Thermodynamic analysis on disproportionation process of cyclohexylamine to dicyclohexylamine

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This work deals with a study of the effect of temperature on the cyclohexylamine disproportionation to dicyclohexylamine, jointly with the thermodynamic analysis of this process. The laboratory experiments were carried out in a glass tubular continuous-flow reactor in a gaseous phase at the reaction temperature 433–463 K over a nickel catalyst. The results show, that the temperature has a trifling effect on equilibrium conversion of cyclohexylamine. However, temperature affects the formation of hydrocarbons, benzene and cyclohexane, and dehydrogenation products of dicyclohexylamine, i.e. N-cyclohexylidenecyclohexanamine and N-phenylcyclohexylamine. The latter one is the dominant product of dicyclohexylamine dehydrogenation. The disproportionation of cyclohexylamine has slightly exothermic character. At the experimental reaction temperature range, the cyclohexylamine disproportionation is spontaneous reaction and other reactions of this process are non-spontaneous.

Keywords: Cyclohexylamine, Dicyclohexylamine, Disproportionation, Chemical equilibrium, Thermodynamics.

INTRODUCTION

Amines are a class of organic compounds that are used as intermediates for the synthesis of biologically active compounds in a variety of applications including agricultural and rubber chemicals, dyes, surfactants and drugs1,2. The cyclohexylamines are cycloaliphatic amines that include unsubstituted primary amine cyclohexylamine (CHA) itself, as well as substituted (C- or N-) cyclohexylamines and secondary amines as dicyclohexylamine (DCHA)3. CHA is used mainly as an intermediate for the production of polymers, vulcanization accelerators, synthetic dyes, plasticizers, medicines and agricultural chemicals4. The salts of dicyclohexylamine, e.g. dicyclohexylamine nitride, are used as corrosion inhibitors4.

CHA is produced by catalytic hydrogenation of aniline (AN), or alternative route to obtain this cycloaliphatic amine is reaction of cyclohexanol (CH-anol) with ammonia5. DCHA is produced as well as CHA by hydrogenation of aniline or amination of cyclohexanol or cyclohexanone (CH-anon)7. Depending on the chosen catalyst and the reaction conditions of aniline hydrogenation, one of these amines can predominate in the hydrogenation products. The cobalt and nickel catalysts are used for the production of both cycloaliphatic amines. Co/Al2O3 catalysts show high selectivity for the primary amine, CHA, whereas the Ni/Al2O3 catalysts are more selective for the secondary amines, DCHA and aromatic amine N-phenylecyclohexylamine (NPCHA)8. Secondary amines arise from the condensation (disproportionation) of two molecules of primary amine9,10. In the case of the CHA disproportionation to DCHA, the reaction scheme (Fig. 1) can be simplified as follows: dehydrogenation of cyclohexylamine (1) to cyclohexylidenamine (2) and their subsequent condensation to N-cyclohexylcyclohexane-1,1-diamine (3). This intermediate releases the molecule of ammonia that gives the imine, N-cyclohexylidenecyclohexanamine (NCCHA, 4), followed by hydrogenation to secondary amine, dicyclohexylamine (5)11.

By a similar route, the condensation reaction of intermediate 2 with aniline, the N-phenylecyclohexylamine (NPCHA) is produced. However, dehydrogenation of DCHA leads to this aromatic amine as well12. The heterogeneously catalyzed hydrogenation of aniline is accompanied by other side reactions. At the elevated temperature, the formation of hydrocarbons benzene (BZ) and cyclohexane (CH-an) occurs and the content of water in the reaction mixture leading to the formation of CH-anol and CH-anon13.

Nowadays, due to increasing demand for DCHA, this amine is produced aside of catalytic hydrogenation of aniline also by the disproportionation of CHA in the gaseous phase over nickel catalysts. This process is frequently performed at the temperature 433–473 K in stream of hydrogen. At this temperature range, CHA disproportionation was studied over a Cu-Zn-Cr/Al2O3 catalyst, leading to a yield of DCHA 50–72.7%14. Popov in his work investigated the catalytic disproportionation of CHA to DCHA at temperature 503 K an atmospheric pressure over the supported nickel catalyst, with the result of the conversion of primary amine of 96%, selectivity with respect to DCHA 35% (yield 32%) and selectivity with respect to NPCHA 54% (yield 50%)15.

In the literature dealing with the production of secondary amines by disproportionation of their primary precursors, especially the disproportionation of CHA to DCHA, are lack of knowledge of equilibrium composition or the temperature dependence of the equilibrium constant. Therefore, the aim of this study is thermodynamic analysis of the disproportionation process of

Figure 1. Scheme of the disproportionation of CHA to DCHA.
CHA to DCHA, with a focus on the effect of reaction temperature on the main and side reactions, particularly the dehydrogenation of DCHA to NCCHA and NPCHA. Both dehydrogenation products, alongside with hydrocarbons are undesirable compounds in commercially produced DCHA.

MATERIALS AND METHODS

Chemicals

All chemicals have been purchased from commercial suppliers and used without any further purification. Cyclohexylamine (99.9%) was acquired from BorsodChem MCHZ. The solvent N,N-dimethylformamide (99.9%) was purchased from Penta Chemicals. The chemicals used as gas chromatography standards, i.e. benzene, cyclohexane, cyclohexanol and cyclohexanone (> 99%) were purchased from Penta Chemicals, aniline (99.9%), dicyclohexylamine (99.9%). N-cyclohexylidenecyclohexanamine (> 50%) and N-phenylcyclohexylamine (> 50%) were acquired from BorsodChem MCHZ. The technical gases, electrolytic hydrogen (grade 3.0) and helium (grade 5.5), were purchased from SIAD Czech spol.

Catalyst

The experiments of disproportionation of CHA to DCHA were carried out using a commercially supported nickel catalyst PRICAT Ni 60/15 (available from Johnson Matthey Catalysts), bulk density 1410 kg/m³. Original cylindrical particles of the catalyst were crushed and sieved. It was used fractions 1.2 to 3.5 mm for experiments.

Experimental apparatus

The experiments were carried out in a glass tubular continuous-flow reactor with an inner diameter of 12 mm and a length of 54 cm. From the gas cylinder hydrogen was fed into the reactor (1). Liquid reactant, cyclohexylamine, was fed into the reactor by a piston pump (2) where it was subsequently vaporized. The reactor was placed in bath of heat transfer (3), the low melting metal alloy Rose’s metal. The outlet gaseous reaction mixture was partially condensed in Liebig condenser (cooled by water) (4) and absorbed at temperature range –15 °C to –18 °C into N,N-dimethylformamide in a freeze trap (5) placed in a bath (6) of the mixture dry ice and ethanol. Waste gases were disposed. The obtained samples of reaction mixture (7) were analysed by the gas chromatography (GC) method (Fig. 2).

Reaction procedure

Disproportionation of CHA was carried out at the reaction temperature range 433–463 K, atmospheric pressure and the 1:15 molar ratio of CHA/H₂. The gas-phase reaction was carried out over a 27.5 g of nickel catalyst (1.2–3.5 mm).

Analytical

Quantitative chromatographic analyses of the chemicals and samples of reaction mixtures were performed using a Shimadzu GC-2010 chromatograph: non-polar column ZB-1 (60 m × 0.25 mm × 1 μm), flame ionization detector using helium as a support gas. The column temperature regime was set as follows: initial temperature 55 °C for 9 min, heating with the first temperature ramp of 10 °C per min up to the temperature of 80 °C for 7 min, heating with the second temperature ramp of 15 °C per min up to the final temperature of 210 °C. The injector and the detector temperatures were set to 250 °C. The substances of the reaction mixtures were identified with the use of GC standards.

Data processing

The obtained chromatographic data, i.e. area units (area %) were converted to mass fractions (wt. %) and subsequently to molar fractions (mol. %). The para-

Figure 2. Schematic diagram of the experimental setup for the disproportionation of CHA to DCHA in gaseous phase in stream of hydrogen.
meters used for the analysis of the reaction system are conversion of CHA and selectivity of products, which are defined as follows:

\[ X_{\text{CHA}} = \left( \frac{x_{\text{CHA, in}}}{x_{\text{CHA, out}}} \right) \cdot 100 \]  

(1)

\[ S_i = \left( \frac{x_{\text{i, out}}}{x_{\text{i, in}}} \right) \cdot 100 \]  

(2)

where \( X_{\text{CHA}} \) is conversion of cyclohexylamine, \( x_{\text{CHA}} \) molar fraction of cyclohexylamine. \( S_i \) the selectivity of species \( i \) and \( x_i \) molar fraction of species \( i \). Subscript \( i \) is a component of carbon products of CHA disproportionation.

The equilibrium constants of the studied reactions of the disproportionation process of CHA were calculated under simplifying premises, that the reaction mixture behaves as the ideal gas and the standard reaction enthalpy of individual reactions does not depend on temperature. Therefore, the equation for equilibrium constant is defined as:

\[ K_p = \prod_{i=1}^{k} \left( \frac{p_i^{\nu_i}}{p^{\nu_i}} \right) = \prod_{i=1}^{k} \left( n_i^{\nu_i} \right) \left( \frac{p^{\nu_i}}{p^{\nu_i}} \right) \]  

(3)

where \( K_p \) is equilibrium constant, \( p_i \) partial pressure of species \( i \), \( p^o \) standard pressure (1 atm), \( n_i \) mole of species \( i \), \( \nu_i \) stoichiometric number, \( p \) pressure of the system (1 atm), \( \Delta \nu \) change of the stoichiometric number. Subscript \( i \) denotes a raw materials hydrogen, cyclohexylamine and products of cyclohexylamine disproportionation. The concentrations of disproportionation produced ammonia and dehydrogenation produced hydrogen were calculated by mass balance.

The standard reaction enthalpy and standard reaction entropy for the reversible reactions were determined by fitting the data using the linear form of Van’t Hoff equation:

\[ \ln K_p = \frac{-\Delta H^o_1}{R} + \frac{\Delta S^o}{R} \]  

(4)

where \( \Delta H^o \) is standard reaction enthalpy, \( \Delta S^o \) standard reaction entropy, \( R \) universal gas constant, \( T \) temperature. Experimental results of standard reaction enthalpy \( \Delta H^o \) of each reaction were compared with the calculated values of \( \Delta H^o \). For this purpose, the Aspen Plus® Simulation Software was used, which compute the \( \Delta H^o \) by summing the standard enthalpies of formation of the reactants and products as follows:

\[ \Delta H^o = \sum_{i=1}^{k} \nu_i \Delta H^o_i \]  

(5)

where \( \Delta H^o \) is standard reaction enthalpy, \( \Delta H^o_i \) standard enthalpy of formation of species \( i \), \( \nu_i \) stoichiometric number.

As a part of thermodynamic analysis of the reaction system, the spontaneity of each reaction was determined, using a change in Gibbs free energy defined as follows:

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]  

(6)

where \( \Delta G^o \) is the change in Gibbs free energy, \( \Delta H^o \) is standard reaction enthalpy, \( \Delta S^o \) standard reaction entropy, \( T \) temperature.

**RESULTS AND DISCUSSION**

**Determination of the equilibrium composition of the CHA disproportionation**

First, the equilibrium composition of the process of CHA disproportionation was scrutinized at the reaction temperature 433 K, pressure 1 atm and 1:15 molar ratio of CHA/H₂. Figure 3 presents the achieving the area of equilibrium composition for the main reaction, the disproportionation of CHA to DCHA. Showed results are described as the variation of CHA conversion with parameter \( W/F_{\text{CHA}} \) (weight of catalyst layer to mass flow of CHA, i.e. catalyst contact time). Over a 27.5 g of nickel catalyst, the equilibrium composition is achieved at the range of mass flow of reactant (CHA) 6–14 g h⁻¹, i.e. at catalyst contact time 4.6–2.0 g cat./(gCHA h⁻¹). The equilibrium conversion of CHA is 53–54% and the equilibrium composition of liquid reaction mixture is ca. 33 wt. % of CHA and 67 wt. % of DCHA.

**Figure 3.** The area of equilibrium composition of the disproportionation of CHA to DCHA at 433 K

Furthermore, Figures 4–6 presents the area of the equilibrium composition of formation of other carbon products of CHA disproportionation, expressed by molar fractions of each species. It can be seen that in the case of the formation of hydrocarbons BZ and CH-an the equilibrium composition is not achieved even at

**Figure 4.** The formation of BZ and CH-an during the disproportionation of CHA to DCHA at 433 K
catalyst contact time range of 4.6–2.0 g_cat./(g_CHA h⁻¹). Nonetheless, the formation of other carbon products as CH-anol, CH-anon, and the dehydrogenation products of both cycloaliphatic amines: AN, NCCHA and NPCHA achieved its equilibrium state at the foregoing range of catalyst contact time.

Effect of the reaction temperature on the CHA disproportionation process

The disproportionation of CHA in a stream of hydrogen over a nickel catalyst was accomplished at different reaction temperatures, i.e. 433–463 K. The results of the conversion of CHA and the values of selectivity of carbon products are displayed in Table 1. The increase of reaction temperature practically does not affects the conversion of CHA, suggests that the disproportionation of CHA to DCHA is slightly dependent on the temperature (i.e. equilibrium conversion of CHA 54–55% at 433–463 K).

These results do not confirm the literary available data, where is stated the conversion of CHA 96% at reaction temperature 503 K. Conversely, the reaction temperature has a significant effect on the selectivity of products. The reaction temperature notably affects the hydrogenolysis of CHA and possibly DCHA to cyclohexane as well (ca. 4% selectivity at 463 K). Noticeably, the formation of benzene is strongly affected by the increasing reaction temperature (ca. 11% selectivity at 463 K). The decrease in the selectivity to DCHA with increasing reaction temperature is due to the increase in the concentration of hydrocarbons (benzene, cyclohexane) and further due to the dehydrogenation reaction of DCHA leading to NCCHA and NPCHA. In addition, this fact does not affirm, that the yield of DCHA increases with temperature. Aromatic amine NPCHA compared with imine NCCHA is dominant product of the dehydrogenation of DCHA and its formation is more affected by the temperature (ca. 2.5% selectivity to NPCHA and 0.2% selectivity to NCCHA at 463 K). It cannot be ruled out that the significant arise in concentration of benzene with increasing temperature is also the result of hydrogenolysis of NPCHA.

Thermodynamic study of the CHA disproportionation process

Based on the results of previous chapters, thermodynamic analysis of the process of disproportionation of CHA to DCHA was simplified (Figure 7) to the reversible reactions: CHA disproportionation to DCHA (R1) and dehydrogenation reactions of DCHA to NCCHA (R2), DCHA to NPCHA (R3), CHA to aniline (R4) and cyclohexanol to cyclohexanone (R5).

![Figure 5. The equilibrium state of the formation of CH-anon and CH-anol during the disproportionation of CHA to DCHA at 433 K.](image)

![Figure 6. The equilibrium state of the formation of AN, NCCHA and NPCHA during the disproportionation of CHA to DCHA at 433 K.](image)

![Figure 7. Scheme of reversible reactions R1–R5 of CHA disproportionation process.](image)

| T [K] | X_{CHA} [%] | Selectivity % of products | CH-an | CH-anon | CH-anon | AN | DCHA | NCCHA | NPCHA |
|-------|-------------|---------------------------|-------|---------|---------|----|------|-------|-------|
| 433   | 54.1        | 0.19                      | 0.34  | 0.88    | 0.03   | 0.01| 96.6 | 0.04  | 0.10  |
| 443   | 55.3        | 0.52                      | 1.04  | 0.84    | 0.04   | 0.06| 97.1 | 0.08  | 0.32  |
| 453   | 55.4        | 1.67                      | 3.74  | 0.87    | 0.06   | 0.17| 92.5 | 0.12  | 0.94  |
| 463   | 55.3        | 3.89                      | 11.05 | 0.71    | 0.09   | 0.54| 81.0 | 0.16  | 2.56  |
Based on equation (3) and the concentrations of the equilibrium state of the corresponding compounds, the thermodynamic parameters of the CHA disproportionation system at the reaction temperature range of 433–463 K were calculated. The equilibrium constants of the reactions (R1–R5) vary with the temperature as presented in Table 2. The exigous decrease of the equilibrium constant with increasing reaction temperature of the main reaction, the disproportionation of CHA to DCHA (R1) indicating that this reaction is slightly exothermic. The equilibrium constant of this reaction at the range of reaction temperature 433–463 K is \( K_P > 1 \), signifies, that the equilibrium is shifted towards the side of products, i.e. DCHA and NH\(_3\). The equilibrium of each dehydrogenation reaction (R2–R5) is shifted towards the side of the reactant \( (K_P < 1) \) due to the large excess of hydrogen (i.e. 1:15 molar ratio of CHA/\( H_2 \)). Nevertheless, there are noticeable differences in each dehydrogenation reactions. In comparison of dehydrogenation of DCHA to NCCHA (R2) and NPCHA (R3), the increasing reaction temperature more affects the increase of \( K_P \) of the latter reaction \( (17 \times 10^{-4} \) for R2, \( 19 \times 10^{-5} \) for R3 at 463 K), consequently, dehydrogenation of DCHA preferably leading to the formation of aromatic amine, NPCHA.

From the data shown in Table 2, the linear plots of ln \( K_P \) versus \( 1/T \) (Figure 8) of each reaction were built and by using equation (4) the respective values of standard reaction enthalpy and entropy were calculated (Table 4). The negative value of the \( \Delta rH^o \) of the reaction R1, the disproportionation of CHA to DCHA, confirms the exothermic character. The \( \Delta rS^o \) of this reaction is almost equal to zero due to the transformation of two molecules of reactant (2 CHA) to two molecules of products (DCHA + \( NH_3 \)). The value of standard reaction enthalpy of the other reactions (R2–R5) is \( \Delta rH^o > 0 \) kJ mol\(^{-1}\) due to the endothermic character of all dehydrogenation reactions. The thermodynamic results of the reactions are \( \Delta rH^o \) (R3, R4) > \( \Delta rH^o \) (R2, R5) and \( \Delta rS^o \) (R3, R4) > \( \Delta rS^o \) (R2, R5) due to the formation of the thermodynamically more stable aromatic ring and increase in disorder, i.e. arise of one molecule of dehydrogenation product plus three molecules of hydrogen, in the case of R3, R4 reactions. The calculated and experimental results of \( \Delta rH^o \) are comparatively consistent, only with discernible difference in the case of reaction R1, however, this can be affected by possible inexactness of the thermochromic data of DCHA in Aspen Plus® Simulation Software database. For the reactions R2, R3 are presented only experimental results of \( \Delta rH^o \) because of lack of any data of compounds NCCHA and NPCHA in Aspen Plus® Simulation Software database.

From the data shown in Table 3, the values change in Gibbs free energy \( \Delta rG^o \) were calculated (Table 4) by using equation (6). At the temperature 433–463 K, the disproportionation of CHA to DCHA (R1) is spontaneous (exergonic) reaction but near to equilibrium due to the value of \( \Delta rG^o \) close to zero (ca. \( -1 \) kJ mol\(^{-1}\)). Compared to that, the rest of the reactions (R2-R5) are non-spontaneous (endergonic) at the reaction conditions of CHA disproportionation, due to the positive value of \( \Delta rG^o \). Nevertheless, with increasing reaction temperature the spontaneous character of reaction R1 grows weaker, due to negative values of both \( \Delta rH^o \) and \( \Delta rS^o \). The opposite situation occurs in the case of reactions R2–R5, when with the increasing temperature the non-spontaneous nature of dehydrogenations weakens, because of positive values of both \( \Delta rH^o \) and \( \Delta rS^o \).

**CONCLUSION**

This study has found, that the liquid equilibrium mixture of disproportionation of CHA to DCHA consists of 33 wt. % of primary and 67 wt. % of secondary amine at 433 K. Increasing reaction temperature has a negligible effect on the equilibrium conversion of CHA, but has a significant outcome on the selectivity of other products. Leading to a decrease in the concentration of DCHA and an increase in the content of hydrogenolysis and dehydrogenation products, especially benzene and NPCHA. Hence, the increasing reaction temperature

*Figure 8. Linear Van’t Hoff plot of ln \( K_P \) versus \( 1/T \) of the reactions R1–R5*

| Table 2. Dependence of the equilibrium constants for each reaction of CHA disproportionation process on the temperature |
| --- |
| \( \bar{T} \) [K] | R1 | R2 | R3 | R4 | R5 |
| --- | --- | --- | --- | --- | --- |
| 433 | 1.33 | \( 5 \times 10^{-4} \) | \( 8 \times 10^{-4} \) | \( 1 \times 10^{-4} \) | \( 33 \times 10^{-4} \) |
| 443 | 1.39 | \( 7 \times 10^{-4} \) | \( 17 \times 10^{-4} \) | \( 4 \times 10^{-4} \) | \( 40 \times 10^{-4} \) |
| 453 | 1.30 | \( 11 \times 10^{-4} \) | \( 64 \times 10^{-4} \) | \( 14 \times 10^{-4} \) | \( 65 \times 10^{-4} \) |
| 463 | 1.21 | \( 17 \times 10^{-4} \) | \( 19 \times 10^{-4} \) | \( 41 \times 10^{-4} \) | \( 97 \times 10^{-4} \) |

*Table 3. Enthalpies of reactions calculated on the basis of thermodynamic data |

| Reaction | \( \Delta rH^o \) [kJ mol\(^{-1}\)] | \( \Delta rS^o \) [kJ mol\(^{-1}\) K\(^{-1}\)] |
| --- | --- | --- |
| R1 | \(-10.2\) | \(-0.01\) |
| R2 | 71.3 | 0.10 |
| R3 | 180.6 | 0.36 |
| R4 | 200.2 | 0.38 |
| R5 | 62.0 | 0.11 |

*\( ^a \) Mean value of \( \Delta rH^o \) at range of 443–463 K. *\( ^b \) No data of compounds NCCHA and NPCHA in Aspen Plus® Simulation Software database.
has almost no effect on the equilibrium constant of CHA disproportionation, however, strongly affects the equilibrium constant of other reversible reactions during this process. The experimental values of the standard reaction enthalpy were obtained for defined reactions of CHA disproportionation process, in particular for the CHA disproportionation, DCHA dehydrogenation to NCCHA and NPCHA: −5.6, 71.3 and 180.6 kJ mol⁻¹.

By the analysis of change in Gibbs free energy with the reaction temperature at the range 433–463 K was found that the main reaction is spontaneous and with increasing temperature leading to equilibrium. The other reactions are non-spontaneous in the direction to products, but with the higher temperature slowly proceed in the reverse direction. In summary, it is appropriate to work at the lower temperature and excess of hydrogen the suppressing the formation of the other products of the cyclohexylamine disproportionation to dicyclohexylamine process.

### NOMENCLATURE

- **AN**: Aniline
- **BZ**: Benzene
- **CHA**: Cyclohexylamine
- **CH-an**: Cyclohexane
- **CH-anol**: Cyclohexanol
- **CH-anon**: Cyclohexanone
- **DCHA**: Dicyclohexylamine
- **GC**: Gas chromatography
- **NCCHA**: N-Cyclohexylidenecyclohexanamine
- **NPCHA**: N-Phenylcyclohexylamine

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