amide/ester group undergoing reaction,[6] and converts reacting groups into neighboring groups. Based on the assumption that, under the conditions of the experiments listed in Table 1, only half of the catalyst is in the active form of a 1:1 ethoxide complex, rate enhancements for reactions catalyzed by the bimetallic vs. monometallic catalyst translate into an effective molarity (EM)[8] value of 0.08 M for the reaction of **3** and one of 0.04 M for the reaction of **5**. We believe that the loss of entropy associated with torsional motions around two C–C and two C–N bonds is largely responsible for these relatively low EM values.[8] Current work is aimed at the construction of more preorganized, and hopefully more efficient, catalysts.

Experimental Section

Ligands **1**[9] and **2**[10] and compounds **3**$\cdot$H$^+$,[11] **4**,[12] **5**$\cdot$H$^+$,[13] and **7**$\cdot$H$^+$[13] were prepared according to published procedures (melting points and/or spectral data in agreement with literature data). The compound **8**$\cdot$H$^+$ was a commercial sample. Acids **3**$\cdot$H$^+$, **5**$\cdot$H$^+$, **7**$\cdot$H$^+$, and **8**$\cdot$H$^+$ were converted in situ into the Me_4N^+ salts by neutralization with Me_4NOEt. Spectrophotometric rate measurements were carried out in the thermostatted cell compartment of a Hewlett Packard HP 8452A diode array spectrometer. For initial rate measurements, a fast mixing accessory, HI-TECH SCIENTIFIC SFA-12, was connected to the spectrometer and the process was monitored at the isosbestic point for the free and the Ba^{2+}-paired reaction product ($\lambda = 276$ nm). Other materials, apparatus and techniques were as reported previously.[4, 5]

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[7] The close similarity of the two values would indicate that the higher affinity for the monometallic complex of the more basic AcO^- ion is substantially counterbalanced by the statistical factor 2 which operates in the binding of the less basic **3** to the bimetallic complex. The fact that the ligand is not exactly the same in the two cases is presumably unimportant.

[8] The effective molarity (EM) for an intramolecular reaction is defined by the ratio $k_{\text{intra}}/k_{\text{inter}}$, where k_{inter} refers to the intermolecular model reaction. For a discussion of structure effects on the EM value see: a) A. J. Kirby, *Adv. Phys. Org. Chem.* **1980**, *17*, 183–278; b) L. Mandolini, *Adv. Phys. Org. Chem.* **1986**, 22, 1–111.

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Continuous Amination of Propanediols in Supercritical Ammonia[**]

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The heterogeneously catalyzed amination of alcohols has been established as the most important industrial process for the manufacture of a variety of aliphatic and aromatic amines.[1–6] However, the yields and selectivities are usually rather low in the synthesis of primary aliphatic diamines from the corresponding diols and ammonia. The transformation of a simple aliphatic alcohol to the corresponding amine on a metal catalyst includes three major reaction steps (Scheme 1): 1) dehydrogenation to a carbonyl compound; 2) condensation with ammonia or an amine to form an imine or an enamine; and 3) hydrogenation to the corresponding amine.[7, 8] Each intermediate and the product amine can undergo various side reactions such as condensation, decarbonylation, disproportionation, and hydrogenolysis.[4, 9–11] The direct transformation of an aliphatic diol to the corresponding diamine requires the repetition of steps 1–3, which favors the formation of the by-product. In addition, the bifunctional intermediates extend the scope of possible side reactions (for example, oligomerization and cyclization).[12, 13] However, reasonable yields have still been reported for the amination of alkanediols with secondary amines, as the tertiary amine product is moderately reactive.[7, 14] Unfortunately, the situation is the reverse in aminations with ammonia, as the reactivities of the inter-

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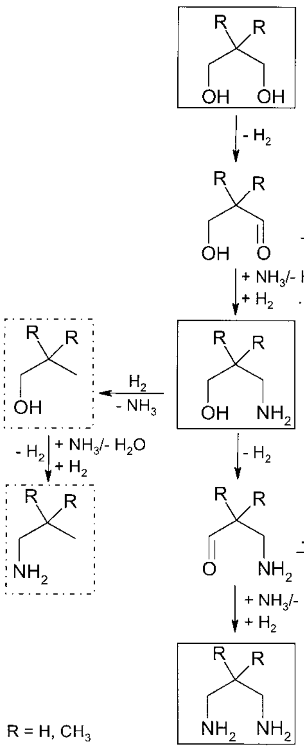

Scheme 1. Important reactions that occur in the amination of alkanediols with ammonia. The continuous and dashed line frames indicate the detected main and by-products, respectively.

mediate and product primary amines are significantly higher than that of ammonia. The above considerations account for the difficulties in the selective synthesis of primary diamines from diols. A practical solution is the separate preparation of the aminoalcohol intermediate and its further amination with ammonia. This method provides good selectivities to diamines.[15–19]

Intrigued by the obvious advantages of the one-step process, we reinvestigated the amination of alkanediols with ammonia in a continuous fixed-bed reactor at pressures where the ammonia forms a supercritical fluid (critical data of ammonia: $T_c = 132.4\,^{\circ}C$, $P_c = 114.8$ bar[20]). The amination of 1,3-propanediol and 2,2-dimethyl-1,3-propanediol were chosen as test reactions. Two types of catalysts were used: an unsupported Co catalyst stabilized by 5 wt% Fe and a commercial silica-supported Ni catalyst. Preliminary experiments indicated that—in agreement with the literature data[21]—a rather high ammonia/alcohol molar ratio in the range of 10/1 to 100/1 was necessary to suppress the dimerization and oligomerization of the intermediate and product amines. A small ratio of hydrogen in the feed (1–5 mol% of the reaction mixture) was sufficient to prevent the undesired dehydrogenation reactions and the formation of nitriles and carbonaceous deposit.

Figure 1 illustrates the role of the total pressure in the amination of 1,3-propanediol over the unsupported Co–Fe catalyst. The conversion varied only from 85 to 99% over the whole pressure range studied. However, a pressure increase from 50 to over 100 bar had a striking effect on the amination selectivity. The technically important cumulative selectivity to 3-amino-1-propanol and 1,3-diaminopropane increased from about 1% to 43–48%.

On the basis of literature data[22–25] it is expected that at 135 bar or above, where the selectivity to the diamine is constant (Figure 1), the reaction mixture is in the supercritical (sc) region. To confirm this assumption the phase composition of the reaction mixture was investigated in a 50 mL quartz autoclave. The presence of a homogeneous fluid at 130 bar and 200 °C was confirmed by visual inspection. Accordingly, we propose that the remarkable improvement in amination selectivity with increasing pressure is connected with the change of the medium in the near critical region of ammonia (110–120 bar) and at the reaction temperature of 60 °C above the critical temperature.

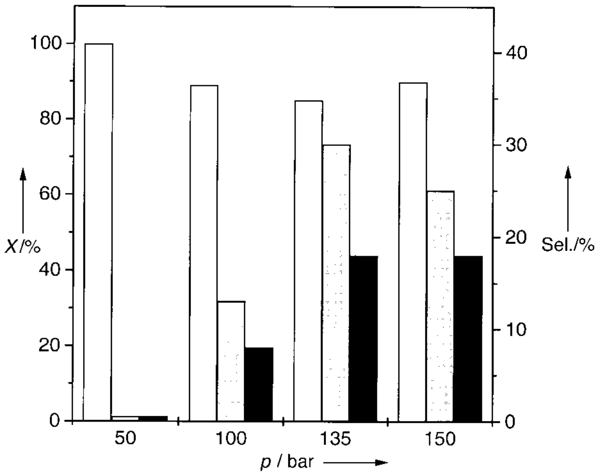

Figure 1. Influence of pressure on the conversion X (□) of propanediol, and the selectivity to 3-amino-1-propanol (▨) and 1,3-diaminopropane (■). Conditions: catalyst: 95 wt% Co and 5 wt% Fe, 195 °C, space time 11 g h mol^{-1}, molar ratio of alcohol/H_2/ammonia: 1/2/60.

It seems from Figure 1 that the amination selectivity increased in both consecutive steps, namely in the formation and in the further amination of the aminoalcohol intermediate. In a control experiment the intermediate 3-amino-1-propanol was fed into the reactor under similar conditions. Figure 2 shows the effect of increasing pressure: likewise a

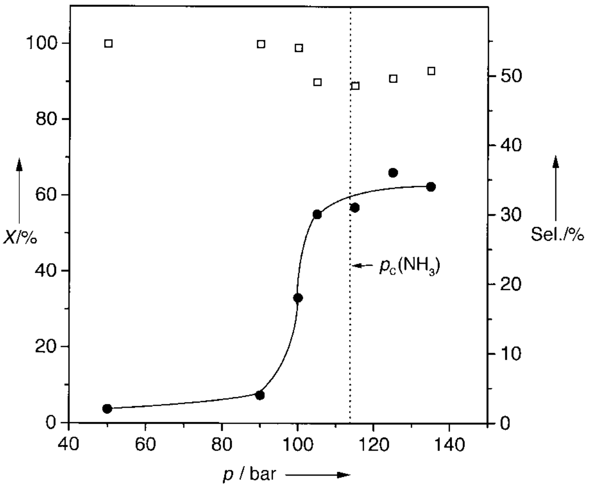

Figure 2. Effect of pressure on the conversion X (□) of 3-amino-1-propanol and the selectivity to 1,3-diaminopropane (●). Conditions: catalyst: 95 wt% Co and 5 wt% Fe, 195 °C, space time 11 g h mol^{-1}, molar ratio of alcohol/H_2/ammonia: 1/2/40.

small drop in conversion and a significant improvement in diamine selectivity was observed in the near critical region. Below and above this region the variations in conversion and selectivity were minor.

The striking effect of supercritical conditions in the amination of alkanediols was not limited to the use of the Co–Fe catalyst or 1,3-propanediol as reactant. Figure 3 presents another example: the amination of 2,2-dimethyl-1,3-propanediol. In this case the reaction was carried out with the supported Ni catalyst. Again, the increasing pressure had only minor influence on the diol conversion, but favored the formation of the aminoalcohol intermediate and especially the desired diamine product. The changes in selectivity were negligible below 90 bar, and only minor above the critical pressure of ammonia.

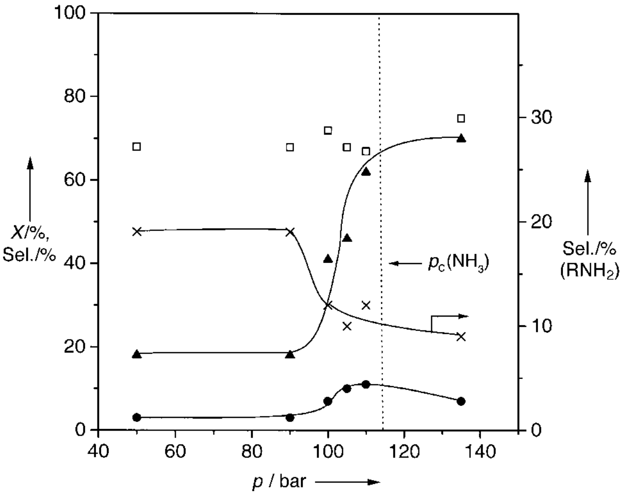

Figure 3. Influence of pressure on the conversion X (□) of 2,2-dimethyl-1,3-propanediol, and the selectivity to 2,2-dimethyl-3-amino-1-propanol (●) and 2,2-dimethyl-1,3-diaminopropane (▲) and alkylamine (×). Conditions: catalyst: 56 wt% Ni on a support (Engelhard Ni-6458), 210 °C, space time 11 g h mol^{-1}, molar ratio of alcohol/H_2/ammonia: 1/2/60.

Before the possible reasons for the observed selectivity enhancement could be discussed we had to ascertain that in the amination of various alkanediols and aminoalcohols the conversion above 60% had only a small influence on the selectivity to the corresponding diamines. For example, the selectivity in the amination of 2,2-dimethyl-1,3-propanediol at 227 °C to 2,2-dimethyl-1,3-diaminopropane decreased from 58 to 53% when the conversion increased (by increasing the contact time) from 61 to 89%. A minor variation in selectivity of about ±2% was observed in the amination of 1,3-propanediol in a similar conversion range. The likely interpretation for the small effect of increasing conversion is that not only is more diamine formed from the aminoalcohol intermediate at higher contact time, but also more is consumed by consecutive side reactions such as disproportionation or hydrogenolysis (degradation). Accordingly, the changes in selectivity with increasing pressure (Figures 1–3) cannot be traced to the small variations in conversion.

At medium pressures (< 90 bar) the reaction mixture consists of two phases: a liquid phase that is rich in the non-volatile alkanediol and amines (depending on the conversion along the catalyst bed), and a gas phase that contains dominantly ammonia. In this pressure range the influence of total pressure on conversion and product composition was minor as illustrated in Figures 1–3. In the near critical region the transformation of the two-phase system to a homogeneous sc fluid generally results in a significant improvement of mass transport because of the elimination of the phase transfer resistance, and the higher diffusion coefficients and lower viscosity, relative to the situation in the liquid phase. Besides, the effect of pressure on the chemical equilibria and reaction rates can also be crucial.[26–28] Unfortunately, for a network of consecutive and parallel reactions the effect of pressure is rather complex because of the different reaction volumes (ΔV_r) and activation volumes ($\Delta V^{\neq}$). We assume that in the supercritical region the surface ammonia concentration is significantly higher than under two phase conditions, which govern in the subcritical region. Although this change is mainly a consequence of the enhanced mass transfer in the sc fluid, a change in adsorption equilibrium (solvent effect) can also contribute. There are some recent examples in the literature on the enhancement of stereoselectivity (*cis*/*trans* ratio) in the hydrogenation of vegetable oils in sc CO_2.[29] The improvement was attributed to the significantly better hydrogen availability on the metal surface that arises from the elimination of mass transport limitations in the sc fluid phase.

A clearer picture is obtained by analysis of the influence of the subcritical–supercritical transition on the main reaction steps and the side reactions. The major side reactions that produce monofunctional alcohols and amines are illustrated in Scheme 1. Decarbonylation of the intermediate aldehydes on the metal surface results in primary alcohols and amines. Amination of the alkanol by-product via the aldehyde intermediate leads to alkylamines. This aldehyde intermediate can also form by the (acid-base catalyzed) retro-aldol reaction.[13] The variation of the total amount of alkylamines detected in the liquid product is illustrated in Figure 3 for the amination of 2,2-dimethyl-1,3-propanediol. The main by-product was isobutylamine. A significant drop in the amount of this by-product in the near critical and supercritical region corroborates the picture discussed above. In the supercritical region of ammonia, the dimerization and oligomerization side reactions were not important.

We suggest that the changes in amination selectivity and alkanediol conversion in the near critical region arise from the increased ammonia concentration at the surface. This change favors the amination and suppresses the degradation-type (hydrogenolysis) side reactions. The situation is rather similar to the well-known, and widely applied, selective poisoning of metal catalysts.[30–32] For example, the presence of strongly adsorbing amines in the hydrogenation of carbonyl compounds hinders the C–O bond hydrogenolysis, and the corresponding alcohols can be prepared in very high yields.

In the amination of alkanediols and alkanolamine (Figures 1 and 2), the small drop in conversion and the strong decrease in the amount of alkylamines by-products in the liquid phase (Figure 3) are clear indications of selective poisoning: the degradation-type reactions are effectively slowed down but also the first step, the dehydrogenation of the alcohol to the carbonyl compound, is affected. On the other hand, the higher ammonia concentration at the surface favors the fast addition of ammonia to the aldehyde-type intermediates, and suppresses the reaction of the alcoholic OH group with the intermediate or product amines that leads to dimerization products. That is, the weaker basicity of ammonia, relative to the product amines, is partly compensated by its higher concentration at the surface. All these effects can contribute to the remarkable enhancements in the overall amination selectivities (Figures 1–3).

In conclusion we can state that the application of $scNH_3$ as a solvent and reactant in the amination of simple alkanediols and aminoalcohol affords significant improvement in selectivities to primary diamines, relative to the procedure at subcritical pressure. Most of the changes in selectivities occur in a narrow pressure range in the near critical region of the medium. The selectivity improvement is attributed to the higher concentration of ammonia at the surface, which favors the amination with ammonia and suppresses the hydrogenolysis-type (degradation) side reactions. It seems that the phenomenon is not limited to a specific catalyst or reactant, though the final selectivity is a function of the structure of the reactant aminoalcohol or diol. We are presently working on the extension to other amination reactions where the low reactivity of ammonia relative to the product amine prevents the efficient synthesis of primary amines.

Experimental Section

The Co–Fe catalyst was prepared by co-precipitation. Aqueous solutions of cobalt nitrate, iron nitrate, and ammonium carbonate were mixed at room temperature and the pH adjusted to 7. The precipitate was filtered off, dried at 120 °C in a vacuum, and calcined at 400 °C for 4 h. The BET surface area was $8\ m^2 g^{-1}$ and the pore volume $0.1\ cm^3 g^{-1}$.

The commercial Ni catalyst (Engelhard No. 6458) contained 56 wt% of pre-reduced Ni. The BET surface area was $180\ m^2 g^{-1}$ and the pore volume $0.3\ cm^3 g^{-1}$.

The amination experiments were carried out isothermally in a continuous tubular reactor with an inner diameter of 13 mm. The reactor was loaded with crushed and sieved catalyst particles of 140 to 400 μm. The liquid ammonia and 1,3-propanediol or the solution of 2,2-dimethyl-1,3-propanediol in ammonia were dosed into the reactor by ISCO D500 syringe pumps. The total pressure in the reaction system was set by a TESCOM back-pressure regulator. Details of the reaction conditions are indicated in the figure captions. The liquid product was separated from the gas and analyzed on an HP 5890 gas chromatograph (HP 1701 column). The products were identified by GC-MS analysis.

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Calcium, Strontium, and Barium Acetylides—New Evidence for Bending in the Structures of Heavy Alkaline Earth Metal Derivatives[**]

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Karin Ruhlandt-Senge*

Since their development in the early 1900s, Grignard reagents have proven to be immensely useful in synthetic chemistry and are among the most common organometallic reagents.[1,2] In contrast, information about beryllium, calcium, strontium, and barium analogues is scarce.[1c,2,3] Organo-

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