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Priority Communication

Mechanism of C–N bond breaking in hydrodenitrogenation

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Abstract

C–N bond rupture is the final step in the hydrodenitrogenation of nitrogen-containing molecules and occurs by substitution of the alkylamine by H_2S to form an alkanethiol and NH_3. To study the mechanism of the C–N bond breaking, we investigated the reactions of the chiral 2-(*S*)-butylamine and of *N*,*N*-dihexylmethylamine. The amine-to-thiol substitution occurred not through a classic organic substitution reaction, but rather through (de)hydrogenation steps via an imine or through redox and (de)protonation steps, in which an alkyliminium cation acts as an intermediate. For alkylamines and dialkylamines, the reaction may well occur via imine intermediates, but for trialkylamines, the intermediate can only be an iminium ion.

Keywords: Hydrodenitrogenation; Mechanism; Substitution; Imine intermediate; Iminium cation; chiral amine; 2-butylamine; *N*,*N*-dihexylmethylamine

1. Introduction

Hydrodenitrogenation (HDN) has been less well studied than hydrodesulfurization (HDS), because oil fractions contain much more sulfur than nitrogen. However, with current and future legislation demanding deeper removal of sulfur from fuels, HDN has become important, because nitrogen-containing molecules inhibit the adsorption of sulfur-containing molecules. Nelson and Levy were the first to propose mechanisms for the HDN of nitrogen-containing aromatic molecules present in oil fractions. They suggested that after the hydrogenation of the strong aromatic C–N bonds into aliphatic C–N bonds, removal of the nitrogen atom from the resulting alkylamines occurs by nucleophilic substitution or Hofmann β-H elimination [1]. Evidence of both mechanisms has been published [2,3], and it has been suggested that the mechanism depends on the alkylamine and on the catalyst [4]. Recently, we found that over sulfided NiMo, CoMo, and Mo on γ-Al_2O_3 catalysts, the substitution mechanism dominated the HDN of alkylamines, with the NH_2 group attached to a primary or secondary carbon atom, and that Hofmann β-H elimination was not important in these alkylamines [5–7]. The large amount of alkenes and alkanes formed in the HDN of alkylamines proved to be the products of the fast decomposition of the alkanethiol formed by substitution of the alkylamine with H_2S. We also proved that the alkanethiol was a primary product and was not formed by the addition of H_2S to the olefin. The only amines that react by elimination are amines with a tertiary carbon atom linked to the nitrogen atom; only these can react through a carbenium ion-type intermediate by an E1 mechanism [6].

Some important questions remain. How does the substitution of the NH_2 group by an SH group occur? Does it take place by classic organic substitution chemistry, catalyzed by acidic or metallic (Lewis acidic) sites, and with inversion of the configuration of the α-carbon atom adjacent to the N atom? This seems unlikely, because it is known in organic chemistry that it is difficult to remove a NH_2 group. Or does the substitution take place by a sequence of reactions, in which dehydrogenated intermediates play an important role? For instance, the sequence dehydrogenation of amine to imine, H_2S addition, ammonia elimination, and hydrogenation of the thioaldehyde may transform an alkylamine into an alkanethiol [8]. A similar reaction sequence is used

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to transform alcohols into alkylamines [9], again because in this case it is difficult to remove the OH group. Answers to these questions were obtained by studying the hydrodenitrogenation reactions of the optically active 2-(*S*)-butylamine and the tertiary amine *N*,*N*-dihexylmethylamine.

2. Experimental

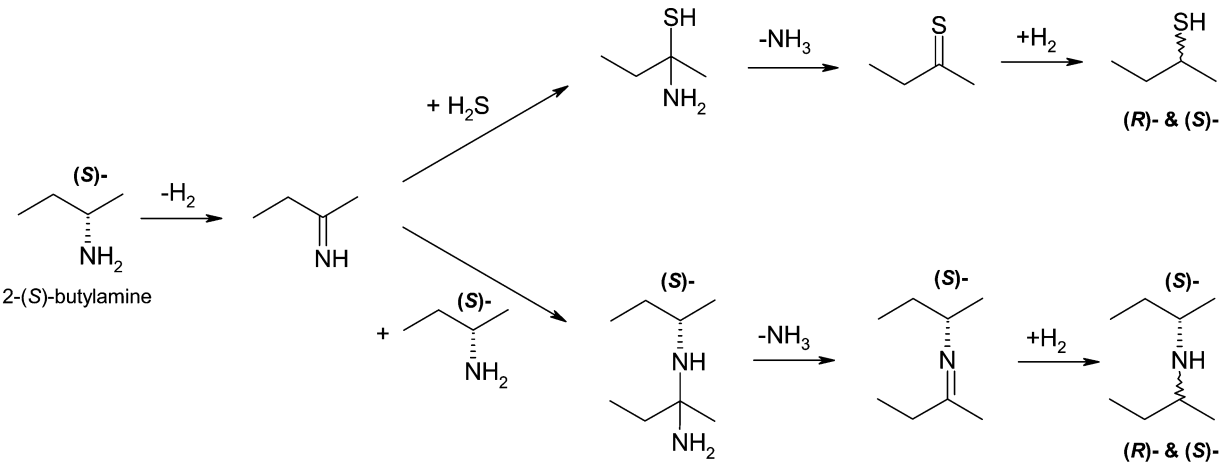
The NiMo/γ-Al_2O_3 catalyst (8 wt% Mo and 3 wt% Ni) was prepared by a two-step pore-volume impregnation of γ-Al_2O_3 as described elsewhere [5]. A sample of 0.05 g catalyst mixed with 8 g of SiC was sulfided in situ in a microflow reactor with 10% H_2S in H_2 at 370 °C and 1 MPa for 4 h. After sulfidation, the pressure was increased to 3 MPa, the temperature was lowered to 300 °C, and the liquid reactant was fed to the reactor. The weight time was varied by changing the flow rates of the liquid and the gaseous reactants, but their ratio was kept constant [5]. 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 ensure that the reactor was free of impurities. To preserve the mass balance of the carbon atoms, 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_p, respectively: $S = (n_P \times Cn_p)/(n_R \times Cn_R)$ [5].

The HDN reaction of 2-(*S*)-butylamine over NiMo/γ-Al_2O_3 was carried out at a weight time of 3.4 g min/mol to give sufficient yields of thiol and dibutylamine for analysis. The HDN reaction of *N*,*N*-dihexylmethylamine was carried out in the presence of 10 kPa H_2S, as in the HDN reactions of other alkylamines [5].

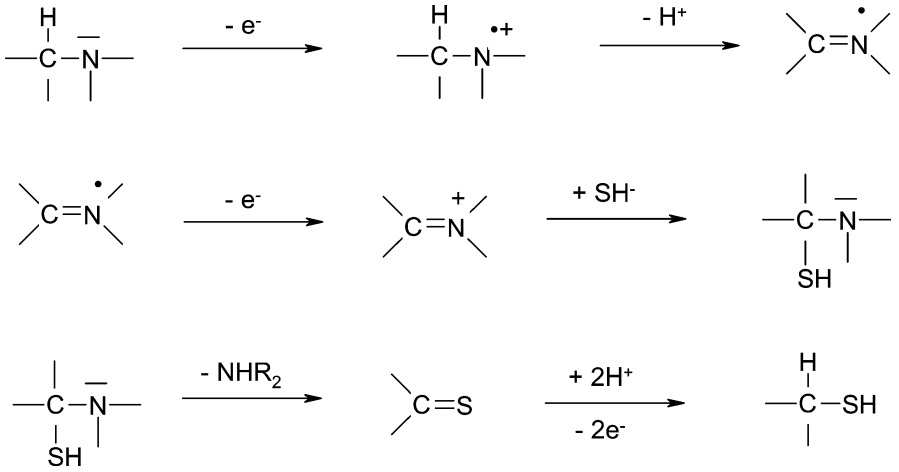
3. Results and discussion

To determine how the substitution of the amine group of an alkylamine by a sulfhydryl group takes place, we reacted 5 kPa 2-(*S*)-butylamine and 100 kPa H_2S at 300 °C, 3 MPa, and a feed rate of 0.15 ml/min over 0.05 g sulfided NiMo/γ-Al_2O_3. The conversion was 57%, and the product selectivity was 45% to butane, 1-butene, *cis*-2-butene, and *trans*-2-butene; 29% to 2-butanethiol; and 26% to di-(2-butyl)amine. The thiol was separated from the amines by extraction, and the thiol and amines were derivatized with the chiral Moscher's acid chloride. Analysis of the diastereoisomers formed from Moscher's acid chloride and 2-butanethiol and 2-butylamine was done on an Agilent GC–MS instrument with a chiral β-DEX 120 capillary column (Supelco; 30 m × 0.25 mm × 0.30 μm). The chromatogram showed that the 2-butanethiol, formed in the reaction of 2-(*S*)-butylamine, was racemic. The optical purity of the 2-(*S*)-butylamine decreased during the HDN reaction; we observed 60% racemization under our reaction conditions.

The equal amounts of 2-(*S*)- and 2-(*R*)-butanethiol formed from pure 2-(*S*)-butylamine demonstrate that the formation of alkanethiol from alkylamine does not proceed stereoselectively. Apparently the reaction proceeds with a loss of chirality of the α-carbon atom. The analysis of the unreacted 2-butylamine showed that racemization of the reactant also occurred; however, the extent of racemization of 2-butylamine was lower (60%) than that of the 2-butanethiol product (100%). This indicates that the racemization of thiol took place during the substitution reaction. This racemization can be explained by an amine-to-thiol reaction by dehydrogenation of 2-butylamine to 2-butylimine, followed by the addition of H_2S to yield a thio-hemiaminal (Scheme 1). Elimination of ammonia from this intermediate and hydrogenation of the resulting thioketone yields racemic 2-butanethiol. The α-carbon atom is involved twice in a double bond, explaining the complete scrambling of the original chirality of this carbon atom. The first racem-



Scheme 1. Substitution of 2-(*S*)-butylamine by H_2S to 2-(*R*)- and 2-(*S*)-butanethiol and by another amine molecule to a di-*sec*-butylamine by means of an imine intermediate.



Scheme 2. Mechanism of the racemization of 2-(*S*)-butylamine by means of an iminium ion.

ization occurs during the dehydrogenation of 2-butylamine to 2-butylimine. We did not observe 2-butylimine in our reaction products, because it is a very reactive intermediate; however, the equilibrium between 2-butylamine and 2-butylimine shifts toward the imine at high reaction temperature, and the racemization of 2-butylamine can only be explained by imine formation.

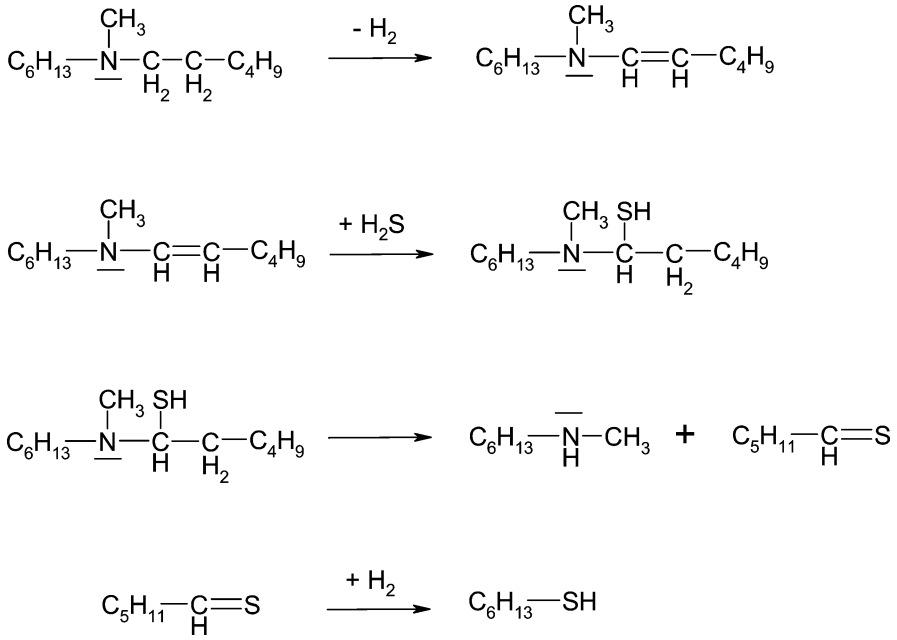
The isomers of di-*sec*-butylamine, produced in the reaction of 2-(*S*)-butylamine, were analyzed directly by chiral gas chromatography on a chiral CP-Chirasil-DEX CB capillary column (Varian; 25 m × 0.25 mm × 0.25 μm), and the following relative amounts were obtained: 20% (*R*,*R*)-, 32% (*S*,*S*)-, and 48% (*R*,*S*)-di-*sec*-butylamine. The formation of di-*sec*-butylamine cannot proceed through 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. If some 2-(*R*)-butylamine formed by isomerization, then 2-(*S*)-butylamine and 2-(*R*)-butylamine should yield equal amounts of the (*S*,*S*) and (*R*,*R*) isomers, which was not the case.

The observed stereoisomers of di-*sec*-butylamine can be explained by a mechanism in which the chirality on the α-carbon atom is lost by double-bond formation. An imine or an iminium ion as the intermediate would explain the observed stereoisomers of 2-butanethiol, 2-butylamine, and di-*sec*-butylamine. For instance, dehydrogenation of 2-(*S*)-butylamine to 2-butylimine, followed by the addition of a molecule of 2-(*S*)-butylamine, elimination of ammonia, and hydrogenation of the resulting di-(2-butyl)imine, would yield an equimolar mixture of (*S*,*S*)- and (*R*,*S*)-di-*sec*-butylamine (Scheme 1). Even if racemization of 2-(*S*)-butylamine occurred, half of the di-*sec*-butylamine product would be (*R*,*S*)-di-*sec*-butylamine, as we observed. The fact that more (*S*,*S*)-di-*sec*-butylamine than (*R*,*R*)-di-*sec*-butylamine was produced is because at the beginning of the reaction, only 2-(*S*)-butylamine was present, whereas later in the reaction, 2-(*R*)-butylamine formed through racemization of 2-(*S*)-butylamine. The racemization of 2-(*S*)-butylamine to 2-(*R*)-butylamine and back occurs via the same 2-butylimine intermediate as proposed for the formation of the 2-butanethiol and di-*sec*-butylamine (Scheme 1).

Thus the HDN products and their configurations, as well as the racemization of the alkylamine reactant can be explained by a mechanism in which imines act as intermediates. Imines have been observed in the HDN of alkylamines over metal sulfide catalysts [6]. 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. Discrete Fourier transform calculations have indicated that the edges of MoS_2 have metallic properties [10,11], and STM studies of MoS_2 crystallites on a gold support have confirmed a high electron density at the edges of the metal and sulfur atoms [12].

But an iminium ion may also explain our observations, however. Scheme 2 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 [13]. Iminium ions can form on a heterogeneous catalyst 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 SH groups at the surface may act as protons. Scheme 2 is not exactly the same as Scheme 1. 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. Therefore, whereas alkylamines and dialkylamines may react through an imine mechanism, trialkylamines will not. In contrast, if a trialkylamine has both α and β hydrogen atoms, then it can form an enamine, which can add H_2S and form an alkanethiol and a dialkylamine.

To determine whether an imine, an enamine, or an iminium ion intermediate is responsible for the observed products of the HDN of alkylamines, we investigated the HDN of *N*,*N*-dihexylmethylamine. This molecule cannot



Scheme 3. Mechanism of the substitution of *N*,*N*-dihexylmethylamine by H_2S to *N*-methylhexylamine and hexanethiol by means of an enamine intermediate.

form an imine and can form an enamine only through dehydrogenation of the hexyl (but not the methyl) group (Scheme 3). Therefore, only the hexyl group can be removed to form a thiol. Consequently, *N*-methylhexylamine, not dihexylamine, should form if an enamine mechanism is in operation. But our results demonstrate that both *N*-methylhexylamine and dihexylamine were formed, in a ratio of about 2:1. This finding demonstrates that the methyl and hexyl groups are removed in a more or less statistical way that cannot be explained by enamine intermediates. However, the related iminium ion intermediate can explain all of our observations. Instead of assuming that the reactions occur through dehydrogenation of the alkylamine, we must assume that the reactions occur due to the removal of electrons and protons. Alkylamines are known to react to iminium cations by double oxidation and proton abstraction (Scheme 2). The methyl group of tertiary amines that carry a methyl group, such as *N*,*N*-dimethylhexylamine and *N*,*N*-dihexylmethylamine, cannot react to an imine but can react to a *N*,*N*-dialkylmethyliminium cation. This explains why the methyl group of these tertiary amines also reacts. It also indicates that the surface of the metal sulfides acts not as a metal, but rather as a redox-proton system. The metal cations function as catalytic reduction–oxidation centers, and the hydrogen atoms on the sulfur atoms act as protons.

4. Conclusion

The final C–N bond rupture in the HDN of nitrogen-containing molecules occurs through a reaction that appears to be an amine–thiol substitution reaction. In reality, this reaction is a complex reaction consisting of redox and (de)protonation steps. For alkylamines and dialkylamines, the reaction may well occur through imine intermediates, but for trialkylamines, the intermediate can only be an iminium ion.

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