Aromatic C-H Bond Rupture; a Density Functional, B3LYP, Study

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Unrestricted Density Functional (B3LYP) calculations with the 6-311G(d) basis were done for benzene (C_6H_6) with successive elongation of one C-H bond. Gradual increase in the total energy resulted til C-H bond length of about 3.7 Å, followed by a sudden decrease in energy on further elongation of the bond. The estimated activation energy for the reaction was 152.346 kcal/mol, much higher than the value calculated with the semiempirical PM3 method.

Key words: Benzene; C-H Rupture; Density Functional; Calculation.

1. Introduction

Aromatic hydrocarbons are frequent components of coal and heavy fractions of mineral oils [1]. On the average, they constitute 3 – 4% of the heavy oil [2]. Various chemical studies exist for the degradation of these compounds to olefins and low molecular weight aromatics that are suitable for industrial purposes [3]. In a theoretical study for the thermal degradation of polyaromatic hydrocarbons [4], applying the semiempirical PM3 SCF-MO [5] method, it was found that the calculated activation energies for the C-H bond breaking reaction are smaller than those for the C-C breaking reactions [6]. The calculated activation energies for the C-H rupture reactions of a series of polyaromatic hydrocarbons ranged from 61 to 117 kcal/mol. Due to the importance of such results for the study of the degradation reaction we found it necessary to recalculate the reaction path applying a more exact method. For this purpose we have chosen the Hartree-Fock density functional method [7], and limited our treatment primarily to the reaction of the aromatic benzene molecule.

C-H bond length (Å)	Energy (kcal/mol)
1.050	0.535
1.085	0.000
2.050	86.474
2.500	121.048
2.550	118.637
2.700	125.528
2.800	129.583
3.000	136.566
3.100	139.562
3.200	141.846
3.300	143.989
3.500	148.915
3.550	149.849
3.700	152.346
4.050	116.012
4.550	116.487
5.050	116.193
5.550	116.204
6.050	116.207

Table 1. UHF-B3LYP total energies calculated for C_6H_6 with different lengths of one C-H bond relative to the energy at the equilibrium C-H distance of benzene (1.083 Å).

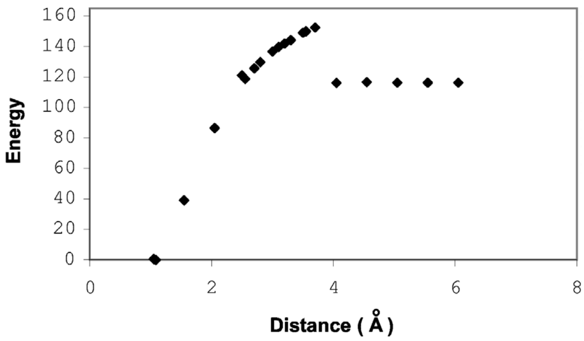

Fig. 1. UHF-B3LYP calculated relative energies (kcal/mol) for the C-H bond rupture in benzene.

2. Method of Calculation

All calculations were done applying the Gaussian 03 program of Pople et al. [8]. Unrestricted Hartree-Fock Density Functional (UHF-B3LYP) calculations were done applying the 6-311G(d) basis. All coordinates of the molecule were varied with the exception of the length for the C-H bond to be ruptured. This was elongated successively during the study of the reaction path.

3. Results and Discussion

The UHF-B3LYP calculation for the C_6H_6 molecule was started with the closed shell structure (D_{6h}) resembling the aromatic benzene. Complete geometry opti-

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mization yielded the total energy values reported in Table 1. Other calculations belong to geometries in which one C-H bond, the same for all points, was elongated and all the other bonds and bond angles varied. Table 1 includes the calculated energies (in kcal/mol) relative to the lowest calculated value, considered to be 0, for the D_{6h} benzene structure.

The study of the data in Table 1 shows that the calculated energy values increase continuously till a C-H distance of approximately 3.7 Å, after which a sudden decline in energy is noticed, followed by an almost constant value of 116.0 kcal/mol. The change in the energy values is best viewed in Fig. 1, the study of which points out:

- bond elongation up to $\sim$ 3.7 Å causes an increase in energy, where a sudden energy decline occurs;
- the energy values for lengths $>$ 3.7 Å are almost constant, $\sim$ 116.0 kcal/mol. Obviously, the values belong to the $C_6H_5^{\bullet} + H^{\bullet}$ molecular system;
- the reaction transition state falls at the distance $\sim$ 3.7 Å much nearer to the reaction product, in accordance with Hammond's postulate for endothermic reactions [9].

It is interesting to note that, the energy difference between benzene of D_{6h} structure and the structure of highest energy along the reaction path, corresponding to a point near the actual reaction transition state, is 152.346 kcal/mol. This calculated (activation) energy is much higher than that calculated applying the semiempirical PM3 method and might be accepted as the correct value for benzene.

A more elaborate discussion of the reaction path and transition state is to be published later in a separate paper [10].

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