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journal homepage: www.elsevier.com/locate/comptcInitial steps in reactions of aquathermolysis of cyclohexyl phenyl sulfide by means of *ab initio* calculations

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ABSTRACT

Aquathermolysis is often proposed as a method to reduce the viscosity of heavy oils. In the present work we have investigated the aquathermolysis reaction of cyclohexyl phenyl sulfide in water medium by means of density functional theory. The water molecule was considered as a reagent and as a catalyst. We have shown that *ab initio* quantum chemistry methods could be applicable for comparative analysis of chemical reaction pathways in aquathermolysis processes. The obtained results could be useful for the systems like tert-alkyl (secondary-alkyl) thiophenyl ethers, which could be formed in heavy oils at harsh conditions. The scheme of different reaction directions with corresponding calculated values of reaction barriers, which are correlated with experimental data, is presented and could be used for comparison with other reaction mechanisms.

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1. Introduction

The heavy oil production keeps increasing globally due to short-fall of conventional light crude oil. The heavy oil consists of high molecular mass compounds, including asphaltenes and resins, which are the main cause of high viscosity. Extremely high viscosity and an abundant amount of heteroatoms (S, O and N) in the structure of heavy oil molecules present major challenges for exploration, transportation and processing of heavy oil. Thus, in order to facilitate production, it is necessary to improve the rheological properties of heavy oil. This can be achieved either by increasing the temperature or by using special chemical transformations during heavy oil processing. One of the proposed methods to reduce the viscosity is aquathermolysis [1–3]. Aquathermolysis is a thermal cracking of large hydrocarbon molecules in the presence of water and in the absence of oxygen. The typical temperatures for aquathermolysis range from about 200 °C up to water critical point conditions (374 °C at 218 atm) [4]. The ability of water to carry out condensation, cleavage, and hydrolysis reactions can be explained by favorable changes in its chemical and physical properties, which at higher temperatures become more compatible with reactions of organic compounds. For example, the dissociation constant (K_w) of water as it approaches the critical point, is

about $10^{-11.30}$, which is about 3 orders of magnitude higher than the value at normal conditions ($10^{-13.99}$) [5], which makes the solvent properties of water at 250–350 °C comparable to properties of polar organic solvents at room temperature. Under those conditions water can act as either acidic or basic catalyst, and its reactivity can often be reinforced by autocatalysis from water-soluble reaction products [6]. Note, however, that once the critical point is passed the value of K_w decreases again dramatically [6].

Over the past decade, significant aquathermolysis processes researches have been focused on the development of the detailed reaction schemes and associated kinetic parameters (see [4] and references therein). However, most of the literature provides only qualitative insights into the chemical interactions of bitumen with steam condensate (or pure steam) while detailed studies of aquathermolysis reactions mechanisms at the molecular level are still relatively rare [7–9]. In Ref. [7] new mechanism for the catalyzed thermal decomposition of formic acid was proposed and analyzed by using B3LYP approach. It was established that decomposition barrier of HCOOH is lowered by 30% in the presence of one water molecule, by 50% in the presence of two water molecules and by 60% in the presence of another HCOOH molecule. In Ref. [8] the *ab initio* calculations of the standard enthalpies of formation, enthalpy of dissociation of the SH and gas-phase acidity for a large number of small sulfur-containing molecules in the gas phase at a temperature of 298.15 K were performed. In Ref. [9] the thermodynamic parameters of conversion reactions of some

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