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Theoretical studies of C–NO_2 bond dissociation energies for chain nitro compounds

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Abstract

In this paper, quantum chemical calculations are used to estimate C–NO_2 bond dissociation energies (BDE) for 16 chain nitro compounds. These compounds are studied by employing four hybrid density functional theory (B3LYP, B3PW91, B3P86 and PBE1PBE) methods in conjunction with the 6-31G*, 6-311G* and 6-311++G** basis sets, and at the same time, the complete basis set CBS-QB3 method is also performed. The obtained results are compared with the available experimental values. It is demonstrated that the B3LYP and B3PW91 methods are not suitable for our nitro compounds system, while B3P86 method is able to give reliable BDE data. The results show that P3P86 together with 6-31G* is also better than CBS-QB3 method for most of molecules. So we can see that the B3P86 method may be more suitable to produce reasonable BDE of C–NO_2 bond for chain nitro compounds. In order to know if the rule is fit to the ring nitro compounds, two molecules have been calculated. The result is not consistent with the former.

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1. Introduction

The energetic materials play an important role in aeronautics, the weapons industry, and other high-tech fields [1–3]. Development of new energetic materials and improvement of existing energetic materials have become the topic of interest for experimentalist and theoreticians. It is known that the strength of weakest bond in the molecule is a good index of relative sensitivity [4], R–ONO_2 series molecule is an important energetic material, and it is believed that RC–NO_2, RO–NO_2 and RN–NO_2 bonds in energetic molecules are key factors in determining sensitivities to impact in a group of nitroaromatics and nitramines. So bond dissociation energy (BDE) is very important for the study of energetic materials.

Although the property of BDE of nitroaromatic energetic materials can be found experimentally, many are difficult to synthesize and some of them are highly unstable. Moreover, different calculational methods are generally applied to compute the BDE for kinds of molecular systems. The investigations for C–NO_2 are still limited. In 1989, MP4 method based on single reference Hartree–Fock configuration has been performed together with a 6-31G* basis set for several simple C–NO_2 molecules [5], It was found that the constant C–NO_2 bond energy is due to two offsetting effects. Namely, substituents which increase the intrinsic bond energy also increase the stability of radical. Betsy et al calculated the BDE for several aromatic ring molecules using DFT method in conjunction with STO-3G basis set [6]. The results indicate a correlation between sensitivity and the BDE for removal of an NO_2 group. Shao et al. have performed a series of calculations for the BDE of nitro energetic materials molecules using different theory methods, including density function theory (DFT), coupled cluster (CCSD) and complete basis set (CBS-Q) methods [7,8]. Due to spin-contamination problems, the widely used unrestricted Hartree–Fork or perturbation methods cannot

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reliably predict the BDE. More sophisticated ab initio methods such as QCISD and CCSD may be better than that HF and MP2 for the BDE calculations. However, resent studies showed that these highly demanding methods still significantly underestimated BDE unless very large basis sets were utilized [10]. MP4 and CCSD method are able to give good results of BDE but need lots of computation resource and time and may not be a good choice to calculate BDEs in this study.

Density Function Theory (DFT) method, which is cheaper than the composite ab initio methods, does not suffer much from the spin contamination problem and therefore, is an attractive computational option for BDEs.

In the present work, our objective is to perform a systematic comparison of the BDEs for C–NO_2 bond dissociation in 16 chain nitro compounds. All the BDEs are calculated by employing the hybrid density functional theory (B3LYP, B3PW91, B3P86 and BPE1PBE) methods and complete basis set (CBS-QB3) method together with the 6-31G*, 6-311G* and 6-311++G** basis sets. By comparing the calculating of three hybrid DFT methods and CBS-QB3 method for reliable bond dissociation energies of C–NO_2 bond for chain nitro compounds is discussed. Two ring nitro molecules are calculated for testing whether the B3P86 is fit to similar system.

2. Theoretical methods

All computational studies were performed with Gaussian03 computational package [9].

For all studied compounds, geometry optimization was conducted. For these situations that are not convergent without any constraint, we performed the EDIIS algorithm forcibly and optimized the structure repetitious as initial configuration. The integral grid (99, 590) is adopted and the criterion convergence 1.0e-8 is taken into account. Each optimized structure including molecule and fragmentation products was confirmed by the calculation to be the real minimum without any imaginary vibration frequency. The equilibrium geometries and bond dissociation energies were obtained at the Becke-style three parameter Density Functional Theory [11] with the Lee–Yang–Parr correlation function (LYP) [12,13], the Perdew–Wang's 91 expression (PW91) [14] and Perdew's 86 (P86, PBE) [15,16]. The 6-31G*, 6-311G* and 6-311++G** basis sets were in combination with the four hybrid DFT methods mentioned above.

The complete basis set method used in this study was developed by Petersson and his co-workers [17–20]. The energy of the chemical system is computed from a series of calculations. The initial calculation starts with geometry optimization and frequency calculation at HF/6-31G(d) theory level. The geometry is further optimized at MP2/6-31G(d) theory level with single point energy calculation at QCISD(T)/6-31G(d), MP4(SDQ), CBS*B4 and MP2/CBSB3, the model also has empirical corrections for spin contamination and a size-consistent, high order correction. Throughout the test, if the theory level is not specified then the discussed energies are obtained through CBS-Q (298.15 K) computational studies.

The C–NO_2 bond strength is obtained by calculating the homolytic bond dissociation energy, which is defined as the enthalpy change of the dissociation reaction:

$$\mathrm{R{-}X} \rightarrow \mathrm{R}' + \mathrm{X}'$$

The bond dissociation energy of R–X bond is computed from the heats of formation at 298.15 K of species involved in the dissociation, i.e.,

$$E_{\mathrm{BDE}} = \Delta_f H^0_{298.15,\mathrm{R}} + \Delta_f H^0_{298.15,f} - \Delta_f H^0_{298.15,\mathrm{RX}}$$

For nitro compounds studied here, the bond dissociation energy 1-nitropropane ($n\mathrm{C_3H_7{-}NO_2}$) is as follows:

$$E_{\mathrm{BDE}} = E(\mathrm{C_3H_7}) + E(\mathrm{NO_2}) - E(\mathrm{C_3H_7NO_2})$$

The average errors of the BDEs for the CBS-QB3, B3LYP, B3P86, B3PW91 and PBE1PBE methods are determined by calculating the average absolute error (Ave. abs. error), defined as

$$\text{Ave. abs. error} = \frac{1}{N}\sum_{i=1}^{n}|x_i - e_i|$$

where e_i represents the experimental data and x_i denotes the calculated values and N is the number of experimental or calculated data.

3. Results and discussions

The R–NO_2 molecules, where R denotes the remainder of the nitroaromatic molecule, the dissociation energies can be obtained by calculating the total energies (including zero-point energies) of each parent nitroaromatic molecules, the corresponding R fragment and NO_2 scission. The results of 18 molecules are given in Tables 1–3 using four different hybrid density function methods B3LYP, B3P86, B3PW91 and PBE1PBE together with three different basis sets 6-31G*, 6-311G* and 6-311++G**. In addition, the complete basis set (CBS-QB3) method has also been performed. Most of experimental values were collected and listed in tables for comparison. In our system, all of molecules have carbon chain structure except for molecules *cyclo*-C_3H_5–NO_2 and 2-nitrofuran, which have a ring structure.

Table 1 lists the bond dissociation energies using different methods in conjunction with a 6-31G* basis set, and all of the experimental values are from the Ref. [21]. Although the hybrid B3LYP method is a popular computational tool, which produces an extraordinary agreement between computed and experimental for small popular molecules [22], the results from B3LYP are rather poorly for our system. Under the 6-31G* basis set, with an average absolute error of 5.1 kcal/mol and a maximum error of 8.9 kcal/mol, which is unacceptable and B3LYP is not suitable to predict the excellent bond dissociation energies for

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