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THERMODYNAMIC ANALYSIS OF TRANSFORMATION REACTIONS OF NITROGEN-CONTAINING COMPOUNDS IN THE HYDROTREATING PROCESS OF DIESEL FRACTIONS BASED ON QUANTUM-CHEMICAL CALCULATIONS

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Abstract

The thermodynamic parameters of the reactions of nitrogen-containing compounds in the hydrotreating process of diesel fractions based on quantum-chemical calculations using the DFT density functional theory (theoretical model of B3LYP approximation, basis 3- 21G) were estimated at 400°C and pressure of 2 MPa.

Based on the thermodynamic analysis, the following groups of nitrogen-containing compounds were identified: monoaromatic hydrocarbons with the position of the nitrogen atom in the ring (pyridine, pyrrole, 3-methylpyridine), diaromatic hydrocarbons with the position of the nitrogen atom in the ring (indole, quinoline, isoquinoline), monosubstituted diaromatic hydrocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring (2-methylquinoline, 4-methylquinoline), three-aromatic hydrocarbons with the position of the nitrogen atom in the ring (acridine, carbazole), alkyl substituted nitriles (3-methylbutanitrile), aromatic nitriles (benzonitrile), aromatic amines (aniline, o-toluidine).

Based on the results of the thermodynamic analysis, the probability of reactions was determined, a reaction scheme for the conversion of hydrocarbons was proposed, which can be used to develop a mathema-tical model for the hydrotreating process of diesel fractions taking into account the transformations of nitrogen-containing compounds.

Keywords: *Hydrotreating, Diesel fractions, Nitrogen-containing compounds, Thermodynamics, Quantum-chemical calculations, Modeling.*

1. Introduction

The hydrotreating process of diesel fractions is widespread, and one of the basic processes in the refining industry nowadays [1-3]. This is largely due to the growth of the production of heavy oils with a high content of nitrogen and sulfur compounds, as well as a change in stand-ards to tighten environmental requirements [4-5]. Reactions of removing heteroatomic com-pounds such as sulfur, nitrogen, oxygen, polycyclic aromatics and olefins take place in the process of hydrotreating diesel fractions [6-7]. But the main purpose of the process is to remove nitrogen and sulfur-containing compounds that cause corrosion of metal equipment and envi-ronmental pollution due to the emission of sulfur and nitrogen-containing gases by diesel engines [8]. In addition, the process of hydrotreating diesel fractions is a supporting process in catalytic technologies, allowing the removal of nitrogenous compounds, which are catalytic poisons [9]. There are non-catalytic methods for removing nitrogen- and sulfur-containing compounds, for example, oxidative or adsorption [10-12]. However, catalytic hydrotreating is currently the most efficient process.

Actual is the direction of increasing the efficiency of the hydrotreating process, in order to increase the degree of nitrogen removal from complex hydrocarbons, for which it is necessary to establish the thermodynamic probability of hydrogenolysis reactions of various nitrogen-containing compounds of the diesel fraction, mainly monoaromatic hydrocarbons with the po-sition of the nitrogen atom in the ring (pyridine, pyrrole, 3-methylpyridine), diaromatic hydro-carbons with the position of the nitrogen atom in the ring (indole, quinoline, isoquinoline),

aromatic nitriles, aromatic amines, alkyl substituted nitriles, etc.. The results of thermody-namic analysis can be used to develop a scheme for the transformation of nitrogen-containing compounds in the mathematical modeling of the hydrotreating process of diesel fractions [13-17].

At present, molecular modeling methods based on quantum chemical calculations are widely used for the calculation of various molecular properties, such as enthalpy, entropy, free Gibbs energy, the total energy of a molecule, and its most stable structure, etc. They take into account the vibrational and rotational motions of atoms, the configuration of electronic orbitals, the effects of the conjugation of double bonds, etc. [18-20], that allows to accurately calculate the energy parameters of molecular structures without binding to narrow classes of organic compounds.

The purpose of this work was to conduct a thermodynamic analysis and determine the probability of the reactions of hydrogenolysis of nitrogen-containing compounds in the process of hydrotreatment of diesel fractions based on quantum chemical modeling.

2. The object of study

The object of the study was the process of hydrotreating diesel fractions, the main purpose of which is to remove nitrogen-containing compounds, such as pyridine, quinoline, acridine, benzonitrile, aniline, etc., proceeding on a nickel-molybdenum catalyst at a temperature of 400°C and a pressure of 2.0 MPa as well as nitrogen-containing compounds and their trans-formations during the reactions of hydrogenation. The straight-run diesel fraction with boiling range 180-360°C was taken as the studied raw materials of this process.
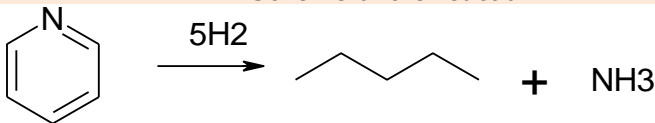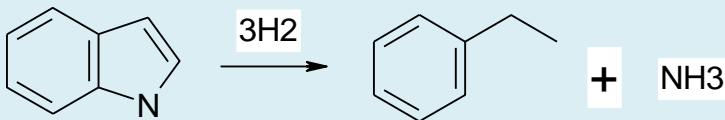
3. Research method

Thermodynamic parameters such as Gibbs energy, enthalpy, and entropy (ΔG_r, ΔH_r, ΔS_r) of hydrogenolysis reactions of various nitrogen-containing compounds during hydrotreatment of diesel fractions were estimated using the DFT density functional theory method (theoretical approximation model B3LYP, basis 3-21G) and Gaussian'09W software.

A distinctive feature of the method used is that it reproduces with high accuracy the struc-ture and energy of hypervalent compounds and provides sufficient accuracy for the qualitative reproduction of many physicochemical properties of molecules. It is known that this method provides the high accuracy of calculations of hydrocarbon molecules containing heteroatoms, and is used to perform thermodynamic analysis under conditions different from standard. The average thermobaric conditions of the hydrotreating process were used for calculations (400°C and 2 MPa).

4. Results and discussion

It is known that hydrogenation reactions of nitrogen-containing compounds, as well as the hydrogenation of olefins, mono- and polyaromatic compounds predominantly proceed during the hydrotreatment process. A list of possible reactions of hydrocarbons contained in the diesel fraction was compiled based on thermodynamic calculations of the parameters of the hydro-genolysis reactions of various nitrogen-containing compounds. The list of reactions used for the research is presented in Table 1.
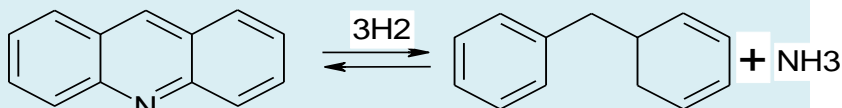
Table 1. Reactions of nitrogen-containing compounds in the hydrotreating process of diesel fractions

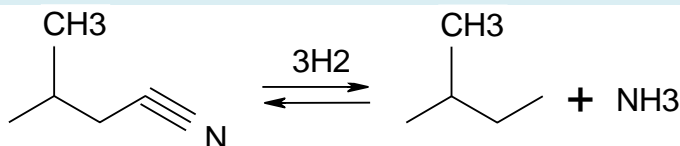| Reaction	Scheme of the reaction
Monoaromatic hydrocarbons with the position of the nitrogen atom in the ring → Paraffins	
Diaromatic hydrocarbons with the position of the nitrogen atom in the ring → Monoaro-matic hydrocarbons	
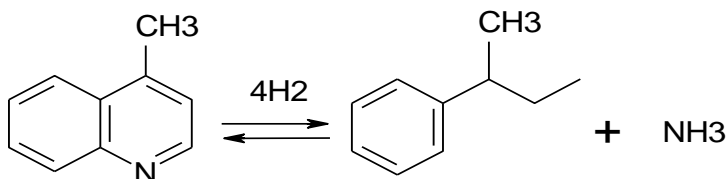
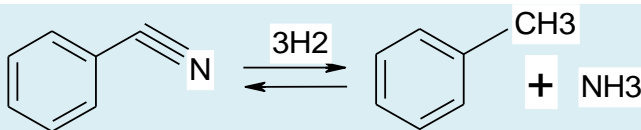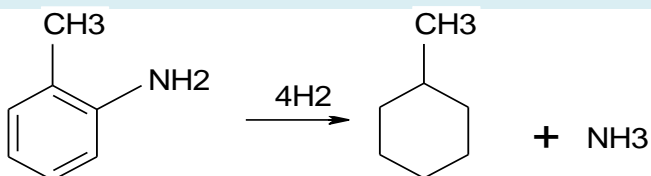| Monosubstituted di-aromatic hy-drocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring → Monoaromatic hydrocarbons | |
Three-aromatic hydrocarbons with the position of the nitrogen atom in the ring → Diaromatic hydrocarbons	
Alkyl substituted nitriles → Paraffins	
Aromatic Nitriles → Monoaromatic hydrocarbons	
Aromatic Amines → Cycloparaffins	

Thermodynamic analysis showed (Table 2) that the probability of hydrogenolysis reactions increases in the row: "Three aromatic hydrocarbons with the position of the nitrogen atom in the ring" < "Monosubstituted diaromatic hydrocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring" < "Alkyl-substituted nitriles" < "Aromatic amines" < "Diaromatic hydrocarbons with the position of the nitrogen atom in the ring" < "Aromatic nitriles" < "Mono-aromatic hydrocarbons with the position of the nitrogen atom in the ring".

Table 2. Values of thermodynamic parameters of reactions of transformations of nitrogen-containing compounds in the hydrotreating process of diesel fractions (T = 400°C, P=2 MPa)

Reaction	ΔH_r, kJ/mol	ΔG_r, kJ/mol	ΔS_r, kJ/(mol*K)
Monoaromatic hydrocarbons with the position of the nitrogen atom in the ring → Paraffins	-317.06	-92.09	-0.34
Diaromatic hydrocarbons with the position of the nitrogen atom in the ring → Monoaromatic hydrocarbons	-209.63	-61.56	-0.22
Monosubstituted di-aromatic hydrocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring → Monoaromatic hydrocarbons	-214.91	-42.56	-0.26
Three-aromatic hydrocarbons with the position of the nitrogen atom in the ring → Diaromatic hydrocarbons	-306.59	-8.54	-0.44
Alkyl substituted nitriles → Paraffins	-173.06	-45.58	-0.19
Aromatic Nitriles → Monoaromatic hydrocarbons	-180.15	-64.47	-0.17
Aromatic Amines → Cycloparaffins	-265.61	-49.38	-0.32

This is due to the increase in their stability and is confirmed by literary data [21]. In this case, the hydrogenolysis reactions of all nitrogen-containing compounds are thermodynamically probable.

The results of thermodynamic analysis showed that the reactions of hydrogenolysis of the compounds such as "Three aromatic hydrocarbons with the position of the nitrogen atom in

the ring", "Monosubstituted diaromatic hydrocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring", "Alkyl-substituted nitriles", "Aromatic amines" proceed reversibly, the average ΔG_r is -8.54 kJ/mol, -42.56 kJ/mol, -45.58 kJ/mol and -49.38 kJ/mol. Moreover, compounds of the group "Monosubstituted diaromatic hydrocarbons with the position of the nitrogen atom in the ring" proceed through the stage of formation of aromatic hydrocarbons, followed by their hydrogenation, first to cycloparaffins and then to paraffins. And the compounds of the group "Aromatic Amines" proceed through the stage of formation of cycloparaffins, followed by their hydrogenation to paraffins.

The hydrogenolysis reactions of nitrogen-containing hydrocarbons such as: "Diaromatic hydrocarbons with the position of the nitrogen atom in the ring", "Aromatic nitriles" and "Monoaromatic hydrocarbons with the position of the nitrogen atom in the ring" are irreversible; the average ΔG_r is -61.56 kJ/mol, -64.47 kJ/mol and -92.09 kJ/mol, respectively. Hydrogenolysis of these compounds proceeds mainly through the stage of hydrogenation.

Thermodynamic analysis of the thermal effects of hydrogenolysis of various nitrogen-containing compounds based on an assessment of their enthalpies at T = 400°C, P=2 MPa, showed (Table 2) that all reactions are exothermic. Hydrogenation reactions of monoaromatic hydrocarbons with the position of the nitrogen atom in the ring to paraffins have the greatest thermal effect. (ΔH_r=-317.06 kJ/mol).

The scheme of transformations of hydrocarbons contained in the diesel fraction was proposed based on the results of thermodynamic analysis of the reactions of nitrogen compounds. The proposed scheme is extended compared to the one proposed by the authors earlier and is presented in Fig. 1.
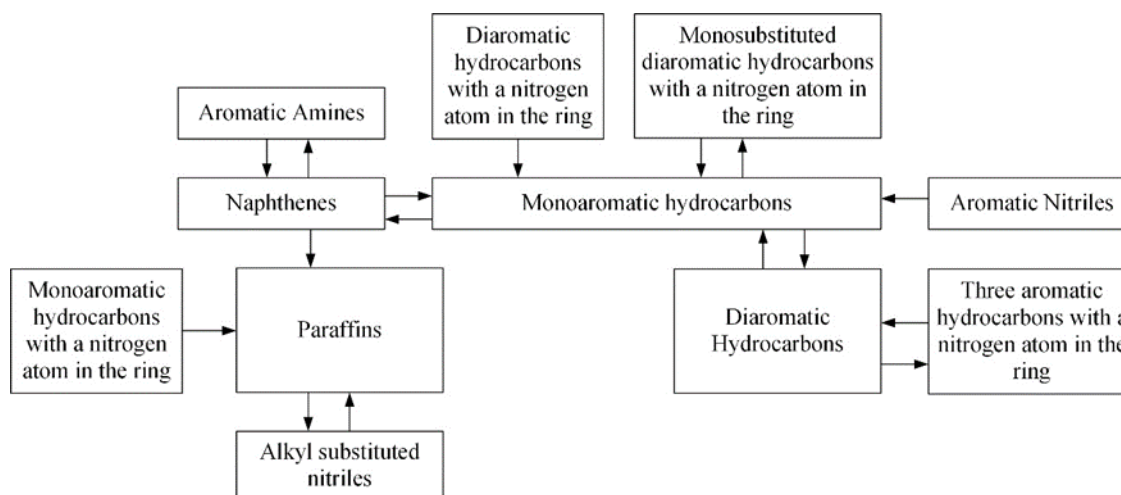

Figure 1. Scheme of hydrocarbon transformations in the hydrotreating process of diesel fractions taking into account the hydrogenolysis reactions of nitrogen-containing compounds

Grouping of hydrocarbons into groups was made based on the probability of reactions taking into account their reversibility. The probability and reversibility of reactions were determined by the values of Gibbs energy under thermobaric conditions of the hydrotreating process (T = 400°C, P=2 MPa) by the following criterion: the reaction is thermodynamically probable and reversible if -50 kJ/mol <ΔG_r <+50 kJ/mol, the reaction is thermodynamically probable and irreversible in the forward direction if ΔG_r <- 50 kJ/mol, the reaction does not proceed in the forward direction if ΔG_r > +50 kJ/mol [22].

The proposed scheme of the transformation of hydrocarbons of diesel fraction taking into account the hydrogenolysis reactions of nitrogen-containing compounds can be used to simulate the process of hydrotreating diesel fractions in order to simplify the mathematical description without losing the sensitivity of the model to the reactivity of nitrogen- and sulfur-containing compounds of various homologous groups.

5. Conclusions

1. It was found that the hydrogenolysis reactions of nitrogen-containing compounds are thermodynamically probable based on the results of the thermodynamic analysis performed by using the DFT quantum-chemical method for calculating (model B3LYP, basis 3-21G) under thermobaric conditions of the diesel hydrotreating process (T=400°C and p = 2 MPa)
2. The proposed level of formalization of nitrogen-containing compounds, which consists of combining hydrocarbons into groups according to a similar structure and thermodynamic probability of their hydrogenolysis reactions.
3. It is shown that the thermodynamic probability of hydrogenolysis reactions of nitrogen-containing compounds increases in the row: "Three aromatic hydrocarbons with the position of the nitrogen atom in the ring" (ΔG_r = -8.54 kJ/mol) < "Monosubstituted diaromatic hydrocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring" (ΔG_r = -42.56 kJ/mol) < "Alkyl-substituted nitriles" (ΔG_r = -45.58 kJ/mol) < "Aromatic amines" (ΔG_r = -49.38 kJ/mol) < "Diaromatic hydrocarbons with the position of the nitrogen atom in the ring" (ΔG_r = -61.56 kJ/mol) < "Aromatic nitriles" (ΔG_r = 64.47 kJ/mol) < "Monoaromatic hydrocarbons with the position of the nitrogen atom in the ring" (ΔG_r = -92.09 kJ/mol).
4. It has been established that under given thermobaric conditions hydrogenolysis of nitrogen-containing hydrocarbons of the type: "Diaromatic hydrocarbons with the position of the nitrogen atom in the ring", "Aromatic nitriles" and "Monoaromatic hydrocarbons with the position of the nitrogen atom in the ring" proceed irreversibly (reaction-direct). And the hydrogenolysis of compounds such as "Three aromatic hydrocarbons with the position of the nitrogen atom in the ring", "Monosubstituted diaromatic hydrocarbons (quinoline derivatives) with the position of the nitrogen atom in the ring", "Alkyl-substituted nitriles", "Aromatic amines" is reversible.
5. The effect of additional benzene rings on the thermodynamic probability of their hydrogenolysis reactions is established. It is shown that with an increase in the number of benzene rings in a molecule, Gibbs energy increases (for pyridine, quinoline, and acridine, ΔG_r is: -97.18 kJ/mol <-58.75 kJ/mol <- 17.15 kJ/mol, respectively).
6. A reaction scheme for the transformation of hydrocarbons based on the results of a thermodynamic analysis of reactions of nitrogen-containing compounds in the hydrotreatment of diesel fractions, which can be used in mathematical modeling and for solving various scientific and applied problems.

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