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Thermodynamics of the Hydrodenitrogenation of Carbazole

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Topical Report

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EXECUTIVE SUMMARY

Catalytic hydrodenitrogenation (HDN) is a key step in upgrading processes for conversion of heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal to economically viable products. Organic nitrogen and sulfur are commonly removed via reaction at 325 to 400° C and 75 to 150 atm. of hydrogen. Under these conditions, hydrogen is consumed not only in breaking carbon-nitrogen and carbon-sulfur bonds, but also in saturating aromatic components in the feed. Hydrogen consumption in excess of 1500 scf/bbl (standard cubic feet per barrel) is common in hydrotreating shale oil, while the amount theoretically required for selective heteroatom removal is only about 600 scf/bbl. Hence, the saving in expensive hydrogen could be enormous if a process for denitrogenation without saturation of the aromatic rings in the feedstock could be developed.

This research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), provides accurate experimental thermochemical and thermophysical properties for "key" organic nitrogen-containing compounds present in the range of alternative feedstocks, and applies the experimental information to thermodynamic analyses of key HDN reaction networks (e.g., quinoline/hydrogen, acridine/hydrogen, indole/hydrogen, carbazole/hydrogen, etc.). Thermodynamic analyses, based on accurate information, can be used to set the boundaries (e.g., temperature range, pressure range, etc.) for efficient processing of materials, and to provide insights for the design of cost-effective methods of nitrogen removal.

A thermodynamic analysis was completed for the key hydrogen-consuming steps in the HDN reaction network for carbazole. The results are compared with literature reaction studies. The "crossover temperature" concept is shown to be a valuable tool in the interpretation of the reaction study results.

The report concludes that the removal of nitrogen from heterocyclic aromatic nitrogen-containing compounds with conventional hydrodesulfurization catalysts, temperatures, and hydrogen pressures results in processing under thermodynamic control with unavoidably high hydrogen consumption. The report also concludes that to reduce hydrogen consumption in the HDN of carbazole, pathways via 1,2,3,4,4a,9a-hexahydrocarbazole must be followed. Conditions under which these processes are possible are discussed.

ABSTRACT

A thermodynamic analysis, based on accurate experimental Gibbs energies of formation, was completed for the key hydrogen-consuming steps in the HDN reaction network for carbazole. The results were compared with literature reaction studies. The concept of "crossover temperature" is shown to be a valuable tool in the interpretation of literature reaction-study results.

Methods of nitrogen removal from aromatic materials are discussed in light of the findings of the thermodynamic analysis. It is concluded that the removal of nitrogen from heterocyclic aromatic nitrogen-containing compounds with conventional hydrodesulfurization catalysts, temperatures, and hydrogen pressures occurs under "thermodynamic control" with unavoidably high hydrogen consumption. The report also concludes that to reduce hydrogen consumption in the HDN of carbazole, pathways via 1,2,3,4,4a,9a-hexahydrocarbazole must be followed. Conditions under which these processes are possible are discussed.

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GLOSSARY

M = molar mass in $\text{g}\cdot\text{mol}^{-1}$

T = temperature

p = pressure

K = equilibrium constant

K' = pseudo-equilibrium constant (defined in NIPER-468)

T_{cross} = crossover temperature (defined in NIPER-468))

k = rate constant

$\Delta_f H_m^\circ$ = molar enthalpy of formation

$\Delta_f S_m^\circ$ = molar entropy of formation

$\Delta_f G_m^\circ$ = molar Gibbs energy of formation

$\Delta_r G_m^\circ$ = molar Gibbs energy of reaction

n = number of moles of substance

1. INTRODUCTION §

Heterocyclic compounds containing nitrogen in a 5- or 6-membered ring -- indoles, carbazoles, quinolines, and benzoquinolines -- constitute the major portion of the nitrogen compounds present in heavy oils and shale oils.^{(1,2)†} The 5-membered ring systems (pyrrolic compounds) are non-basic⁽³⁾ due to the involvement of the nitrogen atom lone pair electrons in the π -electron system of the pyrrole ring. In the 6-membered ring systems (pyridinic compounds) the nitrogen lone pair is not bound within the π -electron system of the pyridine ring and, hence, is available to bind with acids. These compounds are strong bases. Due to the different environments of the lone pair on the nitrogen atom in these systems, each reacts differently with a catalyst surface. Pyrrolic compounds bind to the catalyst surface through an extension of the π -electron system, whereas the pyridinic compounds can also bind through the nitrogen atom and its lone pair as well as through the π -electron system.

Pyrrole

Examples of pyrrolic compounds

Pyridine

Examples of pyridinic compounds

§ This research was funded by the Office of Fossil Energy of the U. S. Department of Energy within its Advanced Extraction and Process Technology (AEPT) research program.

† References are listed in numerical order at the end of the main report.

Catalytic hydrodenitrogenation (HDN) is a process in which organo-nitrogen compounds are removed from hydrocarbon feedstocks to produce processable, stable, and environmentally acceptable liquid fuels and lube base stocks. To date HDN has not been of great concern to refiners because of the small quantities of nitrogen present in conventional petroleum. This situation, however, is changing as the need for the processing of heavier and lower quality stocks (both rich in highly refractory nitrogen compounds) increases. For the present, the catalyst technology used for hydrodesulfurization (HDS) has been adapted for HDN, despite the fact that it is not ideally suited for the purpose.⁽¹⁾

Organic nitrogen and sulfur are commonly removed via reaction at 325°C to 400°C and 75 to 150 atm. of hydrogen. Under these conditions, hydrogen is consumed not only in breaking carbon-nitrogen and carbon-sulfur bonds, but also in saturating aromatic components in the feed. Hydrogen consumption in excess of 1500 scf/bbl (standard cubic feet per barrel) is common in hydrotreating oil shale, while the amount required theoretically for selective heteroatom removal is only about 600 scf/bbl. Hence, the saving in expensive hydrogen used in processing could be enormous if a process for denitrogenation without saturation of the aromatic rings in the feedstock could be developed. Thus, interest in the development of more effective catalysts for HDN has grown, as witnessed by the rapid expansion of the patent literature in the area.⁽⁴⁾

Some key questions concerning hydrodenitrogenation reactions are:

- What are the reaction networks? Alternatively, what stable intermediates are formed?
- What are the reactivities of the various classes of nitrogen-containing compounds?
- Are the reaction networks and commonly accepted generalities about reactivities valid for broad groups of catalysts?

For a proposed reaction network, thermodynamics can be used to ascertain the relative stabilities of reaction intermediates, to determine if a reaction is possible under given reaction conditions (and, if not, whether changing the reaction conditions will make it so), and to determine if the reactions are reversible.

In recent years a series of topical reports⁽⁵⁻²⁰⁾ have detailed the thermodynamic properties of key compounds and intermediates associated with the hydrodenitrogenation (HDN) reactions of heterocyclic aromatic nitrogen-containing compounds. The equilibrium thermodynamics associated with the HDN of pyrrole and indole have been discussed in NIPER-188,⁽⁶⁾ NIPER-264,⁽⁷⁾ and NIPER-415.⁽¹⁵⁾ The HDN of quinoline

was discussed in NIPER-468,⁽¹⁷⁾ where the concept of "crossover temperature" was introduced to give pictorial representations of the various thermodynamic equilibria discussed in the report. The present topical report discusses the role of thermodynamic equilibria in the HDN of carbazole.

2. LITERATURE STUDIES OF THE HYDRODENITROGENATION OF CARBAZOLES

Hydrogen consumption in the HDN of carbazole can range from 2 moles in the direct route carbazole $\rightarrow$ 2-aminobiphenyl $\rightarrow$ biphenyl to 8 moles in the route ending in bicyclohexane (see figure 1). This report discusses the thermodynamics of both these routes and, in addition, two further possible pathways via 2-phenylcyclohexylamine to phenylcyclohexane both of which use 5 moles of hydrogen per mole of carbazole (see figure 1).

Due to experimental difficulties (e.g., the high melting point, 521 K, and low solubility in hydrocarbon solvents) there have been relatively few HDN studies of carbazole reported in the literature. Stern⁽²¹⁾ reported reaction networks for a range of nitrogen-containing heterocyclic compounds including carbazole. His studies used four different presulfided catalysts (CoMo/Al₂O₃, NiMo/Al₂O₃, Re/Al₂O₃, and CoRe/Al₂O₃) at 350°C and 70 atmospheres hydrogen pressure. 1,2,3,4-Tetrahydrocarbazole was the prime product obtained during the time the reaction was followed with only minor amounts of biphenyl and phenylcyclohexane observed. Sarbak⁽²²⁾ studied the HDN reaction using presulfided CoMo/Al₂O₃, and NiW/Al₂O₃, at 367°C and 36 atmospheres hydrogen pressure listing bicyclohexane as the major product with little biphenyl formed and no phenylcyclohexane.

Nagai et al.⁽²³⁻²⁵⁾ reported results from studies of the HDN reaction of carbazole, carbazole + acridine, and carbazole + various sulfur-containing compounds. The studies used reduced and sulfided Mo/Al₂O₃ catalysts within a wide temperature and pressure regime (260 to 360°C, 45 to 125 atmospheres hydrogen pressure). Neither biphenyl nor phenylcyclohexane was a major product of the HDN reaction in these studies. The reaction pathway observed was via 1,2,3,4-tetrahydrocarbazole and perhydrocarbazole to produce fully saturated naphthenes as the products {i.e., complete saturation of the aromatic structures prior to the ring-opening (hydrogenolysis) reactions}.

Ji-Chang Yeh⁽²⁶⁾ studied the HDN reactions of both carbazole, and 9-ethylcarbazole using presulfided CoMo/Al₂O₃, and NiMo/Al₂O₃, at 320°C and

172 atmospheres hydrogen pressure. In agreement with most of the other studies, Yeh failed to report either biphenyl or phenylcyclohexane as a reaction product.

Polinsky et al.⁽²⁷⁾ also studied the hydrogenative conversion of carbazole with a sulfided NiW/Al₂O₃ catalyst in a fixed-bed reactor at 46 bar total pressure, 300°C to 375°C, and a fixed contact time. Their results were explained by assuming that carbazole was rapidly hydrogenated to 1,2,3,4-tetrahydrocarbazole, while subsequent hydrogenation of the heterocyclic ring and splitting of one C-N bond led to 2-cyclohexylaniline. Bicyclohexane was the major HDN product in their study produced via 2-cyclohexylcyclohexylamine. Polinsky et al.⁽²⁷⁾ failed to see the presence of hydrogenated products of carbazole other than 1,2,3,4-tetrahydrocarbazole or the intermediate 2-cyclohexylcyclohexylamine. They also failed to see any perhydrocarbazole. At the highest temperatures studied, significant isomerization of bicyclohexane to methylcyclopentylcyclohexanes was noted.

The HDN model compound studies on carbazole reported in the literature illustrate the failure of "conventional" catalysts to make the reaction scheme follow the pathway of minimum or even partial hydrogenation (i.e., 2-aminobiphenyl → biphenyl or 2-aminobiphenyl → 2-phenylcyclohexylamine → phenylcyclohexane or 1,2,3,4-tetrahydrocarbazole → cis-1,2,3,4,4a,9a-hexahydrocarbazole → 2-phenylcyclohexylamine → phenylcyclohexane). The main product in the model compound studies reported in the literature is bicyclohexane, and, when Al₂O₃ is present, subsequent isomerization reaction to methylcyclopentylcyclohexanes is observed. Thus, the route resulting in the use of the **maximum** amount of hydrogen needed to accomplish HDN is followed.

Figure 1. Reaction scheme for the hydrodenitrogenation of carbazole.

3. THERMODYNAMIC EQUILIBRIA IN THE HYDRODENITROGENATION OF CARBAZOLE

3.1 INTRODUCTION

A possible reaction scheme for the HDN of carbazole is shown on the preceding page (figure 1). This report will not discuss the possible isomerization reactions of the products of the nitrogen removal steps (phenylcyclohexane and bicyclohexane). The presence of acidic sites on the catalyst used to accomplish the HDN reaction ensures the isomerization of the cyclohexane rings to methylcyclopentanes at high temperatures ($>300^{\circ}\text{C}$).⁽²⁷⁾

This section of the report is written in the same format as the earlier report on the HDN of quinoline, NIPER-468.⁽¹⁷⁾ The concept of crossover temperatures introduced in NIPER-468 is used to give a pictorial representation of the derived equilibria equations. The Appendix to this report outlines the thermodynamic relationships used to derive numerical values for the various equilibria in the HDN reaction scheme, and the basics of the concept of crossover temperature. Readers wishing further details on the crossover temperature concept are referred to the Thermodynamic Primer in NIPER-468, where the concept is used to derive the process conditions required to meet the new EPA mandated level of aromatics in diesel fuel.⁽²⁸⁻³⁰⁾ All thermodynamic property values (and their sources) used in the calculation of crossover temperatures, equilibrium constants etc., can be found in the Appendix.

3.2 THE CARBAZOLE $\rightarrow$ 2-AMINOBIPHENYL $\rightarrow$ BIPHENYL ROUTE

This route is the most economic in hydrogen usage. However, it is also the most unlikely thermodynamic route under a pressure of hydrogen. In an earlier topical report, NIPER-482,⁽¹⁹⁾ on the thermodynamic properties of 2-aminobiphenyl, this minimum hydrogen usage route was compared with CH_2 removal from fluorene, and O removal from dibenzofuran. (Biphenyl is formed in each case.)

X = CH₂, NH, and O

The crossover temperature plot given in that report is reproduced here (figure 2) to illustrate the difficulty of direct nitrogen removal from carbazole. Note that for carbazole and fluorene realistic reaction conditions preclude the ring-opening hydrogenation reaction from operating within the kinetic control region. For example, the formation of 2-aminobiphenyl from carbazole under kinetic control at 100 atmospheres hydrogen pressure would require a temperature less than -70°C . In contrast, with a suitable catalyst at 100 atmospheres hydrogen pressure, the ring opening reaction with dibenzofuran could be accomplished in the kinetic control region provided that the temperature was below 210°C .

Under "conventional" processing conditions 325°C to 3400°C and 75 to 150 atmospheres hydrogen pressure all three ring-opening reactions are under thermodynamic control. For carbazole, within the range of conventional processing conditions, thermodynamic calculations (using equation 1 of table A3 in the Appendix) give between 6 and 12 mole per cent 2-aminobiphenyl under equilibrium conditions. For fluorene the corresponding calculations give 67 to 86 mole per cent 2-methylbiphenyl under thermodynamic equilibrium. For dibenzofuran the calculations give the range of conversion to 2-hydroxybiphenyl as 96 to 99 mole per cent.

Figure 2. Crossover-temperatures for dibenzo compound ring opening reactions. Reading from left to right, the curves represent the ring-opening reactions for carbazole, fluorene and dibenzofuran, respectively. For each compound the thermodynamic control region lies to the right of its respective curve. The cross-hatched region represents the range of conventional process conditions.

The fate of the 2-substituted biphenyl formed in the initial step of the HDX reaction is important to the overall consumption of hydrogen. Two pathways are possible for XH_2 removal:

Figure 3 Possible HDX reaction scheme for substituted monoaromatics

Path 1 could continue with subsequent hydrogenation of biphenyl to phenylcyclohexane (Path 3). However, this is not probable in the carbazole or dibenzofuran cases due to the inhibition of the catalyst surface by the nitrogen- or oxygen-containing compounds present. Such a pathway would be more probable for the HDX of fluorene.

For 2-aminobiphenyl, 2-methylbiphenyl, and 2-hydroxybiphenyl on Path 1, thermodynamic calculations (using equations derived in NiPER-402) show the reactions to be in the kinetic-control region under all conceivable reaction conditions with hydrogen present. Under such conditions the relative reaction rates are proportional to the strengths of the aromatic- XH bonds. The bond dissociation energies of Ph-NH_2 , Ph-CH_3 , and Ph-OH , are listed in reference 31 as 439, 418, and 469 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Although the presence of a catalyst will reduce these values somewhat,

high temperatures (>350°C) would be required for the reactions to proceed at measurable rates. Hence Path 2 is the probable route to HDX products.

3.3 2-AMINOBIPHENYL → PHENYLCYCLOHEXYLAMINE ROUTE

This is the Path 2 route to HDN products. Under Path 2 the 2-substituted biphenyl is hydrogenated to the corresponding 2-cyclohexyl compound with subsequent HDX removal. The bond dissociation energies⁽³¹⁾ for cyclohexyl-NH₂, cyclohexyl-CH₃, and cyclohexyl-OH, are 351, 356, and 383 kJ·mol⁻¹, respectively and the rates of reaction will be many powers of ten greater than those under Path 1 provided the reactions are in the kinetic-control region.[§] However, in Path 2 the hydrogenation reaction can be within the thermodynamic-control region under certain conditions; thus, restricting the overall HDX reactions. A detailed discussion of Path 2 requires knowledge of the Gibbs free energies of formation for the substituted cyclohexyl compounds. Research in progress at NIPER (funded by DOE Office of Energy Research) has enabled accurate estimation of such values for trans-2-phenylcyclohexylamine.

The variation of the equilibrium constant with temperature, for the hydrogenation of 2-aminobiphenyl was derived from the estimated Gibbs energies of formation (see tables A2 and A3 of the Appendix). The equation derived is:

$$\ln K' = 22950 (K/T) - 46.08 + 3 [\ln(p_{H_2}/p^\circ)]. \quad (1)$$

The equation relating the crossover temperature T_{cross} to the hydrogen pressure p_{H_2} (see Appendix) is:

$$p_{H_2} = \exp\{(\ln 1000 + 46.08 - 22950/T_{\text{cross}})/3\}. \quad (2)$$

Equation 2 is plotted in figure 4. The figure shows how the pressure needed to keep within the kinetically-controlled region rises exponentially as the temperature is

§ Rate constant = $A e^{-E_a/RT}$; assuming A factors to be the same for the XH₂ formation steps via Path 1 or Path 2 the relative reaction rate constants will be proportional to the difference in bond dissociation energies. Using that assumption calculated factors are 10⁷, 10⁵, and 10⁷ respectively.

increased. This is true for all crossover-temperature plots discussed in this report. At 250° C the pressure for the crossover point into the kinetic region is 21 atm., while at 400° C it is 542 atm. With the proper choice of conditions it would be possible to hydrogenate 2-aminobiphenyl in the kinetic-control region and prevent the intervention of thermodynamic limitations. However, using HDS catalysts, high temperatures (>300° C) are required to break the C-NH₂ bond necessitating that the reactions are in the thermodynamic-control region. Also, since 2-phenylcyclohexylamine is unstable at high temperature, the equilibrium is forced to completion (i.e., the product of the equilibrium is removed by subsequent reaction).

In the quinoline study,⁽¹⁷⁾ the fate of 2-propylaniline in that HDN reaction scheme paralleled that of 2-aminobiphenyl here. The earlier report concluded that at high temperatures (>350°C) the hydrogenation was under thermodynamic control but propylcyclohexane was the ultimate product due to the fast removal of the hydrogenation product, 2-propylcyclohexylamine, (the lower bond-dissociation energy coming into play)

3.4 CARBAZOLE → 1,2,3,4-TETRAHYDROCARBAZOLE ROUTE

Any route for removal of nitrogen from carbazole, except the direct one through 2-aminobiphenyl (discussed above) requires hydrogenation of the aromatic system. The first stable product of ring hydrogenation is 1,2,3,4-tetrahydrocarbazole. Figure 5 shows the relationship between crossover temperature T_{cross} , and hydrogen pressure p_{H_2} , for the carbazole/1,2,3,4-tetrahydrocarbazole system. The plot was derived from the equation:

$$p_{\text{H}_2} = \exp\{(\ln 1000 + 29.17 - 13250/T_{\text{cross}})/2\} . \quad (3)$$

obtained using the information listed in table A3 of the Appendix. At 250° C the pressure for the crossover point into the kinetic region is 215 atm., TEN times that for the 2-aminobiphenyl ⇌ trans-2-phenylcyclohexylamine system discussed above. At 400° C the pressure at the crossover point is over 3600 atmospheres of hydrogen! Therefore, under any practical conditions for the HDN reaction, there will be a thermodynamic equilibrium between carbazole and 1,2,3,4-tetrahydrocarbazole.

Figure 4 Hydrogen pressure against crossover temperature for the 2-aminobiphenyl $\rightleftharpoons$ trans-2-phenylcyclohexylamine system. The cross-hatched region represents the range of conventional process conditions.

Figure 5 Hydrogen pressure against crossover temperature for the carbazole $\rightleftharpoons$ 1,2,3,4-tetrahydrocarbazole system. The cross-hatched region represents the range of conventional process conditions.

3.5 1,2,3,4-TETRAHYDROCARBAZOLE $\rightarrow$ cis-1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE

Subsequent hydrogenation of 1,2,3,4-tetrahydrocarbazole produces 1,2,3,4,4a,9a-hexahydrocarbazole. Figure 6 is a plot of the relationship between crossover temperature T_{cross} , and hydrogen pressure p_{H_2} , for the 1,2,3,4-tetrahydrocarbazole/cis-1,2,3,4,4a,9a-hexahydrocarbazole system. The plot was derived from the equation:

$$p_{\text{H}_2} = \exp\{(\ln 1000 + 13.44 - 3240/T_{\text{cross}})\} . \quad (4)$$

obtained using the information listed in table A3 of the Appendix. At 250° C the hydrogen pressure at the crossover point into the kinetic region is $1.4 \cdot 10^6$ atmospheres of hydrogen, which is 6700 times that for the 2-aminobiphenyl $\rightleftharpoons$ trans-2-phenylcyclohexylamine system discussed above! Therefore, under any practical conditions for the HDN reaction, there will be a thermodynamic equilibrium between 1,2,3,4-tetrahydrocarbazole and cis-1,2,3,4,4a,9a-hexahydrocarbazole.

3.6 CARBAZOLE $\rightarrow$ 1,2,3,4-TETRAHYDROCARBAZOLE $\rightarrow$ cis-1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE

This section considers the combination of sections 3.4 and 3.5, i.e., complete hydrogenation of one of the benzenoid rings of carbazole. The results of the thermodynamic equilibria calculations are shown in figure 7. The plots represent the equilibrium concentrations over the temperature range 100° C to 400° C at the upper and lower pressures (75 and 125 atmospheres hydrogen pressure) used in conventional hydrodesulfurization. Note that the equilibrium concentration of cis-1,2,3,4,4a,9a-hexahydrocarbazole decreases with increase in temperature. Over the temperature range of significance 1,2,3,4-tetrahydrocarbazole is the major product of hydrogenation with the concentration of carbazole only becoming important at high temperature (>300° C). However, >300° C is just where HDN using HDS catalysts is attempted. At thermodynamic equilibrium under "conventional" processing conditions 325 to 400° C and 75 to 150 atmospheres hydrogen pressure, only 1 to 4 mole per cent of cis-1,2,3,4,4a,9a-hexahydrocarbazole is present at thermodynamic equilibrium (see figure 7).

Figure 6 Hydrogen pressure against crossover temperature for the 1,2,3,4-tetrahydrocarbazole $\rightleftharpoons$ cis-1,2,3,4,4a,9a-hexahydrocarbazole system. The cross-hatched region represents the range of conventional process conditions.

Figure 7. The carbazole/tetrahydrocarbazole/hexahydrocarbazole /hydrogen system. Thermodynamic equilibria under 75 and 150 atmospheres hydrogen pressure, respectively. ; 1,2,3,4-tetrahydrocarbazole: ; cis-1,2,3,4,4a,9a-hexahydrocarbazole. Unshaded area represents moles per cent carbazole.

3.7 cis-1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE → trans-2-PHENYL-CYCLOHEXYLAMINE

Note that cis-1,2,3,4,4a,9a-hexahydrocarbazole can form either (cis and/or trans) – 2-phenylcyclohexylamine or 2-cyclohexylaniline via hydrogenolysis (ring-opening) reactions. The formation of 2-phenylcyclohexylamine results in the HDN reaction scheme reverting the 5 moles of hydrogen per mole of carbazole pathway discussed above.

Figure 8 shows the relationship between crossover temperature T_{cross} , and hydrogen pressure p_{H_2} , for the cis-1,2,3,4,4a,9a-hexahydrocarbazole/trans-2-phenylcyclohexylamine system. The plot was derived from the equation:

$$p_{\text{H}_2} = \exp\{(\ln 1000 + 14.02 - 8790/T_{\text{cross}})\} . \quad (5)$$

obtained using the information listed in table A3 of the Appendix. At 250°C the pressure for the crossover point into the kinetic-control region is 62 atm., while at 400°C it is 2610 atm. With the proper choice of conditions (i.e., relatively low temperature) it would be possible to ring open cis-1,2,3,4,4a,9a-hexahydrocarbazole in the kinetic control region and prevent the intervention of thermodynamic limitations. However, using HDS catalysts, high temperatures (>300° C) are required to break the C–NH₂ bond necessitating that the reactions are in the thermodynamic-control region. As noted above during the discussion of the 2-aminobiphenyl/trans-2-phenylcyclohexylamine system, 2-phenylcyclohexylamine is unstable at high temperature. Thus the equilibrium would be forced to completion, if the initial step can be performed

3.8 cis-1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE → 2-CYCLOHEXYLANILINE

Figure 9 shows the relationship between crossover temperature T_{cross} , and hydrogen pressure p_{H_2} , for the cis-1,2,3,4,4a,9a-hexahydrocarbazole/2-cyclohexylaniline system. The plot was derived from the equation:

$$p_{\text{H}_2} = \exp\{(\ln 1000 + 12.37 - 10390/T_{\text{cross}})\} . \quad (6)$$

obtained using the information listed in table A3 of the Appendix. Note from the figure that this hydrogenolysis reaction is under kinetic control under all conditions except those of high temperature (>300° C) and low hydrogen pressure (<50 atmospheres of hydrogen).

Figure 8. Hydrogen pressure against crossover temperature for the cis-1,2,3,4,4a,9a-hexahydrocarbazole $\rightleftharpoons$ trans-2-phenyl-cyclohexylamine system. The cross-hatched region represents the range of conventional process conditions.

Figure 9. Hydrogen pressure against crossover temperature for the cis-1,2,3,4,4a,9a-hexahydrocarbazole $\rightleftharpoons$ 2-cyclohexylaniline system. The cross-hatched region represents the range of conventional process conditions.

3.9 2-CYCLOHEXYLANILINE → 2-CYCLOHEXYLCYCLOHEXYLAMINE

This reaction step is similar to that given earlier for 2-aminobiphenyl → trans-2-phenylcyclohexylamine. The crossover temperature equation:

$$p_{H_2} = \exp\{(\ln 1000 + 47.09 - 22900/T_{\text{cross}})\} . \quad (7)$$

is almost the same as equation 2 above. The reader is referred to figure 4 for a pictorial representation of the crossover temperature function.

4. CONCLUSIONS FROM THERMODYNAMIC ANALYSIS

The results of the thermodynamic analysis show that the minimum-hydrogen-usage pathway for the HDN of carbazole is highly improbable without a specifically designed catalyst.

Even then, thermodynamic control of the reaction sequence will necessitate a low equilibrium concentration of 2-aminobiphenyl and a slow rate of hydrodenitrogenation at temperatures above 300°C. The route:

is also improbable without a specially designed catalyst. Again, formation of 2-aminobiphenyl is the bottleneck.

Thermodynamic analysis shows that HDN routes using 5 mole equivalents of hydrogen with initial ring saturation are more probable. In particular the route carbazole → 1,2,3,4-tetrahydrocarbazole → cis-1,2,3,4,4a,9a-hexahydrocarbazole → trans-2-phenyl-cyclohexylamine → 2-phenylcyclohexane appears

promising. Of more promise is the similar route; carbazole $\rightarrow$ 1,2,3,4-tetrahydrocarbazole $\rightarrow$ cis-1,2,3,4,4a,9a-hexahydrocarbazole $\rightarrow$ 2-cyclohexylaniline $\rightarrow$ 2-phenylcyclohexane where a speciality catalyst is used in the final step aniline to naphthene.

Catalysts for the formation of phenylcyclohexane need to be "poor" hydrogenation catalysts but also "good" hydrogenolysis catalysts to achieve the goal of minimizing hydrogen consumption. Zero valent catalysts appear to fulfill these requirements as shown by the Mo/C catalyst described by Skala et al.⁽³²⁾ However, in the presence of sulfur, the zero valence state of the catalyst is lost with the formation of Mo_xS_y and the reaction can revert to the full ring saturation pathway to HDN.⁽³²⁾

A second possible solution could be the use of a hydrogen donor solvent in the NH_3 formation step. Thermodynamic equilibrium calculations[†] for the overall reaction forming 2-cyclohexylcyclohexylamine via the donation of hydrogen from tetralin:

[†] For the reaction: tetralin $\rightleftharpoons$ naphthalene + 2 H_2 , the pseudo-equilibrium constant is: $\ln K' = -15430/T + 28.43$. This was obtained with Gibbs energies of formation for tetralin and naphthalene from references 33 and 34, respectively.

show that the equilibrium is shifted far to the left. The equilibrium constant is:

$$\ln K = -490/T - 8.89 \quad (8)$$

For the reaction forming phenylcyclohexane by the direct removal of ammonia:

the equilibrium constant is far to the right particularly at high temperature

$$\ln K = -3030/T + 31.51 \quad (9)$$

Hence, use of tetralin in combination with a "good" hydrogenolysis catalyst under low-hydrogen pressure at high temperature should force the reaction in the direction required.

The Re/C in tetralin catalyst used by Shaw,⁽³⁵⁾ in a study of the HDN of 1,2,3,4-tetrahydroquinoline, quinoline, indole, and 2-ethylaniline, is an example of such a catalyst system. For each compound studied, aromatic hydrocarbon selectivity was high; 68 to 77 mole per cent. However, when the catalyst was presulfided, 2-ethylaniline was converted mainly to ethylcyclohexane (76 moles per cent), the opposite of that observed when no sulfur was present. (Reaction with sulfur altered the valency of the catalyst.) At the low pressures used by Shaw (< 5 atm. H₂), less than 0.5 per cent 2-propylcyclohexylamine was present at equilibrium. Because the rate of ammonia loss from this molecule is more rapid than from its aromatic counterpart, the presence of a few percent 2-propylcyclohexylamine is sufficient to result in mostly saturated product.

The success of HDN reactions of carbazole resulting in the formation of phenylcyclohexane as the main product depends on the relative stability of one intermediate; namely hexahydrocarbazole. The thermodynamic analysis shows that

cis-1,2,3,4,4a,9a-hexahydrocarbazole is not a stable compound in the absence of a large excess of hydrogen. To amplify the point the equilibrium constant for the reaction:

is given by the following expression

$$\ln K = 6774/T - 2.28 \quad , \quad (10)$$

emphasizing the relative instability of the hexahydro compound. The instability of cis-1,2,3,4,4a,9a-hexahydrocarbazole was shown in a thermal stability study of a sample supplied by the Oklahoma State University Synthesis Group.

In the initial study of the thermal stability of cis-1,2,3,4,4a,9a-hexahydrocarbazole a 10.6 mg sample was subjected to the usual heat-hold-heat cycles used to determine heat capacities of organic compounds.⁽³⁶⁾ In the liquid phase (above 390 K) the heat capacities were linear in temperature to approximately 560 K where a sharp positive divergence from the straight line indicated an exothermic reaction, and hence, sample decomposition. Since in the planned adiabatic heat-capacity measurements the sample could spend long periods of time above the melting point, and would require several freeze/melt cycles, further studies were undertaken to test the "long-term" stability in the liquid phase.

A 9 mg sample was held at 500 K for 64 hours in a cell in the differential scanning calorimeter (dsc). The sample had decomposed since it was not possible to solidify the sample at any temperature above that of liquid nitrogen. A further 7 mg sample was held at 450 K 2 hours. Subsequent glc analysis of the products of that heat treatment showed two peaks. The "new" peak was identified as 1,2,3,4-tetrahydrocarbazole by measuring the retention time of a known sample under identical conditions to that used in the analysis of the dsc sample.

The samples were dissolved in high-purity pentane with a little methylene chloride added to promote solubility for the glc analyses. To confirm the presence of 1,2,3,4-tetrahydrocarbazole in the dsc sample, some was added to enhance its peak height. However, in addition to the peak height enhancement, a third peak appeared. Subsequent tests showed the third peak to be carbazole.

The results of this sojourn from the field of thermodynamics into the realms of analytical chemistry has confirmed that cis-1,2,3,4,4a,9a-hexahydrocarbazole is indeed very unstable in its liquid phase. Furthermore, in the presence of excess 1,2,3,4-tetrahydrocarbazole, in solution in the vicinity of room temperature hydrogen is further "shuttled," resulting in the formation of the parent aromatic system carbazole. Additional studies are required to elucidate the full reaction scheme and the relative kinetics of the system, but that is left to others more expert in the fields of kinetics and analytical chemistry.

In the spectrum of fossil fuel materials from heavy petroleum through the liquids formed in the liquefaction of coal, a myriad of aromatic nitrogen-containing compounds are observed. When such a mixture is subjected to HDN under thermodynamic control the different nitrogen-containing systems will react in a particular order. Research into the relative thermodynamics of the HDN reaction for 2 and 3-ring aromatic heterocyclic aromatic nitrogen-containing compounds is in progress at present. Preliminary results point to an "excess stability" for alkyl-carbazoles, which is not present in quinolines, indoles, or even, benzocarbazoles. Details of the research will be published in a Topical Report in September.

5. CONCLUSIONS

- Removal of nitrogen from heterocyclic aromatic nitrogen-containing compounds using conventional hydrodesulfurization catalysts, temperatures, and hydrogen pressures *results in processing under thermodynamic control with high hydrogen consumptions.*
- To reduce hydrogen consumption in the hydrodenitrogenation of carbazole, special conditions are required.
- Use of a zero valent transition metal catalyst with or without the addition of a hydrogen donor solvent results in the formation of aromatics as the major products of the HDN reaction.
- HDN reactions in the presence of zero valent transition metal catalysts require prior removal of sulfur-containing compounds.
- Preliminary research points to carbazole HDN being difficult to accomplish even when hydrogen usage is not considered a major problem.

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APPENDIX

LISTING OF THERMODYNAMIC PROPERTY VALUES AND SOURCES

THERMODYNAMIC EQUILIBRIA

The calculation of thermodynamic equilibria in organic systems has been outlined in previous reports from this research group.^(A1,A2,A3) The methodology can be summarized as follows. For the general reaction:

the equilibrium constant, K , is approximately:

$$K = [p_{\text{product}} / p_{\text{reactant}}] \cdot p_{\text{H}_2}^{-n}, \quad (\text{A1})$$

and the Gibbs energies of formation, $\Delta_f G_m^\circ$, for reactants and products are directly related to the equilibrium constant through the relations:

$$\sum \Delta_f G_m^\circ(\text{products}) - \sum \Delta_f G_m^\circ(\text{reactants}) = \Delta_r G_m^\circ = -RT \ln K. \quad (\text{A2})$$

[Thus, the experimental Gibbs energies of formation for nitrogen compounds derived in this and earlier reports in this series provide the means to accurately determine equilibrium constants without performing a single reaction. In a more rigorous treatment, the partial pressures are replaced by fugacities. For the experimental conditions discussed in this report, the difference is not significant.] To explicitly demonstrate the effect of hydrogen pressure on the equilibria, a "pseudo-equilibrium" constant, K' , is defined:

$$K' = [p_{\text{product}} / p_{\text{reactant}}] = K \cdot p_{\text{H}_2}^n, \quad (\text{A3})$$

and with equation (A2), K' is related to the Gibbs energy of reaction, $\Delta_r G_m^\circ$:

$$\ln K' = -\Delta_r G_m^\circ / RT + n [\ln(p_{\text{H}_2} / p^\circ)], \quad (\text{A4})$$

where p° is the standard state pressure used in the thermodynamic calculations (101.325 kPa, 1 atm. in this report). As has been noted in previous reports,^(A1,A2) if $\ln K'$ is plotted versus $1/T$, near linear curves are obtained. This facilitates extrapolation of the experimental values obtained at relatively low temperature into the range of commercial processes.*

* $\Delta_r G_m^\circ$ can be split into an enthalpy and entropy contribution. Then, equation (A4) can be written:

$$\ln K' = -\Delta_r H_m^\circ / RT + \Delta_r S_m^\circ / R + n [\ln(p_{\text{H}_2} / p^\circ)]. \quad (\text{A4a})$$

CROSSOVER TEMPERATURE

In order to give as visual a picture as possible of the use of thermodynamics in process engineering, a new concept was introduced in reference A3: the "crossover temperature." For any hydrogenation reaction with a negative Gibbs energy of reaction (i.e., a possible reaction) a crossover temperature can be defined such that below that temperature the reaction is "kinetically controlled." Below the crossover temperature (in the "kinetic-control region"), equilibrium constants derived from Gibbs energies indicate that the reaction can go to completion, though a catalyst may be required for it to go at a measurable rate. In this region, the extent of reaction will increase as the temperature is increased; roughly doubling every 15° C. *Hence, for optimal efficiency the reaction should be performed at the maximum temperature practical (i.e., near as possible to the crossover temperature).*

Above the crossover temperature, the reaction conditions are in the "thermodynamic-control region." In this region an equilibrium exists between the reactants and the products and **increasing the temperature** further results in a **decrease** in the yield of the products. In the thermodynamic-control region, the presence of a catalyst will hasten the attainment of the equilibrium, but will not change the yield. To change the equilibrium condition, special procedures are required such as continuous removal of a product. In the thermodynamic region, increasing the temperature while maintaining all other conditions the same will result in **less** product formation. A pictorial view of the crossover-temperature concept is given in figure A1.

Thus, the slope of a $\ln K'$ versus $1/T$ plot is directly proportional to the enthalpy of reaction, $-\Delta_r H_m^\circ$. This feature is used in the main report to estimate "heats" of reaction.

Figure A1. Pictorial view of the crossover-temperature concept. The filled circle denotes the maximum yield of products obtained at temperature T_1 ; the unfilled circle denotes the maximum yield of products at temperature T_2 . (Note the same value for the yield.) Therefore, increasing the temperature can fail to increase the yield since the reaction can change zones from the kinetic-control zone to the thermodynamic-equilibrium-control zone. Maximum process efficiency is obtained within the box marked on the figure i.e., at the crossover temperature,

GIBBS ENERGIES OF FORMATION

GENERAL DETAILS

Enthalpies and entropies for equilibrium hydrogen, oxygen, and nitrogen used in the derivation of the ideal-gas thermodynamic properties of each compound were determined from JANAF tables.^(A4) Enthalpies and entropies for graphite were determined with the polynomial^(A5) used to calculate the values from 298.15 K to 6000 K listed in the JANAF tables. Values for the enthalpies of formation for CO₂(g) and H₂O(l) used to derive enthalpies of formation for each compound were those listed by CODATA.^(A6) Details of the sources and/or methods of estimation of the ideal-gas thermodynamic properties of each compound follow. The derived values for the Gibbs energies of formation are reported in table A1.[¶] Uncertainty intervals (one standard deviation) in the estimated Gibbs energies of formation reported in table A1 vary, depending on the degree of estimation used in the derivations. Since the values were used to determine Gibbs energies of reaction in a closed system (in the thermodynamic sense) the uncertainties in the enthalpies and entropies of the elements as assessed by JANAF^(A4) cancel in the equilibrium calculations reported in the main text. Neglecting the uncertainties in the elements the uncertainty interval for the dimensionless Gibbs energies of formation (i.e., $\Delta_f G_m^\circ/RT$) for each compound listed in table A1 probably lies in the range ± 0.2 to ± 0.5 .

[¶] All tables are listed at the end of this Appendix.

CARBAZOLE

Due to its high melting point (521 K) direct thermodynamic property measurements on carbazole are not possible in the available apparatus at NIPER. However, with the availability of measurements on 9-methylcarbazole (a liquid at room temperature) and 1-methylpyrrole, reliable values for carbazole itself can be estimated. As can be seen in the above figure the molecular environment of each atom within the balanced equation is approximately the same maintaining the rules of group additivity for property estimation.

The ideal gas thermodynamic functions for 9-methylcarbazole in the temperature range 298.15 K to 760 K were reported in NIPER-520.^(A7) Ideal gas thermodynamic functions for 1-methylpyrrole in the temperature range 0 to 1000 K were reported in reference A8.

The ideal-gas thermodynamic functions derived for carbazole are in serious disagreement with those listed in the American Petroleum Institute (API) Monograph Series Publication 716.^(A9) The ideal-gas thermodynamic functions reported in the monograph were derived using molecular property data from reference A10 and vibrational frequencies from reference A11. The vibrational frequencies listed in reference A11 are for the solid phase or from solution IR spectra and their use to calculate ideal-gas functions is not to be recommended. The carbazole results were then used in the American Petroleum Institute (API) Monograph Series

Publication 719(A12) to estimate ideal-gas thermodynamic properties for indole. The indole thermodynamic functions reported were also in serious disagreement with those reported by this group in reference A13. Both API Monographs need revision to include the recent experimental measurements.[§]

1,2,3,4-TETRAHYDROCARBAZOLE

Ideal gas thermodynamic functions for 9-methyl-1,2,3,4-tetrahydrocarbazole in the temperature range 298.15 K to 680 K were reported in NIPER-520.(A7) Functions for 1,2,3,4-tetrahydrocarbazole were estimated using the same procedure as that used for carbazole. The estimation procedure is represented by the following figure.

2-AMINOBIPHENYL

The thermodynamic functions for 2-aminobiphenyl are reported in reference A15.

BIPHENYL

The thermodynamic functions for biphenyl are reported in reference A16.

[§] Note in proof: The standard enthalpy of formation of carbazole in the ideal gas phase estimated in this research was $204.2 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ which is in excellent agreement with the value of $205.0 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$ recently obtained by Jiménez et al.⁽¹⁴⁾ Jiménez's value was significantly different from earlier values reported in the literature and used in the API Monographs.

AMMONIA

The thermodynamic functions for ammonia listed in reference A4 were used in the calculations.

trans-2-PHENYLCYCLOHEXYLAMINE

The method of increments^(A17) was used to estimate the ideal-gas thermodynamic functions for trans-2-phenylcyclohexylamine using the formula:

trans-2-phenylcyclohexylamine =

$$\text{trans-2-ethylcyclohexylamine} + \text{phenylcyclohexane} - \text{ethylcyclohexane} - \{R \ln 4\} . \quad (\text{A.5})$$

In A.5 the symmetry numbers from left to right are 4, 6, 2, and 3, respectively. The logarithmic term corrects for the discrepancy in total symmetry numbers for over-all and internal rotation in the formula A.5 as written. It is necessary in the calculations of the entropies but not the enthalpies of formation. Values from NIPER-415^(A13) were used for trans-2-ethylcyclohexylamine, from NIPER-403^(A18) for phenylcyclohexane, and from Stull, Westrum, and Sinke^(A17) for ethylcyclohexane.

PHENYLCYCLOHEXANE

Values of the thermodynamic functions for phenylcyclohexane were estimated in NIPER-403.^(A18)

cis-1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE

As detailed in the main text, cis-1,2,3,4,4a,9a-hexahydrocarbazole is unstable above the melting point (372 K). Therefore the ideal gas thermodynamic properties cannot be determined directly from conventional measurements. The direct application of group additivity methods^(A19) is also not possible due to the absence of ring correction terms for the

ring system.

In this report another approach has been taken to estimate the ideal gas Gibbs energies of formation of cis-1,2,3,4,4a,9a-hexahydrocarbazole. Shaw and Stapp^(A20) report results of a study of the hydrogenation of carbazole using a platinum on alumina catalyst (where no hydrogenolysis occurred at the temperature of the study). They found that, at 500 K under 152 atmosphere hydrogen pressure, the equilibrium ratio of cis-1,2,3,4,4a,9a-hexahydrocarbazole to 1,2,3,4-tetrahydrocarbazole was 1:7. Hence

$$\ln K' = -\Delta_r H_m^\circ / RT + \Delta_r S_m^\circ / R + n[\ln(p_{H_2}/p^\circ)]$$

becomes

$$\ln (1/7) = -\Delta_r H_m^\circ / 500R + \Delta_r S_m^\circ / R + \ln 152$$

Assuming that the entropy change for the addition of one mole of hydrogen to 1,2,3,4-tetrahydrocarbazole is approximately the same as the addition of one mole of hydrogen to indole to form indoline, then $\Delta_r S_m^\circ / R$ is -13.44.^(A17) Hence $-\Delta_r H_m^\circ / R$ is then 3230 and the equation for the reaction

1,2,3,4-TETRAHYDROCARBAZOLE $\rightarrow$ cis-1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE
is

$$\ln K' = 3240/T - 13.44 + [\ln(P_{H_2} / P^\circ)].$$

This equation is used to estimate the Gibbs energies of formation and reaction reported in tables A1 and A2 respectively.

2-CYCLOHEXYLANILINE

The method of increments^(A17) was used to estimate the ideal-gas thermodynamic functions for 2-cyclohexylaniline using the formula:

$$\text{2-cyclohexylaniline} = \text{2-methylaniline} + \text{phenylcyclohexane} - \text{toluene} - \{R \ln 2\} \quad (\text{A.6})$$

In **A.6** the symmetry numbers from left to right are 2, 6, 2, and 6, respectively. Values from NIPER-459^(A21) were used for 2-methylaniline, from NIPER-403^(A18) for phenylcyclohexane, and from Stull, Westrum, and Sinke^(A17) for toluene.

trans-2-CYCLOHEXYLCYCLOHEXYLAMINE

The method of increments^(A17) was used to estimate the ideal-gas thermodynamic functions for trans-2-cyclohexylcyclohexylamine using the formula:

$$\begin{aligned} \text{trans-2-cyclohexylcyclohexylamine} = \\ \text{trans-2-ethylcyclohexylamine} + \text{bicyclohexane} - \text{ethylcyclohexane} - \{R \ln 4\} \quad (\text{A.7}) \end{aligned}$$

In **A.7** the symmetry numbers from left to right are 4, 6, 2, and 3, respectively. Values from NIPER-415^(A13) were used for trans-2-ethylcyclohexylamine, from NIPER-403^(A18) for bicyclohexane, and from Stull, Westrum, and Sinke^(A17) for ethylcyclohexane.

BICYCLOHEXANE

Values of the thermodynamic functions for bicyclohexane were estimated in NIPER-403.^(A18)

GIBBS ENERGIES OF REACTION

Values of $\Delta_r G_m^\circ$ for each of the reactions depicted in figure A2 are listed in table A2. Equations in the form of **A4a** are listed in table A3 for each of the reactions (the reaction numbers given in table A2 are those used to denote the equilibria in table A3).

FIGURE A2 The hydrodenitrogenation of carbazole. The numbering sequence depicts the reaction equilibria used in tables A2 and A3.

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TABLE A1 Gibbs energies of formation ^a
(R = 8.31451 J·K⁻¹·mol⁻¹ and p° = 101.325 kPa)

T/K	$\Delta_f G_m^\circ / RT$			
	carbazole	2-aminobiphenyl	biphenyl	ammonia
300	126.41	129.12	112.90	-6.41
400	106.27	111.00	94.99	-1.72
500	94.53	100.53	84.62	1.21
600	86.86	93.73	77.89	3.22
700	81.48	88.91	73.14	4.71
	THC	<u>trans</u> -2-PChA	phenylcyclohexane	
300	111.48	98.96	76.20	
400	102.19	99.39	78.40	
500	97.15	100.52	80.47	
600	94.04	101.59	82.23	
700		102.48	83.68	
	HHC	2-cyclohexylaniline	<u>trans</u> -2-ChChA	bicyclohexane
300	114.13	91.93	62.87	41.49
400	107.54	93.84	83.39	63.79
500	104.11	95.68	96.92	78.26
600	102.09	97.22	106.35	88.38
700				95.86

- ^a THC = 1,2,3,4-tetrahydrocarbazole;
trans-2-PChA = trans-2-phenylcyclohexylamine;
HHC = cis-1,2,3,4,4a,9a-hexahydrocarbazole;
trans-2-ChChA = trans-2-cyclohexylcyclohexylamine.

TABLE A3 Equations to represent the equilibria given in figure A2

Reaction #	
1	CARBAZOLE → 2-AMINOBIHENYL $\ln K' = 2490 \text{ K/T} - 10.99 + [\ln(P_{H_2} / P^\circ)]$
2	2-AMINOBIHENYL → BIHENYL + AMMONIA $\ln K' = 6057 \text{ K/T} + 2.51 + [\ln(P_{H_2} / P^\circ)]$
3	CARBAZOLE → 1,2,3,4-TETRAHYDROCARBAZOLE $\ln K' = 13250 \text{ K/T} - 29.17 + 2 \cdot [\ln(P_{H_2} / P^\circ)]$
4	2-AMINOBIHENYL → <u>trans</u> -2-PHENYLCYCLOHEXYLAMINE $\ln K' = 22950 \text{ K/T} - 46.08 + 3 \cdot [\ln(P_{H_2} / P^\circ)]$
5	<u>trans</u> -2-PHENYLCYCLOHEXYLAMINE → PHENYLCYCLOHEXANE + AMMONIA $\ln K' = 7880 \text{ K/T} + 2.97 + [\ln(P_{H_2} / P^\circ)]$
6	1,2,3,4-TETRAHYDROCARBAZOLE → <u>cis</u> -1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE $\ln K' = 3240 \text{ K/T} - 13.44 + [\ln(P_{H_2} / P^\circ)]$
7	<u>cis</u> -1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE → <u>trans</u> -2-PHENYLCYCLOHEXYLAMINE $\ln K' = 8790 \text{ K/T} - 14.02 + [\ln(P_{H_2} / P^\circ)]$
8	<u>cis</u> -1,2,3,4,4a,9a-HEXAHYDROCARBAZOLE → 2-CYCLOHEXYLANILINE $\ln K' = 10390 \text{ K/T} - 12.37 + [\ln(P_{H_2} / P^\circ)]$
9	2-CYCLOHEXYLANILINE → <u>trans</u> -2-CYCLOHEXYLCYCLOHEXYLAMINE $\ln K' = 22900 \text{ K/T} - 47.09 + 3 \cdot [\ln(P_{H_2} / P^\circ)]$
10	<u>trans</u> -2-CYCLOHEXYLCYCLOHEXYLAMINE → BICYCLOHEXANE + AMMONIA $\ln K' = 7807 \text{ K/T} + 1.79 + [\ln(P_{H_2} / P^\circ)]$

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