Journal of Catalysis **200,** 389–399 (2001)
doi:10.1006/jcat.2001.3218, available online at http://www.idealibrary.com on IDEAL®

Stereochemistry of Hydrodenitrogenation: The Mechanism of Elimination of the Amino Group from Cyclohexylamines over Sulfided Ni–Mo/γ-Al_2O_3 Catalysts

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Received January 26, 2001; revised March 12, 2001; accepted March 12, 2001; published online May 15, 2001

The hydrodenitrogenation of cyclohexylamine and of the diastereomers of 2-methylcyclohexylamine and 2,6-dimethylcyclohexylamine was studied at 200 to 350°C and 50 bar pressure over a sulfided Ni–Mo/γ-Al_2O_3 catalyst. The removal of the amino group from cyclohexylamines occurs primarily by means of a β elimination mechanism. Elimination of a β hydrogen atom attached to a tertiary carbon atom is faster than that of a β hydrogen atom attached to a secondary carbon atom. The rate of elimination also depended on the stereochemical configuration of the amino group with respect to the β hydrogen atoms. Elimination was more rapid when the configuration of the amino group was *anti* periplanar to the β hydrogen atom (in a chair conformation) than when it was *syn* periplanar (in a boat conformation). This is consistent with an E2 elimination mechanism. The relative elimination rates of all the diastereomers of the substituted cyclohexylamines were rationalized in terms of the stereochemical relation between the amino group and a β hydrogen atom, the number and type of β hydrogen atoms, and the energy required to attain the required chair/boat conformation(s). In contrast to previous proposals for *anti* elimination of H_2O from alcohols, it was shown that an *anti* elimination mechanism is possible on the surface of heterogeneous catalysts if SH or OH groups protrude from the catalyst surface.

Key Words: **hydrodenitrogenation; Ni–Mo/γ-Al_2O_3; cyclohexylamines; β elimination, E2; stereochemistry.**

1. INTRODUCTION

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are among the most important catalytic processes in the petroleum industry, because during these processes sulfur and nitrogen are removed in the form of hydrogen sulfide and ammonia from oil fractions. Sulfided Ni–Mo or Co–Mo supported on γ-alumina is typically employed as a catalyst. Compounds containing sulfur or nitrogen in oil fractions are mainly polycyclic aromatic molecules, such as benzothiophene and dibenzothiophene, and quinoline, indole, acridine, and carbazole, respectively (1). Removal of nitrogen from heteroaromatic compounds with sulfided Ni–Mo catalysts occurs mainly after hydrogenation of these compounds. Therefore, industrial HDN essentially consists of two types of reactions: hydrogenation followed by nitrogen removal. Both reactions occur on the same catalyst, although it is not known if they occur on the same catalytic site.

Studying the stereochemistry of these reactions should provide important information about the mechanism of the reaction on the surface of the catalyst as well as about the structure of the catalytic site. Sulfided catalysts were employed in the past for hydrogenation reactions of organic molecules (2), but they were largely superseded by supported metal catalysts, which are active under much milder reaction conditions. Consequently, the stereochemistry of hydrogenation over catalysts sulfided catalysts has hardly been studied (3, 4). We have even less information about the stereochemistry of the elimination reaction. There are very few stereochemical investigations of elimination reactions over heterogeneous catalysts, a notable exception being the elimination of the hydroxyl group over acidic alumina (5–10). We report the very first investigation of the stereochemistry of elimination of substituted cyclohexylamines over sulfided catalysts.

Several authors have studied networks of HDN reactions with different model compounds containing nitrogen. *o*-Alkylanilines are formed as intermediates in the HDN of a majority of nitrogen-containing molecules in oil. Investigation of the HDN network of *o*-toluidine as a model compound is being studied in our laboratory (11–13). The HDN network of a simple model compound such as *o*-toluidine is quite complex, as indicated in Scheme 1. The aromatic C–N bond is considerably stronger than the aliphatic C–N bond, and hence the direct conversion of *o*-toluidine to toluene takes place only to a minor extent under the typical process conditions employed for HDN (350°C and 50 bar) (11). Thus, 2-methylcyclohexylamine is an important intermediate in the HDN network of *o*-toluidine. Although there are

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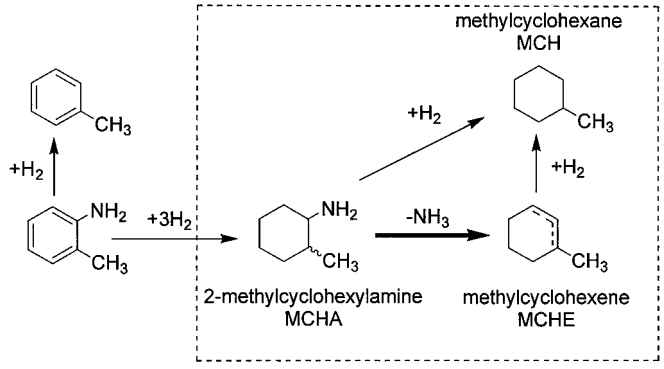


SCHEME 1

two pathways from 2-methylcyclohexylamine to methylcyclohexane, the ultimate product of the HDN of *o*-toluidine, the path involving direct scission of the aliphatic C–N bond, plays a minor role (5–10%) (11). The crucial step, which involves nitrogen removal, takes place mainly via elimination. Ni–Mo or Co–Mo catalysts are typically sulfided before and during their use in HDN reactions. Sulfidation enhances the C–N bond cleavage of the catalyst but decreases hydrogenation (14, 15). Thus, although 2-methylcyclohexylamine is an important intermediate in the HDN network of *o*-toluidine, only traces of it are detectable, because the hydrogenation of the aromatic ring is the rate-limiting step. It is clear that the stereochemistry of elimination cannot be investigated starting from *o*-toluidine, because 2-methylcyclohexylamine is observed in very small amounts. Therefore, we synthesized and then studied the HDN of the *cis* and *trans* isomers of 2-methylcyclohexylamine. The reactivity of 2-methylcyclohexylamine was also compared with the reactivity of cyclohexylamine and of the diastereomers of 2,6-dimethylcyclohexylamines to provide additional support for our conclusions.

2. EXPERIMENTAL

Preparation of Catalyst and HDN Experiments

The Ni–Mo/γ-Al_2O_3 catalyst used in this work contained 8 wt% Mo and 3 wt% Ni and was prepared by successive incipient wetness impregnation of γ-Al_2O_3 (CONDEA, pore volume 0.5 $cm^3\,g^{-1}$, specific area 230 $m^2\,g^{-1}$) with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich) followed by an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (Aldrich). After each impregnation step, the catalyst was dried in air at ambient temperature for 4 h and then dried in an oven at 120°C for 15 h. The catalyst was subsequently calcined at 500°C for 4 h. It was crushed and sieved to a particle size below 60 μm to avoid diffusion effects on product distribution and conversion (11).

Reactions were conducted in a continuous mode in a fixed-bed reactor with a hastelloy tube (15-mm i.d., 320 mm long) that was heated by an oven. The temperature inside the bed was monitored with a thermocouple inside the reactor. The active Ni–Mo catalyst (0.05 g) was diluted with 8 g SiC to achieve plug-flow conditions in the fixed-bed reactor and was held in place by glass wool. The catalyst was sulfided *in situ* with a mixture of 10% H_2S in H_2 at 370°C and 10 bar for 4 h. The reactant feed was prepared by dissolving the amine in octane; heptane was added as an internal standard. Octane was used as a solvent to simulate the presence of hydrocarbons during HDN, as in actual refinery operations. After sulfidation of the catalyst, the pressure was increased to 50 bar; the liquid reactant was vaporized in a preheater at 200 to 300°C and was fed concurrently with the gases to the reactor by means of a high-pressure syringe pump (flow rate, 0.02–0.25 ml min^{-1}). The catalyst was maintained in the sulfided state throughout the reaction by allowing H_2S and H_2 to flow over the catalyst bed. Weight time was defined as $\tau = w_c/n_{feed}$, where w_c denotes the catalyst weight and n_{feed} the total molar flow to the reactor. The weight time (τ) was changed by varying the flow rates of the liquid and the gaseous reactants while keeping their ratio constant. Reactions were performed at 0.2 bar H_2S partial pressure. The flow rate of H_2 was adapted using mass flow controllers so as to keep the H_2 partial pressure at 48 bar. The total pressure was maintained at 50 bar using a backpressure regulator. Reactions were conducted at four different reaction temperatures ranging from 200 to 350°C. Samples were collected every 45 min at the reactor outlet using an automated valve maintained at 300°C and at the same pressure as the reactor. The reaction products were injected from the valve into a gas chromatograph equipped with a 30-m DB-5 fused-silica capillary column (J & W Scientific, 0.32-mm i.d., 0.25-μm film thickness) for quantitative analyses. Detection was made with a flame ionization detector as well as with a pulsed flame photometric detector, which is especially sensitive to compounds containing nitrogen and sulfur. The reaction was stable after 3 to 4 h following a change in temperature or in the flow rate. This entailed the use of about 10 g of amine per investigation at one single temperature. Very little deactivation of the catalyst occurred even after prolonged operation of the reactor. The mass balance was between 95 and 100% for all reactions. The activity of the reactor without the active catalyst (but filled with alumina support and SiC, and sulfided as the catalyst) was only about 20 to 30% that with the catalysts. This and the fact that sulfided Ni–Mo on carbon catalysts had a similar activity for elimination as NiMo/γ-Al_2O_3 catalysts (16, 17) indicate that the Ni–Mo sulfide and not the alumina enables the NH_3 elimination.

Synthesis of 2-Methylcyclohexylamine and 2,6-Dimethylcyclohexylamine Diastereomers

The *trans* diastereomer of 2-methylcyclohexylamine was obtained by repeated crystallization of the hydrogen

chloride salt of a commercially available mixture of the *cis* and *trans* diasteromers (1 : 4, Fluka). The purity of the *trans* diastereomer was 95 to 98%; it contained a small amount of water (up to 0.5 wt%) as determined by Karl–Fischer titration. The *cis* diastereomer of 2-methylcyclohexylamine was prepared according to two methods. The first method involved a transamination procedure starting from 2-methylcyclohexanone and 1-phenylethylamine (18). The second method involved hydrogenation of *o*-toluidine over a noble metal catalyst followed by separation of the *cis* diastereomer from the by-products by crystallization. The purity of the *cis* diastereomer was 92 to 96%. 2,6-Dimethylcyclohexylamines were synthesized from 2,6-dimethylaniline (BASF) by hydrogenation over a ruthenium catalyst. The product was separated into two fractions, namely, a fraction consisting of crystals of the *cis,cis* diastereomer and a fraction containing a 1 : 1 mixture of *cis,cis* and *cis,trans* diastereomers together with a small amount of the *trans,trans* diastereomer. Both fractions were used in HDN studies after purification. The purity of the *cis,cis* diastereomer was 98%, while that of the mixture of the *cis,cis* and the *cis,trans* diastereomers was 97%. The crystals of pure *cis*-2-methylcyclohexylamine and *cis,cis*-2,6-dimethylcyclohexylamine were insoluble in octane, but were soluble after adding small amounts of water (up to 0.7 wt%). Additional details on the synthesis, purification, and solubilization of 2-methylcyclohexylamines and 2,6-dimethylcyclohexylamines are given in the Appendix. The HDN of pure cyclohexylamine (Fluka) produced a substantial amount of the secondary dicyclohexylamine, which reduced the activity of the catalyst. The HDN reactions were therefore conducted after adding small amounts of water (up to 1.5 wt%), since water was found to effectively suppress the formation of this by-product. Satterfield *et al.* reported a higher rate of HDN reactions for sulfided Ni–Mo catalysts due to water (19, 20). The concentration of water in our experiments, however, was much lower than that reported by Satterfield *et al.* as being necessary for a significant effect on the reaction rates. We did not observe an increase in the rate of the HDN of cyclohexylamine after adding various amounts of water, ranging from 0 to 1.5 wt%, to the cyclohexylamine in the feed.

3. RESULTS

HDN of 2-Methylcyclohexylamines at 350°C

Our initial experiments to determine the stereochemical effects during HDN were conducted at 50 bar and 350°C, conditions typically used in industry. As shown in Scheme 1 and discussed in the Introduction, the removal of the amino group from 2-methylcyclohexylamine can occur by two pathways, namely, the direct conversion of the amine to methylcyclohexane and the elimination of the amino group to give methylcyclohexenes and their subsequent

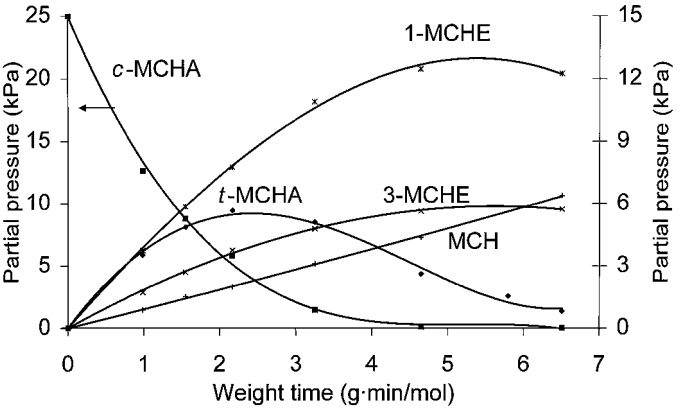


FIG. 1. Product distribution as a function of weight time in the HDN of *cis*-2-methylcyclohexylamine (*c*-MCHA) at 350°C. Left-hand scale for the *c*-MCHA educt; right-hand scale for the products methylcyclohexene (MCHE), methylcyclohexane (MCH), and *trans*-2-methylcyclohexylamine (*t*-MCHA).

hydrogenation to methylcyclohexane. The former pathway plays only a minor role under the present experimental conditions. The latter pathway leads to 1-methylcyclohexene and 3-methylcyclohexene, the relative amounts of which depend on the precise mechanism of elimination. The presence of amine inhibits the hydrogenation of the methylcyclohexenes, and, therefore, only a small amount of methylcyclohexane is formed as long as a substantial amount of amine is present.

The conversion of the almost pure *cis* and *trans* diastereomers of 2-methylcyclohexylamine with increasing weight time is shown in Figs. 1 and 2. It is clear that the *cis* diastereomer is consumed faster than the *trans* diastereomer. Figure 1 reveals that the *cis* diastereomer isomerizes to the *trans* diastereomer during HDN, and that the concentration

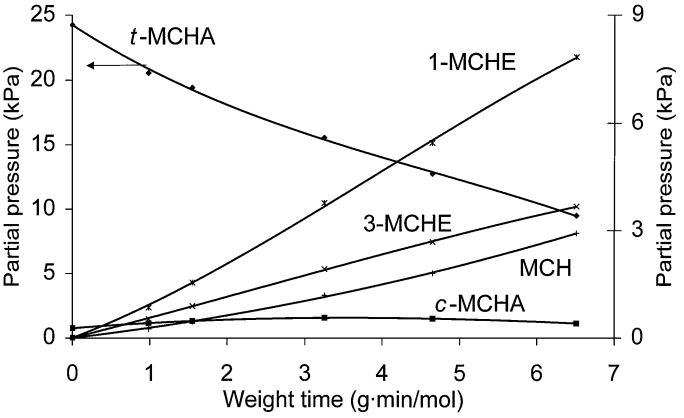


FIG. 2. Product distribution as a function of weight time in the HDN of *trans*-2-methylcyclohexylamine (*t*-MCHA) at 350°C. Left-hand scale for the *t*-MCHA educt; right-hand scale for the products methylcyclohexene (MCHE), methylcyclohexane (MCH), and *cis*-2-methylcyclohexylamine (*c*-MCHA).

of the *trans* diastereomer goes through a maximum. In contrast, Fig. 2 reveals that the concentration of the *cis* diastereomer does not increase significantly. Therefore, either the isomerization of the *trans* diastereomer takes place only to a small extent, or the *cis* diastereomer is formed from the *trans* diastereomer and is consumed at an equal rate. Two olefinic products, 1-methylcyclohexene and 3-methylcyclohexene, were obtained directly from the *cis* and *trans* diastereomers on elimination of the amino group. The evolution of these products during HDN of the *cis* and *trans* diastereomers is also shown in Figs. 1 and 2, respectively. The selectivity between 1-methylcyclohexene and 3-methylcyclohexene is about 68 : 32 for the *cis* diastereomer and hardly changes with weight time. For the *trans* diastereomer, this selectivity is about 61 : 39 at the beginning and slowly reaches the value obtained for the *cis* diastereomer with increasing weight time. Substantial amounts of methylcyclohexane are obtained at higher weight times because of the low concentration of the diastereomeric amines at higher conversion.

To determine whether the olefins isomerize at 350°C, we conducted experiments with a mixture of 3-methylcyclohexene and cyclohexylamine. Cyclohexylamine (without water) was added to simulate the presence of 2-methylcyclohexylamine during the reaction. The HDN of cyclohexylamine produces cyclohexene, which does not interfere with the analysis of the methylcyclohexenes. Furthermore, cyclohexylamine retards the isomerization of methylcyclohexene products by deactivating the acid sites of the catalyst as well as inhibiting further hydrogenation to methylcyclohexane. Three experiments were conducted in this way at three temperatures (350, 295, and 250°C). We did not conduct similar investigations using 1-methylcyclohexene as the reactant feed, because it is the more stable isomer (Saytzeff's rule) and because isomerization of methylcyclohexenes, if it proceeds at all, should lead to the formation of 1-methylcyclohexene from 3-methylcyclohexene. The formation of 1-methylcyclohexene from 3-methylcyclohexene at three reaction temperatures is shown in Fig. 3. At 350°C, there is rapid isomerization of 3-methylcyclohexene, and the molar ratio of the two olefins approaches a value close to that obtained in the HDN of *cis*- and *trans*-2-methylcyclohexylamine. Isomerization is retarded to a significant extent at 295°C, whereas at 250°C it is almost completely suppressed. In an experiment at 350°C, in which a 66 : 34 mixture of 1-methylcyclohexene and 3-methylcyclohexene was used instead of pure 3-methylcyclohexylamine, this ratio remained unchanged with increasing space time, indicating that this is the thermodynamic equilibrium value at 350°C. The selectivity between 1-methylcyclohexene and 3-methylcyclohexene, obtained in the HDN of the *cis* and *trans* diastereomers of 2-methylcyclohexylamine at 350°C, is thus very close to the equilibrium value.

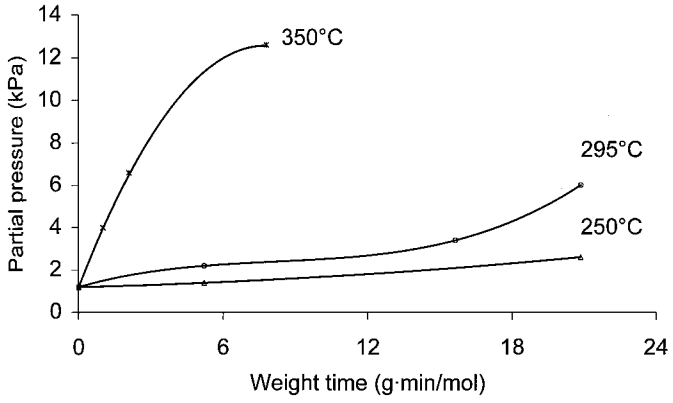


FIG. 3. Formation of 1-methylcyclohexene (1-MCHE) by isomerization of 20 kPa 3-methylcyclohexene as a function of weight time at various temperatures.

HDN of Substituted Cyclohexylamines at Temperatures Lower than 350°C

The above results indicate that there is considerable isomerization not only of the *cis* and *trans* diastereomers of 2-methylcyclohexylamine, but also of the two olefinic products 1-methylcyclohexene and 3-methylcyclohexene. To elucidate the HDN mechanism the reaction temperature must be lowered. Conversion of the *cis* diastereomer of 2-methylcyclohexylamine as a function of weight time at 295°C is plotted in Fig. 4. Figure 4 shows that the concentration of the *trans* diastereomer does not change with weight time, whereas Fig. 1 shows that it does, indicating that isomerization was considerably retarded at 295°C. The concentration of methylcyclohexane is considerably lower in Fig. 4 than in Fig. 1, even at higher weight times. The ratio of 1-methylcyclohexene and 3-methylcyclohexene is approximately 80 : 20 (Fig. 4) and does not change with

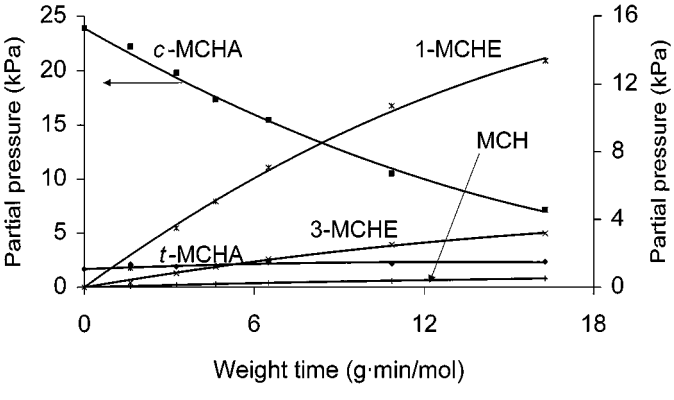


FIG. 4. Product distribution as a function of weight time in the HDN of *cis*-2-methylcyclohexylamine (*c*-MCHA) at 295°C. Left-hand scale for the *c*-MCHA educt; right-hand scale for the products methylcyclohexene (MCHE), methylcyclohexane (MCH), and *trans*-2-methylcyclohexylamine (*t*-MCHA).

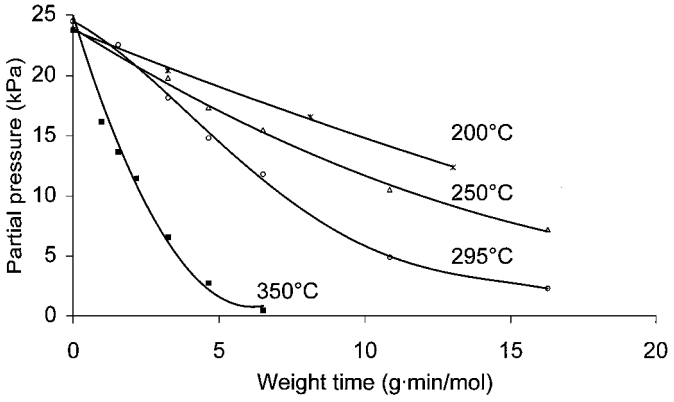


FIG. 5. Conversion of *cis*-2-methylcyclohexylamine as a function of weight time at different reaction temperatures.

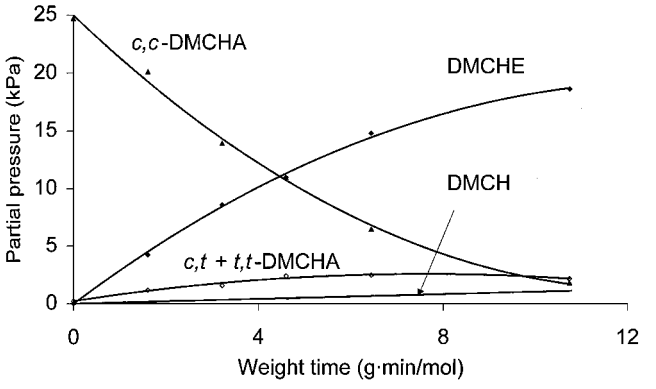


FIG. 7. Product distribution of dimethylcyclohexene (DMCHE), dimethylcyclohexane (DMCH), and isomers of *cis,cis*-2,6-methylcyclohexylamine (*c,t*-+*t,t*-DMCHA) as a function of weight time in the HDN of *c,c*-DMCHA at 295°C.

weight time. The reaction rate of the *cis* diastereomer is clearly lower at 295°C (Fig. 4) than at 350°C (Fig. 1). This is due not only to the slower elimination, but also to the slower isomerization of the *cis* diastereomer to the *trans* diastereomer. Figure 5 presents a comparison of the reaction rates of the *cis* diastereomer at different temperatures. Because of the extensive isomerization of the *cis* diastereomer at 350°C, the sum of the partial pressures of the *cis* and *trans* diastereomers is plotted at this temperature. The reaction rate decreases as the temperature decreases, as would be expected from an Arrhenius-type relation between temperature and reaction rate.

The HDN of the *trans* diastereomer at 295°C gives a plot (not shown) similar to that presented in Fig. 2 except that the reaction rate is lower. The selectivity between 1-methylcyclohexene and 3-methylcyclohexene is about 67:33 and changes little with weight time. The conversions of the *cis* and the *trans* diastereomers of 2-methylcyclohexylamine with weight time at 295°C are shown in Fig. 6. It is seen that the *cis* diastereomer reacts about 1.5 times faster than the *trans* diastereomer. In addition to the HDN of 2-methylcyclohexylamine, the HDN of cyclohexylamine and 2,6-dimethylcyclohexylamine was also studied. The HDN of cyclohexylamine may result in only one olefinic product, namely, cyclohexene. Similarly, the HDN of 2,6-dimethylcyclohexylamine gives only 1,3-dimethylcyclohexene. Figure 7 shows the evolution of the products in the HDN of cis,cis-2,6-dimethylcyclohexylamine at 295°C. Isomerization of the *cis,cis* diastereomer to the *cis,trans* and *trans,trans* diastereomers occurs to a small extent. A small amount of 1,3-dimethylcyclohexane is formed by the hydrogenation of 1,3-dimethylcyclohexene. The conversion of cyclohexylamine and *cis,cis*-2,6-dimethylcyclohexylamine with weight time is also included in Fig. 6. Cyclohexylamine reacts slower, while *cis,cis*-2,6-dimethylcyclohexylamine reacts faster than the *cis* and *trans* diastereomers of 2-methylcyclohexylamine. In the HDN of a 1:1 mixture of the *cis,cis* and *cis,trans* diastereomers of 2,6-dimethylcyclohexylamine (not shown), the reaction rate of the *cis,trans* diastereomer was about 0.75 times the reaction rate of the *cis,cis* diastereomer.

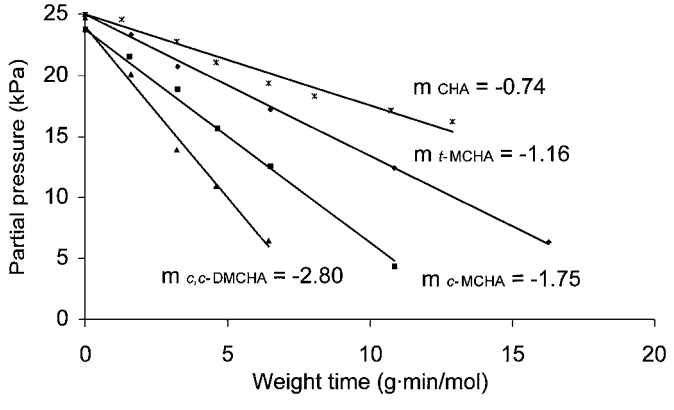


FIG. 6. Conversion of cyclohexylamine (CHA), *cis* and *trans* diastereomers of 2-methylcyclohexylamine (*c*- and *t*-MCHA), and *cis,cis*-2,6-dimethylcyclohexylamine (*c,c*-DMCHA) as a function of weight time at 295°C.

Comparison of Rates of Formation and Distribution of Olefinic Products in the HDN of Substituted Cyclohexylamines

Formation of 1-methylcyclohexene from 2-methylcyclohexylamine involves the elimination of the amino group and of a hydrogen atom on the tertiary β carbon atom. This reaction is comparable to the reaction involved in the elimination of 2,6-dimethylcyclohexylamine to 1,3-dimethylcyclohexene. Hence, Table 1 presents a comparison of the formation of 1-methylcyclohexene from the *cis* and the *trans* diastereomers of 2-methylcyclohexylamine with the formation of 1,3-dimethylcyclohexene from *cis,cis*-2,6-dimethylcyclohexylamine at 295°C. The partial

TABLE 1

Rates of Elimination (in kPa · mol g^{-1} cat min^{-1}) of the Amino Group and a β Hydrogen Atom in Substituted Cyclohexylamines at Different Reaction Temperatures

	Elimination with H on a tert β carbon atom			Elimination with H on a sec β carbon atom		
				Mainly *anti*		
T°C	*anti* *c,c*-DMCHA → DMCHE	*anti* *c*-MCHA → 1-MCHE	*syn* *t*-MCHA → 1-MCHE	CHA → CHE	*c*-MCHA → 3-MCHE	*t*-MCHA → 3-MCHE
295	2.38	1.30	0.65	0.70	0.33	0.31
250	—	1.02	0.19	0.45	0.24	0.09
200	—	0.64	—	0.34	0.15	—

pressures of all olefinic products increased linearly with increasing weight time. Because of this zero order, the rate constants were determined directly from the rates of formation. The rate of formation of 1,3-dimethylcyclohexene is about double the rate of formation of 1-methylcyclohexene from *cis*-2-methylcyclohexylamine, which is in turn approximately twice as fast as the formation of 1-methylcyclohexene from *trans*-2-methylcyclohexylamine. Formation of 3-methylcyclohexene from either the *cis* or the *trans* diastereomer involves elimination of the amino group together with a hydrogen atom on a secondary β carbon atom. This is comparable to the process that takes place in the elimination reaction of cyclohexylamine to cyclohexene. Table 1 shows a comparison of the formation of 3-methylcyclohexene from the *cis* and *trans* diastereomers of 2-methylcyclohexylamine with the formation of cyclohexene from cyclohexylamine at 295°C. The rates of formation of 3-methylcyclohexene from the *cis* and *trans* diastereomers of 2-methylcyclohexylamine are about the same and are about half the rate of formation of cyclohexene formed from cyclohexylamine.

Table 1 also presents the rates of the formation of olefinic products in the HDN of cyclohexylamine and the *cis* and *trans* diastereomers of 2-methylcyclohexylamine at 250 and 200°C. Because of problems with the mass balance, we did not obtain reliable results for the HDN of *cis,cis*-2,6-dimethylcyclohexylamine below 295°C. The rates of formation of 1-methylcyclohexene and 3-methylcyclohexene from *trans*-2-methylcyclohexylamine decrease with temperature at a faster rate than the formation from the *cis* diastereomer. At 250°C, only about 10% of the *trans* diastereomer reacted at the highest weight time used and, hence, we did not conduct the reaction of the *trans* diastereomer at 200°C. The rate of formation of cyclohexene from cyclohexylamine is approximately twice as fast as the formation of 3-methylcyclohexene from *cis*-2-methylcyclohexylamine at 250 and 200°C. The data presented in Table 1 show that the dependency of the reaction rate on temperature is greater for the *trans* diastereomer than for the *cis* diastereomer.

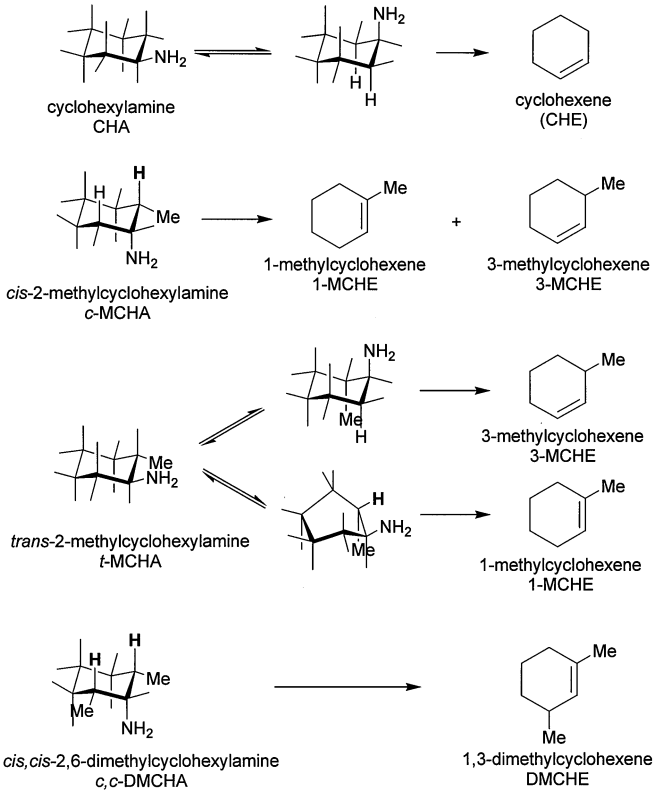
4. DISCUSSION

The HDN of aromatic nitrogen heterocycles proceeds over sulfided Ni–Mo catalysts mainly after complete saturation of the α and β carbon atoms (21). The HDN activity of the resulting aliphatic or alicyclic compounds is strongly dependent on the number of hydrogen atoms on carbon atoms in β position relative to the carbon bearing the amino group (22). This suggests that the primary mechanism of removal of the amino group is β elimination. Only the HDN of amines that do not have β hydrogen atoms proceeds via a substitution mechanism (primarily S_N2), for example, in neopentylamine and benzylamine (23, 24). A substitution mechanism also occurs to a lesser extent in molecules with β hydrogen atoms. By a substitution mechanism we mean either direct substitution of the amino group by hydrogen or a two-step process involving substitution by a sulfhydryl group and then by hydrogen. Only 5 to 10% of the final product in our reactions was obtained via these mechanisms. This leaves only two mechanisms for the elimination reactions, namely, E1 and E2. In the E1 mechanism, the first step in the removal of the amino group is rate controlling, and the second step in the removal of a β hydrogen should have no influence on the overall reaction rate. If this E1 mechanism were to occur, then we would expect almost no differences between the reaction rates of the different diastereomers of 2-methylcyclohexylamine and 2,6-dimethylcyclohexylamine. Furthermore, the E1 reaction of these amines involves the formation of a secondary carbenium ion, which should isomerize significantly to a tertiary carbenium ion in the case of alkyl-substituted cyclohexylamines. This should lead to rearrangement of the carbon skeleton to give products like ethylcyclopentane from the 2-methylcyclohexyl carbenium ion. Such products were, however, observed only to a very small extent (~2%), indicating that the primary mechanism under the present experimental conditions is most likely E2.

An E2 mechanism involves the single-step removal of the amino group together with a hydrogen atom on the β carbon atom. In single-phase reactions, the E2 mechanism

has a first-order dependence on the concentration of the base and the substrate. This implies that if elimination takes place by an E2 mechanism under these conditions, then the reaction should have a first-order dependence on the amine concentration on the surface and in the base (which is widely assumed to be the sulfhydryl group attached to a surface molybdenum atom). It is very difficult to change the surface concentration of basic species on a surface and keep other properties of a heterogeneous catalyst the same. It is not easy to monitor the dependence of the reaction rate on the surface concentration of the amine. This is because amines adsorb very strongly on the surface of the sulfide catalyst and, therefore, almost completely cover the catalyst surface, even if their concentration in the gas phase is very low. Thus, a zero-order dependence of the reaction rate on the concentration of amine in the gas phase is observed. This is advantageous, because a zero-order dependence simplifies the calculation of reaction rates for parallel reactions. The plots show the zero-order dependence of the reaction rate on the concentration of amines in the gas phase; namely, the concentration of the amines decreases linearly with weight time (e.g., Fig. 6), and the concentration of the olefinic products increases linearly with weight time. Only toward the end of the reaction do the plots become nonlinear because of competitive adsorption of ammonia, a product of the elimination reaction (see Fig. 5). Thus, it is not possible to determine the reaction mechanism from the dependence of the reaction rate on the concentration of the base and the catalyst.

Stereochemistry is a very effective tool for determining the existence of an E2 mechanism. The isomerization of diastereomers at 350°C, however, did not result in the determination of the mechanism, and hence the reaction temperature was lowered. E2 elimination takes place preferably when the hydrogen atom and the amino group to be eliminated are in either a *syn* periplanar or an *anti* periplanar configuration (25–27). In *anti* elimination, the hydrogen atom and the amino group are on opposite sides of the C–C bond, while in *syn* elimination the hydrogen atom and the amino group are on the same side of the C–C bond. The *anti* periplanar configuration is preferable, because it minimizes steric interaction with substituents on the adjacent carbon atoms involved in the elimination process. *Anti* elimination is even more favorable in reactions of substituted cyclohexanes, because this configuration can be easily attained in its more stable chair conformation. *Syn* elimination with ideal geometry, i.e., periplanar, is impossible in the chair conformation whereas it is possible in the less stable boat or boat-like conformation. Scheme 2 presents the elimination of the amino group from cyclohexylamine, the *cis* and *trans* diastereomers of 2-methylcyclohexylamine, and *cis,cis*-2,6-dimethylcyclohexylamine. Only the hydrogen atoms involved in the elimination reaction are indicated. The most stable conformers of the amines are shown on the left. In the



SCHEME 2

most stable conformation of cyclohexylamine, the amino group is found in an equatorial position and cannot be eliminated. For elimination to occur, the chair has to flip over so that the amino group is in the axial position. *Anti* elimination can now take place in either direction to cyclohexene. *Cis*-2-methylcyclohexylamine is already in the preferred conformation for elimination, i.e., with the amino group in the axial position and the methyl group in the equatorial position. Once again, elimination can take place on either side, but it is easier to eliminate the hydrogen atom on the tertiary carbon atom bearing the methyl group. The formation of 1-methylcyclohexene is also favored because of its higher stability (Saytzeff's rule) (25). Thus, the formation of 1-methylcyclohexene from *cis*-2-methylcyclohexylamine occurs more often than the formation of 3-methylcyclohexene at all reaction temperatures (cf. Table 1). Surprisingly, the product distribution is hardly affected by temperature (below 300°C) and the selectivity between the two products is always close to 80 : 20. As mentioned above, the process of elimination of a hydrogen atom from the secondary β carbon atom of *cis*-2-methylcyclohexylamine is comparable to the elimination of a hydrogen atom from the secondary β carbon atom of cyclohexylamine. This is illustrated very well by our experiments, because the rate of formation of cyclohexene is approximately double the rate of formation of 3-methylcyclohexene at all reaction temperatures

investigated (cf. Table 1). Although additional activation energy is necessary to flip the more stable chair conformer of cyclohexylamine to its less stable chair conformer for elimination, this energy is insufficient to retard the reaction rate, probably because of the small size of the amino group.

In the most favorable conformation of the *cis,cis*-2,6-dimethylcyclohexylamine, the amino group is in an axial position, whereas the two methyl groups are in equatorial positions. The stereochemical configuration is thus ideal for *anti* elimination in either direction. There are now two hydrogen atoms on a tertiary β carbon atom which can be eliminated with the amino group compared with only one in the case of *cis*-2-methylcyclohexene. In agreement with these stereochemical situations, the rate of formation of 1,3-dimethylcyclohexene is approximately twice as high as the rate of formation of 1-methylcyclohexene at 295°C (cf. Table 1). The fact that elimination of a hydrogen atom on a tertiary β carbon atom is easier than that of a hydrogen atom on a secondary β carbon atom is supported by the observation that the rate of elimination of *cis,cis*-2,6-dimethylcyclohexylamine (2.38) is higher than the sum of the two elimination reaction rates of *cis*-2-methylcyclohexylamine (1.63), which in turn is higher than the elimination rate of cyclohexylamine (0.7) (cf. Table 1).

In the most stable conformation of the *trans*-2-methylcyclohexylamine, both amino and methyl groups are in equatorial positions. As in the case of cyclohexylamine, the chair must flip over so that both groups are in an axial position; only then can the elimination of the amino group together with a hydrogen atom on the secondary β carbon atom occur. The results of experiments at 295°C indicate that the rate of formation of 3-methylcyclohexene from the *trans* diastereomer is about the same as that from the *cis* diastereomer (cf. Table 1). At a lower reaction temperature, however, the rate of the *trans* diastereomer is much lower than that of the *cis* diastereomer. A higher activation energy is apparently necessary for the *trans* diastereomer to flip, because in this process two groups must attain the unfavorable axial positions. This higher activation energy results in a significant change in the reaction rate, in contrast to the case of cyclohexylamine. *Anti* elimination of the hydrogen atom on the tertiary β carbon atom together with the amino group of the *trans*-2-methylcyclohexylamine is impossible, but *syn* elimination can take place if a boat or a boat-like conformation is attained. This process is clearly much less favorable than a similar *anti* elimination from a chair conformation. Accordingly, the rate of formation of 1-methylcyclohexene from the *trans* diastereomer is about half the rate of the corresponding rate from the *cis* diastereomer at 295°C (cf. Table 1). This result agrees well with the results obtained for the HDN of the mixture of *cis,cis* and *cis,trans* diastereomers of 2,6-dimethylcyclohexylamine. The stereochemical relationship of the amino group with the hydrogen atom on tertiary β carbon atoms in the case of the *cis,trans* diastereomer of 2,6-dimethylcyclohexylamine is similar to that of the *cis*-2-methylcyclohexylamine on the one hand and to that of the *trans*-2-methylcyclohexylamine on the other. Thus, the *cis,trans*-2,6-dimethylcyclohexylamine reaction rate should be about the same as the sum of the rates of formation of 1-methylcyclohexene from the *cis* and *trans* diastereomers of 2-methylcyclohexylamine. Accordingly, the reaction rate of the *cis,trans* diastereomer is about 0.75 times the reaction rate of the *cis,cis* diastereomer or 1.5 times the rate of formation of 1-methylcyclohexene from the *cis* diastereomer. The rate of formation of 1-methylcyclohexene from *trans*-2-methylcyclohexylamine decreases much faster with decreasing temperature than the corresponding rate from the *cis* diastereomer (Table 1), as expected because a higher activation energy is necessary to attain the required boat/boat-like form for *syn* elimination (Scheme 2). However, since the hydrogen atom involved in the elimination is attached to a tertiary β carbon atom, apparently its elimination is still easier than the *anti* elimination involving the hydrogen atom on the secondary β carbon atom.

To the best of our knowledge, a comparable investigation of elimination reactions over heterogeneous catalysts with a quantitative comparison between the reaction rates of different molecules and at different temperatures has not been made. Considerable work has been done on the dehydration of alcohols over alumina catalysts (e.g., Pines *et al.*, Knözinger *et al.*, and Kochloefl *et al.*) (5–8, 28, 29). Pines and Manassen illustrated the prevalence of *anti* elimination in the dehydration of menthol and *neo*-menthol (5). The stereochemical relation between the hydroxy group and the hydrogen atom on the tertiary β carbon atom in menthol and *neo*-menthol is similar to the corresponding relation between the amino group and hydrogen atom in the *cis* and *trans* diastereomers of 2-methylcyclohexylamine respectively. It is surprising that they report that only a very small amount of *neo*-menthol reacted by *syn* elimination. Beránek *et al.* (28) studied the dehydration of several cyclohexanols and found that the *cis* diastereomers of 2-alkylcyclohexanols always reacted much faster than the *trans* diastereomers at 200°C. In line with their observations, our investigations show that the *cis* diastereomers of alkyl-substituted cyclohexylamines react faster than the corresponding *trans* diastereomers. They, however, did not report the composition of the olefinic products in their reactions and, hence, no parallels can be drawn with our results in this respect. Bauer and Thomke investigated the mechanism of elimination of the methoxy group of *erythro*-2-methoxybutane-3-D over heterogeneous alumina catalysts (30). After taking into account the kinetic isotope effects, they found that the elimination reaction proceeds by the *syn* pathway (30%) and by the *anti* pathway (about 70%) at 220°C. This agrees qualitatively with our results because,

as in their investigations, we found significant *syn* elimination for molecules for which comparable *anti* elimination was not possible.

Pines and co-workers already discussed how difficult it is to explain how *anti* E2 elimination can take place on the surface of a heterogeneous catalyst (5, 8). The hydrogen atom and the leaving group, although oriented in opposite directions, must be coordinated simultaneously to the catalyst surface for the reaction to occur. It is much easier to explain a *syn* E2 elimination, because the hydrogen atom and the leaving group are on the same side and can coordinate easily with the catalytic surface. Pines suggested that *anti* E2 elimination takes place in crevices where opposite walls coordinate with the hydrogen atom and the leaving group. It is obvious that this explanation takes for granted that only a small part of the catalyst is active since only a few pores have molecular dimensions. Also, the explanation lacks generality. Knözinger *et al.* tried to solve this problem by suggesting that a rocking vibration of the whole molecule may take place (9). The resulting inclination of the molecule should then enable the β hydrogen to reach the basic site. Closer inspection of the geometry involved in the coordination of molecules with the surface reveals, however, that *anti* elimination is indeed possible over catalyst surfaces, even if the reaction does not take place on opposite walls or is not aided by rocking vibrations.

Acidic sites and basic sites are necessary for elimination. On an MoS_2 surface, the sulfhydryl groups may behave as basic sites, while the molybdenum atoms can act as Lewis acid sites. These sites coordinate with the hydrogen atom on a β carbon atom and the amino group, respectively. Figure 8 shows how *anti* and *syn* elimination can occur from *cis*- and *trans*-2-methylcyclohexylamine on an MoS_2 surface. The basic difference between these and former models is that the MoS_2 edge surface is not considered to be a single row of Mo and S atoms. Recent DFT calculations demonstrate that, in the absence of H_2S, the $(10\bar{1}0)$ edge surface of MoS_2 contains Mo atoms that are bonded to four sulfur atoms (31–33). In the presence of some H_2S, however, additional sulfur atoms become bonded to these surface Mo atoms. These sulfur atoms may be singly bonded (on top position, as in Fig. 8) or doubly bonded (between two surface Mo atoms). In either case, the surface is not flat, because sulfur atoms protrude from the Mo plane.

The occurrence of *syn* elimination over such an MoS_2 surface is easy to explain, because the amino group and the hydrogen atom can point toward the surface (Fig. 8A). Since the sulfhydryl group protrudes from the surface, *anti* elimination can easily occur as well, as illustrated by the docking of the *cis* diastereomer (Fig. 8B). Previous reports on elimination reactions did not explain *anti* E2 eliminations on catalyst surfaces, because the surface was assumed to be flat. This is not the case with MoS_2 where protruding

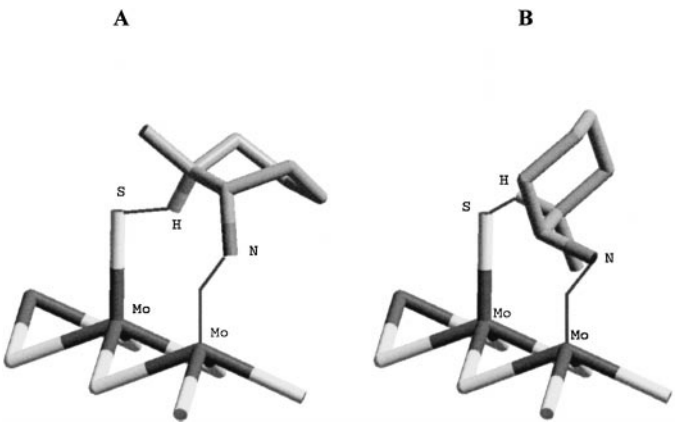
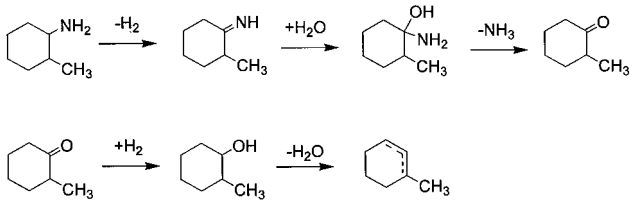


FIG. 8. Pictorial presentation of *syn* elimination of *trans*-2-methylcyclohexylamine (left) and *anti* elimination of *cis*-2-methylcyclohexylamine (right) on an MoS_2 surface.

sulfhydryl groups are found under typical reaction conditions. Furthermore, it had been assumed that the C, N, and Mo atoms are colinear (9). The dehydration of alcohols on alumina is easily explained in an analogous way, because an acidic alumina catalyst has protruding hydroxyl groups attached to the surface, thus providing the necessary geometry for *anti* elimination. In Fig. 8 we show only the edge of MoS_2, but in case of nickel decoration, a nickel atom could replace a Mo atom as proposed by Raybaud *et al.* (33).

Our mechanism also explains why elimination preferentially leads to *cis* olefins in the removal of water from butanol-2 (9). Instead of assuming the *anti* position in the transition state, as in liquid phase elimination, the methyl groups preferably take up the *gauche* position during elimination on a solid surface because then both methyl groups can be turned away from the surface (cf. Fig. 8). This argument has already been proposed by Knözinger *et al.* (9). Their model does not, however, explain the preferential formation of 1-methylcyclohexene rather than 3-methylcyclohexene from *cis*-2-methylcyclohexylamine. Since they assumed a flat catalyst surface and a C_α–O bond vertical to the catalyst surface, the steric hindrance between the methyl group and the catalyst surface does not enable elimination to occur in their model.

The stereochemical results of the elimination of NH_3 from *cis*- and *trans*-2-methylcyclohexylamine also enable us to discard a mechanism that explained HDN by dehydrogenation of an amine to an imine, followed by reaction with water to a ketone and hydrogenation to an alcohol, with final elimination of water to an olefin (Scheme 3) (34). The metal sulfide would be responsible for the (de)hydrogenation and elimination, and water would act as a cocatalyst. The intermediate formation of a ketone would, however, lead to a mixture of *cis*- and *trans*-2-methylcyclohexanol.



SCHEME 3

5. CONCLUSION

We demonstrated the influence of stereochemical factors in HDN reactions over sulfided catalysts and reported one of the very few detailed mechanistic investigations of elimination reactions over heterogeneous catalysts. We have shown that the rate of HDN of alkyl-substituted cyclohexylamines over sulfided Ni–Mo catalysts depends not only on the number of β hydrogen atoms, but also on their stereochemical relation to the amino group. Isomerization of olefinic products and the amines prevented meaningful mechanistic investigations at 350°C, a temperature typically employed in HDN. Our results were obtained at lower reaction temperatures and can be explained by the E2 elimination mechanism which, together with its conformation requirements, accounts for the quantitative relationships between the rates of the HDN of various amines and the rates of formation of different olefinic products. The *cis* diastereomers react faster than the *trans* diastereomers, because they allow for an *anti* geometric relationship in the chair conformation between the amino group and a hydrogen atom on a β carbon atom. The *syn* elimination takes place to a considerable extent at higher temperatures in molecules that are unable to undergo *anti* elimination. The activation energy of *anti* elimination is lower than that of *syn* elimination, and the activation energy of *anti* elimination involving a hydrogen atom attached to a tertiary β carbon atom is lower than that involving a hydrogen atom attached to secondary β carbon atom. Finally, we demonstrated the possibility of *anti* as well as *syn* elimination on the surface of the catalyst without assuming the geometry of the catalytic pores.

APPENDIX: SUPPLEMENTARY INFORMATION

Synthesis of cis- and trans-2-methylcyclohexylamine

A commercially available mixture of *cis*- and *trans*-2-methylcyclohexylamine (*cis*:*trans* 78:22, Fluka) was cooled with an ice-water bath and neutralized with hydrochloric acid to give the chloride salt. Repeated crystallization of the salt mixture in water or in a water–ethanol mixture gave crystals of the chloride salt of *trans*-2-methylcyclohexylamine of increasing purity. Sufficiently pure crystals (95–98%) were treated with NaOH in water, and the free amine was extracted with diethyl ether. The ether extracts were dried with sodium sulfate, and the ether was evaporated in a rotary evaporator. The isolated product was then distilled under vacuum (bp. 73°C) to yield the *trans* diastereomer with 95 to 98% purity, the main impurity being the *cis* diastereomer.

Cis-2-methylcyclohexylamine was synthesized by two methods. The first method involved transamination of 1-phenylethylamine to 2-methylcyclohexanone, as reported by Knupp and Frahm (18). The chloride salt of *cis* 2-methylcyclohexylamine obtained at the end of the procedure was neutralized with NaOH and treated further as for the *trans*-2-methylcyclohexylamine. The *cis* diastereomer was obtained with about 98% purity as a colorless liquid after vacuum distillation (bp. 74°C). In the second method, 120 g of *o*-toluidine was hydrogenated over a Rh/C (Aldrich) catalyst (substrate-to-metal weight ratio = 400) in glacial acetic acid at 50°C and 100 bar hydrogen pressure in an autoclave for 2 days. In addition to *cis*- and *trans*-2-methylcyclohexylamine, significant amounts of secondary amines (approximately 40% by weight), resulting from the coupling of the primary amine products, were obtained. It was not possible to separate the individual amines by distillation because of azeotrope formation. Therefore, after filtration of the catalyst and removal of solvent, the product was separated into three fractions by vacuum distillation. The fraction that boiled at 118 to 121°C was isolated as a thick colorless oil (approximately 130 g). Two hundred grams of ethyl acetate was added to this fraction and the solution was stirred slowly at room temperature overnight. White microcrystals of *cis*-2-methylcyclohexylamine (40 g) were obtained. The crystals were filtered and washed with ethyl acetate and then recrystallized using ethyl acetate to increase the purity if necessary. The purity of these crystals was 92 to 96%, the main impurity being the *trans* diastereomer. The *cis* diastereomer synthesized according to the second method was, however, insoluble in octane, the solvent used for dissolving the reactant feed. It was found that traces of water (up to 0.8% by weight) stabilized/dissolved the *cis* diastereomer synthesized according to the first method in octane. Hence, the *cis* diastereomer obtained according to the second method was neutralized by hydrochloric acid and the free amine isolated via treatment with NaOH and extraction, as reported for the *trans* diastereomer. The resulting *cis* diastereomer was then obtained (~20 g) as a colorless liquid with 92% purity after vacuum distillation (bp. 74°C).

Synthesis of 2,6-Dimethylcyclohexylamine Diastereomers

2,6-Dimethylcyclohexylamines occur in three diastereomeric forms, *cis,cis*, *cis,trans*, and *trans,trans*. The configuration of the diastereomers was identified by referring to the ^{1}H NMR data published by Feltkamp (35). A mixture of the three isomers was synthesized by hydrogenation of 100 g 2,6-xylidene (a gift from BASF AG) in an ethanol–acetic acid mixture (2:1 weight ratio) over Ru/C (Aldrich, substrate-to-metal weight ratio = 400) at 80°C

and 100 bar hydrogen pressure. After the hydrogenation reaction, a solid mass was obtained as the product after cooling the autoclave to room temperature. The products could be dissolved again when more ethanol was added. The products consisted mainly of the *cis,cis* and *cis,trans* diastereomers with a small amount of *trans,trans* diastereomer. After the catalyst was filtered off, ethanol was removed in a rotary evaporator and the remaining acetic acid in the resulting liquid was neutralized with NaOH after dissolving in water. The insoluble amine diastereomers formed a separate organic layer consisting of crystals and liquid. Separation of the organic layer was facilitated by the addition of ethyl acetate. The crystals, although insoluble in ethyl acetate, collected preferentially in the organic layer. The aqueous layer was extracted twice with ethyl acetate, and all the ethyl acetate fractions were collected. The crystals were made up primarily of the *cis,cis* diastereomer and were removed by filtration from ethyl acetate. The ethyl acetate from the filtrate was evaporated in a rotary evaporator. Vacuum distillation of the liquid extract after removal of the solvent yielded 42 g of an azeotropic mixture (bp. 88–90°C) of 5% *trans,trans* diastereomer, 45% *cis,cis*, and 50% *cis,trans* diastereomer. A solid residue was left after distillation and consisted mainly of crystals of the *cis,cis* diastereomer. These crystals were collected and purified by recrystallization from a diisopropyl ether–ethanol mixture. The *cis,cis* diastereomer of 2,6-dimethylcyclohexylamine obtained according to this method presented a problem. Like the *cis* diastereomer of 2-methylcyclohexylamine synthesized by the second method, it was insoluble in octane. To make it soluble, traces of water were sufficient. *Cis*-2-methylcyclohexylamine became soluble after converting the amine to its chloride salt and back again to the free amine using NaOH. The free amine was extracted with diethyl ether and was obtained as a colorless liquid (∼22 g) after removing the ether in a rotary evaporator; it was purified (97%) by vacuum distillation (bp 84°C).

REFERENCES

1. Ho, T. C., *Catal. Rev.-Sci. Eng.* **30**, 117 (1988).
2. Weisser, O., and Landa, S., "Sulphide Catalysts, Their Properties and Applications." Pergamon Press, Oxford, 1973.
3. Shabtai, J., Nag, N. K., and Massoth, F. E., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 1, p. 1. Chem. Inst. of Canada, Calgary, 1988.
4. Fischer, L., Harlé, V., and Kasztelan, S., *Stud. Surf. Sci. Catal.* **127**, 261 (1999).
5. Pines, H., and Manassen, J., *Adv. Catal.* **16**, 49 (1966).
6. Knözinger, H., *Angew. Chem. Int. Ed. Engl.* **7**, 791 (1968).
7. Knözinger, H., and Scheglila, A., *J. Catal.* **17**, 252 (1970).
8. Pines, H., and Haag, W. D., *J. Am. Chem. Soc.* **83**, 2847 (1961).
9. Knözinger, H., Bühl, H., and Kochloefl, K., *J. Catal.* **22**, 57 (1972).
10. Knözinger, H., and Ress, E., *Z. Phys. Chem. NF* **54**, 136 (1967).
11. Rota, F., and Prins, R., *Stud. Surf. Sci. Catal.* **127**, 319 (1999).
12. Rota, F., and Prins, R., *J. Mol. Catal. A* **162**, 359 (2000).
13. Rota, F., and Prins, R., *Top. Catal.* **11**, 327 (2000).
14. Yang, S. H., and Satterfield, C. N., *J. Catal.* **81**, 168 (1983).
15. Olalde, A., and Perot, G., *Appl. Catal.* **13**, 373 (1985).
16. Eijsbouts, S., Sudhakar, C., de Beer, V. H. J., and Prins, R., *J. Catal.* **127**, 605 (1991).
17. Hillerova, E., Vit, Z., Zdrazil, M., Shkuropat, S. A., Bogdanets, E. N., and Startsev, A. N., *Appl. Catal.* **67**, 231 (1991).
18. Knupp, G., and Frahm, A. W., *Chem. Ber.* **117**, 2076 (1984).
19. Satterfield, C. N., Smith, C. M., and Ingalls, M., *Ind. Eng. Chem. Process Des. Dev.* **24**, 1000 (1985).
20. Satterfield, C. N., and Yang, S. H., *J. Catal.* **81**, 335 (1983).
21. Nelson, N., and Levy, R. B., *J. Catal.* **58**, 485 (1979).
22. Portefaix, J. L., Cattenot, M., Guerriche, M., Thivolle-Cazat, J., and Breysse, M., *Catal. Today* **10**, 473 (1991).
23. Vivier, L., Dominguez, V., Pérot, G., and Kasztelan, S., *J. Mol. Catal.* **67**, 267 (1991).
24. Cattenot, M., Portefaix, J.-L., Afonso, J., Breysse, M., Lacroix, M., and Perot, G., *J. Catal.* **173**, 366 (1998).
25. March, J., "Advanced Organic Chemistry." Wiley, New York, 1992.
26. Sicher, J., *Angew. Chem. Int. Ed.* **11**, 200 (1972).
27. Bartsch, R. A., and Závada, J., *Chem. Rev.* **80**, 453 (1980).
28. Beránek, L., Kraus, M., Kochloefl, K., and Bazant, V., *Collect. Czech. Chem. Commun.* **25**, 2513 (1960).
29. Kochloefl, K., Kraus, M., Chin-Shen, C., Beránek, L., and Bazant, V., *Collect. Czech. Chem. Commun.* **27**, 1199 (1962).
30. Bauer, R., and Thomke, K., *J. Mol. Catal.* **79**, 311 (1993).
31. Byskov, L. S., Nørskov, J. K., Clausen, B. S., and Topsøe, H., *J. Catal.* **187**, 109 (1999).
32. Raybaud, P., Hafner, J., Kresse, G., Kasztelan, S., and Toulhoat, H., *J. Catal.* **189**, 129 (2000).
33. Raybaud, H., Hafner, J., Kresse, G., Kasztelan, S., and Toulhoat, H., *J. Catal.* **190**, 128 (2000).
34. Prins, R., *in* "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 4, p. 1908. VCH, Weinheim, 1997.
35. Feltkamp, H. Z., *Anal. Chem.* **235**, 39 (1968).