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Alkanolysis simulation of lignite-related model compounds using density functional theory

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HIGHLIGHTS

- LRMC alkanolysis includes nucleophilic attack, hydrogen transfer and bond cleavage.
- Reactivities of the LRMCs toward alkanolysis are: BOB > anisole > PEB > ODB.
- For the same LRMC, ethanolysis proceeds much easier than methanolysis.

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ABSTRACT

Benzyloxybenzene (BOB), phenethoxybenzene (PEB), oxydibenzene (ODB), and anisole were selected as lignite-related model compounds (LRMCs). Theoretical simulation on the LRMC alkanolysis was conducted to understand the mechanism for lignite alkanolysis using density functional theory in terms of bond order, transition state (TS), charge distribution of TS, bond length, and activation energy (AE). The alkanolysis includes nucleophilic attack of the oxygen atom in an alkanol on the carbon atom in the oxygen-containing bridged bond (OCBB) of a LRMC, hydrogen transfer from OH in the alkanol to oxygen atom in the OCBB, and subsequent cleavage of the OCBB. According to the calculated AE, under the same conditions, the reactivities of the LRMCs toward alkanolysis decrease in the order: BOB > anisole > PEB > ODB; for the same LRMC, ethanolysis proceeds much easier than methanolysis. The rate constant of BOB ethanolysis is ten times more than that of BOB methanolysis at the same temperature.

1. Introduction

Lignites are inferior fuel because of their high ash yield, high water content, low calorific value, poor thermal stability, and easy spontaneous combustion. However, many organic chemicals (OCs), especially oxygen-containing OCs, can be obtained from lignites due to their high oxygen content [1]. Hence, converting lignites to value-added chemicals (VACs) is more promising compared with lignite utilization as fuel, while lignite degradation (LD) in a proper solvent under mild conditions is a crucial step for converting lignites to VACs. Methanol [2–5], ethanol [5–7], and isopropanol [5,8] were reported to be effective solvents for coal liquefaction due to their hydrogen-donating and alkylating abilities [9–12]. Mondragon et al. [13] investigated the reaction of a vitrinite concentrate of Taiheiyo coal with various alkanols using $ZnCl_2$ as a catalyst under nitrogen pressure. They found that more soluble portion was obtained using branched alkanols than using straight alkanols. Shishido et al. [14] considered that ethanol could attack coal structure to yield a considerable amount of coal liquid. The results from sequential thermal dissolution of Huolinguole lignite (HL) in methanol and ethanol show that ethanolysis is much more effective than methanolysis for HL degradation and nucleophilic attack of oxygen atom in methanol or ethanol on carbon atom in oxygen-containing bridged bonds (OCBBs) of HL is a crucial reaction [15]. Such an attack makes LD possible at temperatures much lower than those for lignite pyrolysis, since radical formation is not involved in the alkanolysis.

Understanding the mechanism for lignite alkanolysis (LA) facilitates LA optimization. Theoretical calculation based on quantum chemistry provided systematic and convincing explanation on the mechanisms for many organic reactions [16–26]. Lignites retain more macromolecular structures (MMSs) of coal-forming plants (CFPs) and contain larger amounts of oxygen-containing moieties, including OCBBs, than higher-rank coals [27,28]. Lignin is an important moiety in CFPs and underwent less change during coal-forming process because of its structural stability compared with cellulose and hemicellulose in CFPs.

According to a structural model (Fig. S1) of lignin proposed by Adler [29], anisole, oxydibenzene (ODB), benzyloxybenzene

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Nomenclature

BOB	benzyloxybenzene
PEB	phenethoxybenzene
ODB	oxydibenzene
LRMCs	lignite-related model compounds
TS	transition state
AE	activation energy
OCBB	oxygen-containing bridged bond
OCs	organic chemicals
VACs	value-added chemicals
LD	lignite degradation
HL	Huolinguole lignite
LA	lignite alkanolysis
MMSs	macromolecular structures
CFPs	coal-forming plants
DFT	density functional theory
BO	bond order
CD	charge distribution
BL	bond length
k	rate constant
C_{alk}	carbon atom in CH_2
IF	imaginary frequency
TC	total charge
O_m	oxygen atom in methanol
O_{BOB}	oxygen atom in BOB
C_{ar}	carbon atom in aromatic ring

(BOB), and phenethoxybenzene (PEB) are important moieties in lignin. Such moieties could also exist in MMSs of lignites. Hence, we selected anisole, ODB, BOB, and PEB as lignite-related model compounds (LRMCs) and investigated the alkanolysis of the LRMCs using density functional theory (DFT).

2. Computational approach

Scheme 1 displays methanolysis and ethanolysis of the LRMCs. Quantum chemistry software Materials Studio was used to investigate the detailed mechanisms for the LRMC alkanolysis. Generalized gradient approximation, Becke and Perdew functional, double numerical plus polarization, and Fine and Octupole were selected as method, functional, basis set, and self-consistent field tolerance and aux_density, respectively. The related parameters to LRMC alkanolysis include bond order (BO), transition state (TS), charge distribution (CD) of TS, bond length (BL), and activation energy (AE). The TS was searched by linear and quadratic synchronous transits. In addition, the rate constants (k) for BOB alkanolysis at 298, 373, 473, 513, 543, 573, and 603 K were calculated according to the following formula [30]:

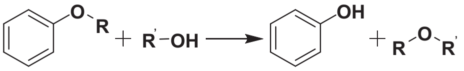
$$k = \frac{k_bT}{h}\left(\frac{p^o}{RT}\right)^{1-n}\exp\left(\frac{-E_a}{RT}\right)$$

where k_b, T, h, R, p^o, E_a, and n denote Boltzmann constant, reaction temperature, Plank constant, universal gas constant, standard atmospheric pressure, AE, and the mole number of reactants, respectively.

3. Results and discussion

3.1. BOs in LRMCs

BO, which reflects chemical bond strength, is half of the difference value between bonding electrons and anti-bonding electrons. The larger the BO is, the stronger the chemical bond will be. As Fig. 1 exhibits, the BO of C_{alk}–O bond in BOB (0.510) is the smallest. Similarly, the BOs of C_{alk}–O bond in PEB (0.514), ODB (0.564) and anisole (0.519) are also the smallest. The results suggest that such OCBBs are not stable and susceptible to decomposition, including alkanolysis.



Scheme 1. LRMC alkanolysis. R denotes methyl, phenyl, benzyl or phenylethyl group, and R′ denotes methyl or ethyl group.

3.2. TS structure

Understanding TS structure is essential for revealing related reaction mechanism. However, in most cases, separating TS species from a reaction system is very difficult due to lability of the species. Simulation using DFT facilitates understanding TS structure. There is only one imaginary frequency (IF) in TS from BOB methanolysis (IF-90.3 cm^{-1}) and ethanolysis (IF-7.4 cm^{-1}) via vibrational analysis. As Fig. 2 illustrates, during the reaction of BOB with methanol or ethanol, as a nucleophilic atom in methanol or ethanol, oxygen with two pairs of lone electron would attack the carbon atom in the OCBB and subsequently cleave the OCBB.

3.3. CD of TS

CD of atoms can be obtained by Mulliken population analysis. As shown in Fig. 2, total charge (TC) of each group in TS can be figured up. The charges of methanol and ethanol are 0.025 and 0.039 (Table 1), respectively, corresponding to their nucleophilicities in terms of pK_a (ethanol 15.9 and methanol 15.5) [31]. The higher nucleophilicity of ethanol than that of methanol makes ethanol more effective than methanol for HL degradation [15].

3.4. BL of reactants and TS

As Fig. 3 and Scheme 2 exhibit, the distance between C_{alk} in BOB and oxygen atom (O_m) in methanol changed from 464.1 to 273.5 pm, while the distance between oxygen atom (O_{BOB}) in BOB and hydrogen atom in OH in methanol changed from 360.3 to 173.0 pm. The O_m attacks the C_{alk}, weakening the O–H bond (i.e., increase in O–H BL from 97.0 to 100.2 pm) and decreasing C–O BL from 143.1 to 142.3 pm in methanol. Such an attack also

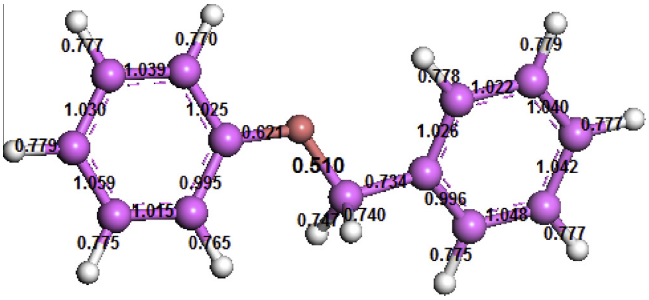


Fig. 1. BOs in BOB.