylamine$^{*,+}$	70% (*S*) + 30% (*R*) and vice versa

25% (*R*,*R*)-, 25% (*S*,*S*)-, and 50% (*R*,*S*)-isomer (mesoform). When the HDN reaction was performed with chiral 2-(*S*)-butylamine, we obtained 20% (*R*,*R*)-, 32% (*S*,*S*)-, and 48% (*R*,*S*)-di-*sec*-butylamine and 28% (*R*,*R*)-, 22% (*S*,*S*)-, and 50% (*R*,*S*)-di-*sec*-butylamine when the reaction was performed with 2-(*R*)-butylamine (Fig. 2).

To prove that the catalyst, and not the support, is responsible for the observed reactions, we carried out an experiment in which only catalyst support (alumina) was placed in the reactor. Under the same reaction conditions, we observed no conversion or racemization of 2-(*R*)-butylamine. This means that the Ni–Mo sulfide phase is responsible not only for the catalytic activity in the HDN reaction, but also for the racemization of 2-butylamine.

4. Discussion

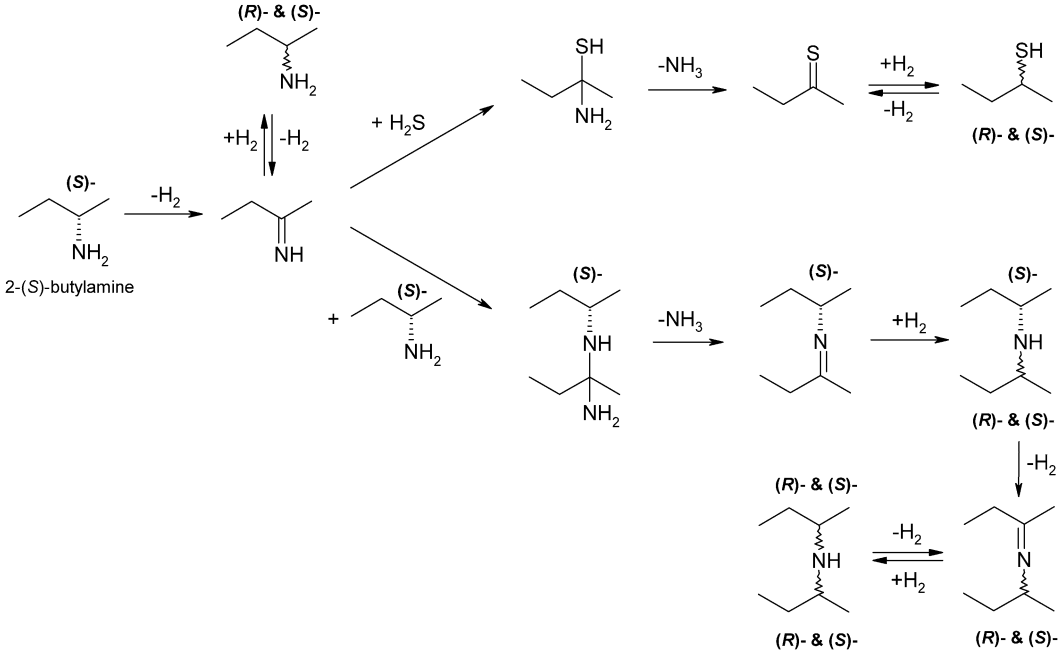
The equal amounts of 2-(*S*)-butanethiol and 2-(*R*)-butanethiol formed from pure 2-(*S*)-butylamine or 2-(*R*)-butylamine (Table 1) show that the formation of alkanethiol from alkylamine did not proceed stereoselectively. The reason for this may be that the nucleophilic substitution did not follow a purely S_N2 mechanism with Walden inversion, but rather proceeded partly by an S_N1 reaction. An S_N1 reaction can be excluded, however, because the partial pressure of H_2S was found to influence the reaction rate [16–18]. Another possibility is that the reaction proceeded through a mechanism in which the chirality of the α-carbon atom was lost. Determination of the stereoconfiguration of the unreacted 2-butylamine indeed showed that racemization of the reactant itself had occurred; however, the extent of racemization during the HDN reaction was insufficient to explain the observed equal amounts of 2-(*S*)-butanethiol and 2-(*R*)-butanethiol. If the racemization of the reactant 2-butylamine was the reason for the occurrence of both 2-(*S*)-butanethiol and 2-(*R*)-butanethiol, then one would expect an excess of 2-(*R*)-butanethiol (between 100 and 70%, the percentage of 2-(*S*)-butylamine in 2-butylamine observed at the exit of the reactor) for an S_N2 mechanism with Walden inversion from amine to thiol, or an equally large excess of 2-(*S*)-butanethiol in case of retention of configuration. We therefore conclude that the racemization occurred during the substitution reaction itself. A possible explanation for the racemization is that the amine-

to-thiol reaction went though a dehydrogenated intermediate. Dehydrogenation of 2-butylamine to 2-butylimine, followed by addition of H_2S would give a thio-hemiaminal (Scheme 2). Elimination of ammonia from this intermediate and hydrogenation of the resulting thioketone gives 2-butanethiol. The α-carbon atom is twice involved in a double bond, which explains the complete scrambling of the original chirality at this carbon atom.

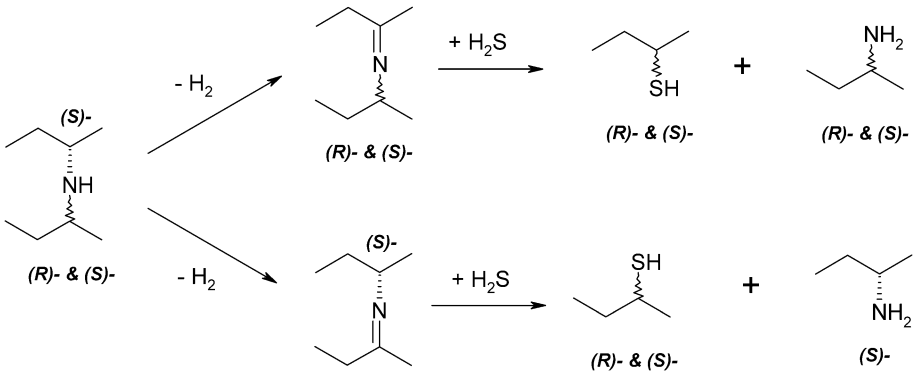
The formation of di-*sec*-butylamine cannot proceed by a classic organic disproportionation reaction, in which a 2-(*S*)-butylamine molecule reacts with another 2-(*S*)-butylamine molecule to di-*sec*-butylamine and ammonia, because in that case the only product would be (*R*,*S*)-di-*sec*-butylamine, the mesoform. The reason is that the molecule, which is attacked in an S_N2 reaction, changes its configuration while the chiral configuration of the attacking molecule does not change. The (*S*,*S*) and (*R*,*R*) isomers present in the reaction mixture (Table 1) can, in a classic S_N2 reaction, be formed only by the reaction between 2-(*S*)-butylamine and 2-(*R*)-butylamine formed by racemization of 2-(*S*)-butylamine. If an (*S*) molecule attacks an (*R*) molecule, then the di-*sec*-butylamine product has the (*S*,*S*) configuration, and if an (*R*) molecule attacks an (*S*) molecule, then the configuration of the resulting di-*sec*-butylamine is (*R*,*R*). This means that for an S_N2 mechanism, the amounts of (*S*,*S*) and (*R*,*R*) should be equal, which was not the case. In addition, the observed percentage of the (*R*,*S*) isomer was too low (48%) and that of the (*S*,*S*) isomer was too high (32%); namely, the differential selectivity of the (*R*,*S*) isomer was $(1-\alpha)^2+\alpha^2$ and that of the (*S*,*S*) and (*R*,*R*) isomers was $\alpha(1-\alpha)$, in which α is the instantaneous molar $(R)/((S)+(R))$ ratio. Thus, in an S_N2 reaction and with 60% racemization of 2-(*S*)-butylamine to 2-(*R*)-butylamine ($\alpha = 0.3$), the integral (*R*,*S*) selectivity should be between 100 and 58% and the (*S*,*S*) selectivity should be between 0 and 21%. A mechanism in which the configuration of both amine molecules that form dialkylamine is retained can be rejected in the same way. In that case, the differential (*S*,*S*) selectivity is equal to $(1-\alpha)^2$ and the integral (*S*,*S*) selectivity should be between 100 and 49%, whereas the differential (*R*,*S*) selectivity of $2\alpha(1-\alpha)$ would lead to an integral (*R*,*S*) selectivity between 0 and 42%. The same conclusions can be drawn from the results of the experiment starting with 2-(*R*)-butylamine (see Table 1).

Like for 2-butanethiol, the observed stereoisomers of di-*sec*-butylamine can be easily explained by a mechanism in which imines are intermediates. Dehydrogenation of 2-(*S*)-butylamine to 2-butylimine, followed by addition of a molecule of 2-(*S*)-butylamine, elimination of ammonia, and hydrogenation of the resulting di-(2-butyl)imine, would give an equimolar mixture of (*S*,*S*)- and (*R*,*S*)-di-*sec*-butylamine (Scheme 2). In the same way, 2-(*R*)-butylamine would give an equimolar mixture of (*R*,*R*)- and (*R*,*S*)-di-*sec*-butylamine. In all cases, when racemization of 2-(*S*)-butylamine takes place, half of the di-*sec*-butylamine product would be (*R*,*S*)-di-*sec*-butylamine. This is exactly what we observed. The larger amount of (*S*,*S*)-di-*sec*-butylamine compared with (*R*,*R*)-di-*sec*-butylamine (see Table 1) is due to the fact that in the beginning of the reaction, only 2-(*S*)-butylamine is present, whereas later, 2-(*R*)-butylamine is formed by racemization of 2-(*S*)-butylamine. In fact, with differential selectivities of $0.5(1-\alpha)$ for (*S*,*S*), 0.5α for (*R*,*R*), and 0.5 for (*R*,*S*), the integral selectivity for (*S*,*S*) should be between 50 and 35% for (*R*,*R*) between 0 and 15%, and should always be 50% for (*R*,*S*).

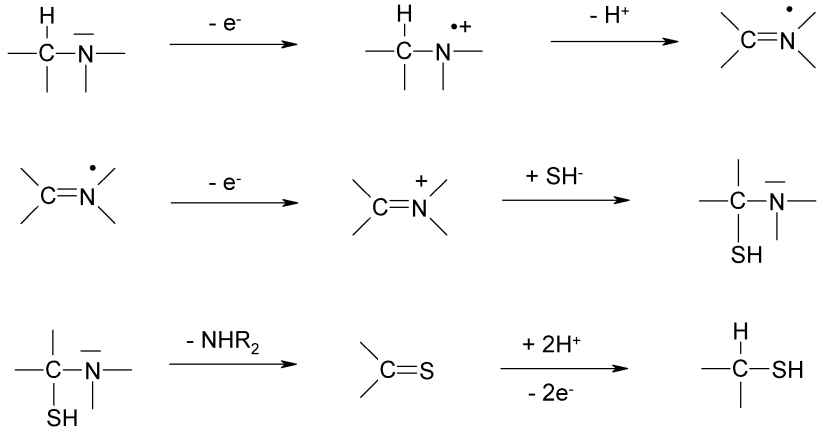
The racemization of 2-(*S*)-butylamine to 2-(*R*)-butylamine and back can occur via the same 2-butylimine intermediate as proposed for the formation of 2-butanethiol and di-*sec*-butylamine (Scheme 2). Another possibility for racemization of



Scheme 2. Substitution of 2-(*S*)-butylamine with H_2S to racemic butanethiol and by another amine molecule to a di-*sec*-butylamine via the formation of an imine intermediate.



Scheme 3. Substitution of a dialkylamine by H_2S to form an alkanethiol and an alkylamine by means of an imine intermediate.



Scheme 4. Mechanism of the substitution of an alkylamine with H_2S to an alkanethiol by means of an imine cation intermediate.

the starting amine is through the consecutive reaction of di-*sec*-butylamine with H_2S to 2-butylamine and 2-butanethiol. Like the substitution of the NH_2 group of 2-butylamine by the SH group (Scheme 2), the substitution of the 2-butyl-NH group of di-*sec*-butylamine by SH will go through an imine (Scheme 3). The equimolar mixture of (*S*,*S*)- and (*R*,*S*)-di-*sec*-butylamine initially formed from 2-(*S*)-butylamine (Scheme 2) will then form racemic 2-butanethiol, 75% 2-(*S*)-butylamine, and 25% 2-(*R*)-butylamine.

The HDN products and their configurations, as well as the racemization of the alkylamine reactant, thus can very well be explained by a mechanism in which imines act as intermediates. 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]. Although 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. In the HDN of neopentylamine and 2-adamantylamine, we have observed substantial amounts of di-neopentylimine and di-(2-adamantyl)imine, respectively (unpublished results). The formation of imines would be in accordance with recent studies demonstrating that the edges of MoS_2 and Co- and Ni-promoted MoS_2 have metallic properties. DFT calculations predict that the band gap in bulk MoS_2 disappears at the edge surface as a result of the reduced coordination of the surface Mo and S atoms [22–26]. STM studies of MoS_2 crystallites on gold supports confirmed this prediction by showing high electron density on the metal and sulfur atoms at the edges [27].

Our results may be explained not only with imine molecules, but also with iminium ions. Scheme 4 demonstrates that, through a sequence of electron and proton transfer reactions, substitution of the NH_2 group by the SH group can occur through an iminium ion. Such cations are well-known intermediates in organic radical reactions [28]. On a heterogeneous catalyst, iminium ions can be formed when the surface contains reduction-oxidation centers as well as protons, as is the case for metal sulfides, in which the metal ions may undergo redox reactions and the H atoms of surface SH groups may act as protons. Scheme 4 is similar but not equal to Scheme 2. The formation of an imine from an amine requires a hydrogen atom on the N atom as well as on the α-carbon atom, but the formation of an iminium ion does not require a hydrogen atom on the N atom. As a consequence, whereas alkylamines and dialkylamines may react by an imine mechanism, trialkylamines cannot. Nevertheless, trialkylamines react rapidly with H_2S to dialkylamines and thiols [16]; Scheme 4 (but not Scheme 2) can explain this reaction. Moreover, we have obtained an additional indication from the HDN of *N*,*N*-dihexylmethylamine that the imine cation intermediate is involved in the reaction mechanism. We are currently investigating this topic and will present the results in the future.

5. Conclusions

Using a chiral alkylamine allowed us to determine how alkylamines undergo substitution by H_2S and by another alkylamine molecule to form an alkanethiol and a dialkylamine, respectively. Complete loss of chirality occurred in the formation of thiol in the reaction of 2-(*S*)-butylamine, and the product distribution of the di-*sec*-butylamine was 50% (*R*,*S*), and more (*S*,*S*) than (*R*,*R*). These results can be explained by a mechanism in which loss of the chiral information on the α-atom occurs by dehydrogenation of the alkylamine to an alkylimine or to an alkylimine cation. Formation of both an imine molecule and an iminium ion is possible on the surface of MoS_2 and cobalt- or nickel-promoted MoS_2.

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