

## Simulation of the Destructive Hydrogenation of Coal Asphaltene (Short Communication)

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**Abstract**—Data of the computer simulation of the destructive hydrogenation of coal asphaltene are reported. These data were obtained by quantum-chemical methods for refining the geometric configurations of the asphaltene molecule and its radical fragments (UPM3) and the directions of the unimolecular thermal degradation and hydrogenation of a radical fragment (UHF/6-311 + G(d,p)).

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It is well known [1] that various radical fragments, which are stabilized by a hydrogen radical, are formed upon the destructive hydrogenation of heavy hydrocarbon raw materials. These radical fragments are coal and petroleum asphaltenes—the high-molecular-weight degradation products of coal and oil.

Although a large number of studies were devoted to the model samples of multicomponent hydrocarbon-type systems, published data on the results of the quantum-chemical studies of the degradation of these compounds are scanty. At the same time, quantum-chemical simulation is of interest for understanding the microstructure of the test systems.

The aim of this work was to calculate the electronic structure of the model molecule of a coal asphaltene

and its radical fragments and also the most probable reaction paths of the destructive hydrogenation of asphaltene.

Aromatic and heterocyclic rings are the constituents of coal (petroleum) asphaltenes. However, oxygen and sulfur are the main heteroatoms in coal and petroleum asphaltenes, respectively.

Coal asphaltene was chosen as a test material and a model of hydrocarbon raw materials; the geometric configuration (Fig. 1) of the asphaltene and its radical fragments was calculated by the UHF/PM3 (UPM3) method with the full geometry optimization [2].

According to the results of the calculations, the lengths of C–C bonds in benzene rings fall in a range of 1.38–1.41 Å; the carbon–carbon bonds with a

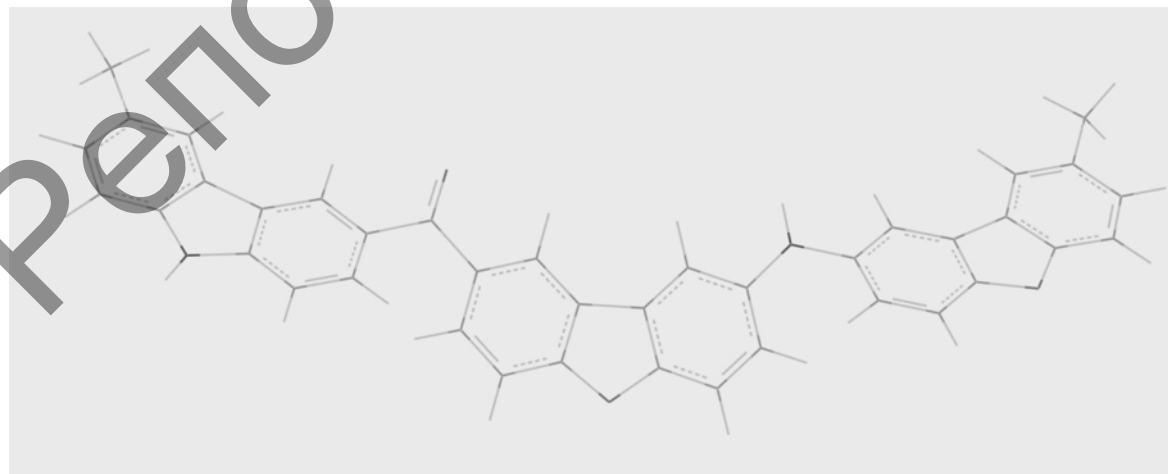
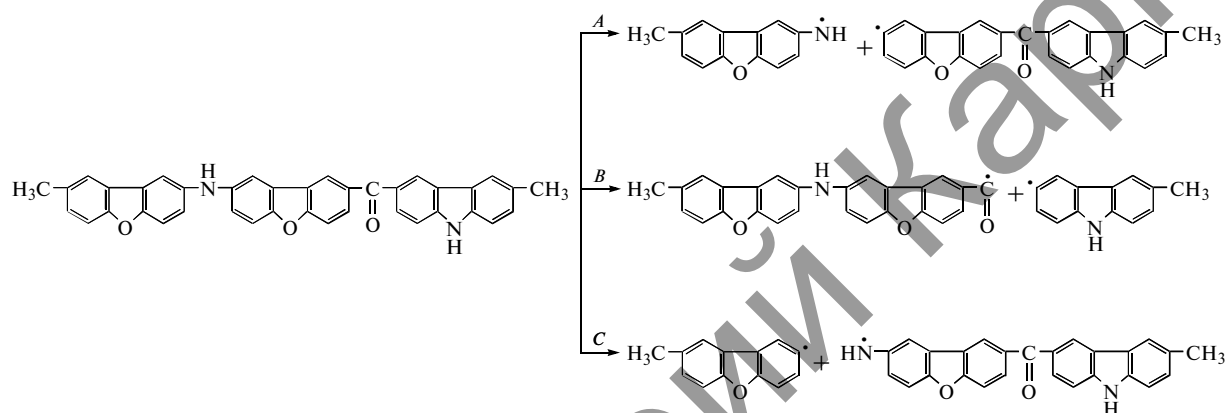


Fig. 1. Spatial molecular configuration of coal asphaltene.

length of 1.46–1.48 Å belong to interring bonds, and the values of 1.52–1.53 Å correspond to out-of-ring C–C(CH<sub>3</sub>, O) bonds. All of the C–H bonds of benzene rings have a length of 1.08 Å, and they are shorter than the C–H bonds of methyl groups (1.09 Å). As expected based on the electronegativities of carbon and nitrogen, nitrogen–hydrogen bonds are even shorter (1.02–1.03 Å). The bond lengths of carbon with heteroatoms also have characteristic values ([C–O(N)] 1.39–1.45 Å). The bond angles fall within the ranges of 118–122° for benzene rings, 105–108° for heterocycles, and 120–133° for interring angles and angles between other bonds. The angles between the

ring planes connected by a carbonyl bridge and an imine bridge are 57 and 49°, respectively. From the analysis of the geometry, it follows that no discrepancy between the bond lengths and bond angles calculated by the PM3 semiempirical method and the standard values is not observed. Therefore, the optimized geometric configurations of the asphaltene molecule and radical fragments were used in nonempirical calculations.

Earlier [2], the following reaction scheme was proposed for determining the most probable reaction path of coal asphaltene degradation in accordance with published data [3]:



With the use of numerous techniques including <sup>1</sup>H NMR, UV, and IR spectroscopy, it was demonstrated that asphaltenes differ in molecular weights, elemental compositions, and heteroelement contents; that is, the above asphaltene structure is one of the conceivable structures. Published data [4] indicate that a less stable structure is formed upon linking two aromatic rings by –CO–, –NH–, and –CH(OH)– bridges than that upon linking by –CH<sub>2</sub>– and –O– bridges. Therefore, reaction paths A–C can be the possible routes of degradation. Allen and Gavalas [3] performed a comparative quantum-chemical evaluation of the bond dissociation energies of asphaltene. In this work, we refined these energies (see the table) with the use of the UHF/6-311 + G(d,p) nonempirical method and the GAUSSIAN program package [4].

The comparative analysis of data showed that the qualitative result remained unchanged: the C–C bond possesses the greatest strength (route B). The UHF/6-311 + G(d,p) method, as previously the UHF/3-21G method, suggested a difference in the dissociation energies of bonds along routes A and C, whereas both semiempirical and spin-restricted Hartree–Fock methods gave the same energy values. Both routes A and C lead to C–N bond cleavage; however, the resulting radicals are structurally different (although similar), and this fact is correctly reflected in the results of

two calculations by an unrestricted method. In the latter case [the UHF/6-311 + G(d,p)\*\* method], the proximity of the values (routes A and C) corresponds to the similarity of radical fragments.

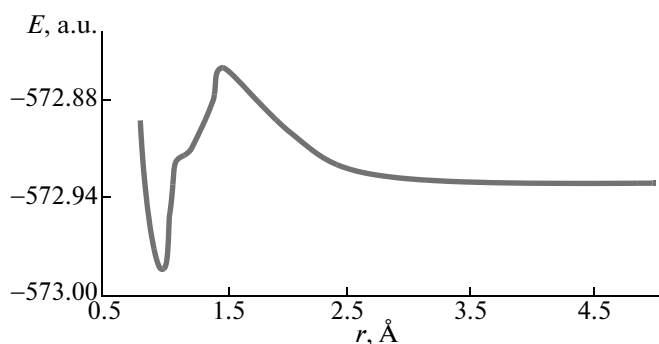
In turn, in the destructive hydrogenation, radical fragments are stabilized by a hydrogen atom. One of these stabilization pathways is considered below. A radical with the smallest number of atoms formed in reaction path C was chosen for the calculations. The energy change of the radical–hydrogen atom system on approaching the latter to the reaction center was calculated by the UHF/6-311 + G(d,p) method

#### Asphaltene bond dissociation energies

Method	Bond dissociation energy $\Delta E(R-X)$ , kJ/mol		
	A	B	C
UPM3 (PM3)*	220.59	227.51	220.78
ROHF/3-21G*	387.76	421.13	387.59
UHF/3-21G*	318.79	413.22	382.99
UHF/6-311 + G(d,p)**	239.69	357.28	247.50

Notes: \* Published data [2].

\*\* This work.



**Fig. 2.** Energy profile of the radical–hydrogen atom system according to UHF/6-311 + G(d,p) data.

(Fig. 2). It is evident that the reaction requires an activation energy.

Thus, as a result of refining the energy of the destructive hydrogenation of coal asphaltene with the aid of nonempirical calculations, the qualitative result of early studies on the greatest strength of the carbon–

carbon bond upon the thermal degradation of asphaltene was confirmed. It was hypothesized that the radical fragment can be stabilized by a hydrogen atom as a result of an electron spin inversion in a particle.

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