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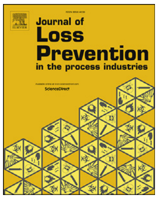

Prediction of heat of formation for *exo*-Dicyclopentadiene

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ABSTRACT

Dicyclopentadiene (DCPD) is an organic compound with two structural isomers, the *exo* and *endo* isomers. There have been several thermal runaway accidents related to this hazardous compound. It is well known that heat of formation is one of the most important parameters to investigate thermal runaway reactions. The heat of formation for the *endo* isomer has been characterized via computational and experimental studies. However, there is no thorough computational or experimental study on the heat of formation for the *exo* isomer. In this work, computational chemistry methods with homodesmotic reaction schemes were proposed to predict the heat of formation for the *exo* isomer. First, the computational methodology was validated by comparing predicted results of the *endo* isomer with its existing experimental value (42.2 ± 0.6 kcal/mol). The results from high level *ab-initio*, density functional theory, and composite methods were shown in a good agreement with the experimental value. The same methodology was then applied to predict the heat of formation for the *exo* isomer. The energy difference of heat of formation between two isomers was estimated at 0.7 ± 0.1 kcal/mol based on various computational methods. Therefore, combining the experimental and computational data, the predicted heat of formation for the *exo* isomer is 41.5 ± 0.6 kcal/mol. This work could provide reliable thermochemical data for inherently safer design of any processes involving DCPD.

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1. Introduction

Dicyclopentadiene (DCPD) is an organic compound with the chemical formula being $C_{10}H_{12}$. It was obtained primarily from steam cracking of naphtha or crude feed in the C5 stream. There has been a strong interest in the polymerization of DCPD via the ring opening metathesis polymerization (ROMP) using metallic catalysts (Hayano et al., 2006) due to its unique properties and new applications including self-healing polymers (Mauldin et al., 2007) and cryogenic storage (Toplosky and Walsh, 2006). There are two structural isomers: the *endo* and the *exo* isomer (Fig. 1). The *endo* isomer has been a subject of many computational (Feng et al., 2012; Guner et al., 2003) and experimental studies (Hayano and Tsunogae, 2005; Liu et al., 1999; Burcat and Dvinyaninov, 1997). To the best of our knowledge, there has never been a thorough computational study on the *exo* isomer. The *exo* isomer is preferred over the *endo* isomer in the ring opening metathesis polymerization due to its kinetics and the exothermic nature of the process (Davidson et al., 1996), which has also attracted lots of attention as a potential high density fuel (Krishnamachary et al., 2014).

Despite its valuable applications, there have been questions of its safety issue (Herndon and Manion, 1968). Previous experiments in the dimerization of cyclopentadiene (CPD) (Ende et al., 2007) showed that the dimerization of CPD was highly exothermic which ruptured the test cell. Herndon et al. (Herndon et al., 1967) showed experimentally that the dimer decomposed to CPD before forming the *endo* isomer thus indicating that the *exo* isomer cannot change its conformation to *endo* directly. Harkness et al. studied the kinetics of CPD to *endo*-DCPD using spectroscopy (Harkness et al., 1937). Recently, Guner et al. (Guner et al., 2003) benchmarked the reaction energy of CPD to *endo*-DCPD as part of a proposed set

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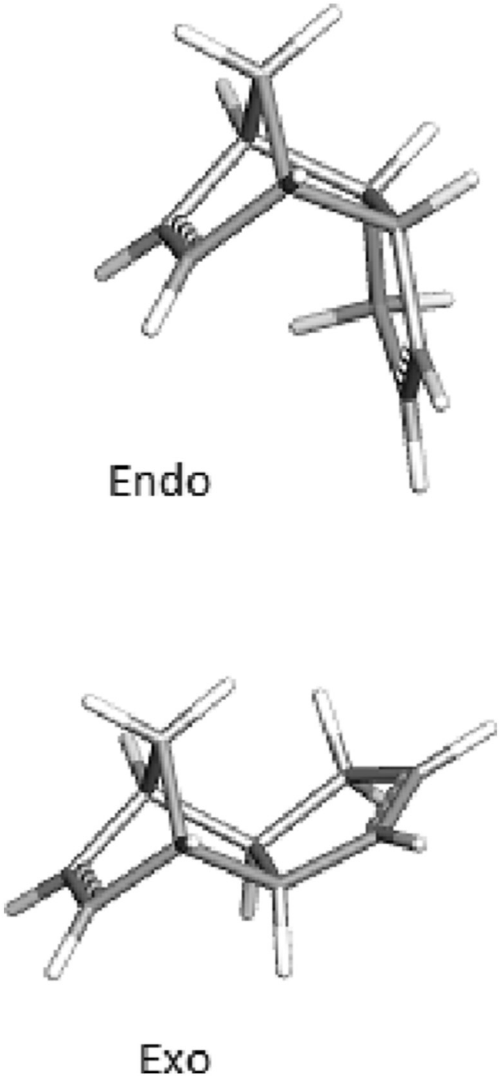

Fig. 1. Structures of the *endo* and *exo* isomers.

of pericyclic reactions for benchmarking new computational methods. A computational study on DCPD was conducted by Jamróz et al. (Jamróz et al., 2003) and the geometries of the 14 possible isomers were calculated and compared with available experimental values using the B3PW91 functional.

DCPD has been involved in a catastrophic incident of a plant manufacturing synthetic resins. The incident at Nevcin Polymers in Netherlands on July 2nd, 1992 resulted in 3 fatalities and a large scale destruction of the city due to a thermal runaway initiated by charging wrong amounts of DCPD mixture into a reactor. The recommended preparation of *exo*-DCPD took place at more than 150 °C in an Argon atmosphere (Nelson and Kuo, 1975), but the product is often not pure enough to characterize the compound using conventional calorimetry. Many researchers reported novel methods to convert the *endo* isomer to the *exo* isomer (Zhang et al., 2007) in order to prepare fuels and polymers. However, due to its reactivity the normal characterization of *exo*-DCPD and measurement of its heat of formation at standard conditions is challenging.

Computational chemistry has been extensively applied to compare the reaction pathways (Wang et al., 2009a,b, 2010) and estimate the heat of formation or heat of reaction for runaway reactions in our previous studies (Saraf et al., 2003; Wang et al., 2009a,b; Wang and Mannan, 2010). The heat of formation is an important data for safe design of chemical process and characterizing the thermodynamics of the compound and kinetic pathways. Given the considerable industrial interest in the ring opening metathesis polymerization of *exo*-DCPD (Henna and Larock, 2009; Rule and Moore, 2002; Mol, 2004) and obtaining high accurate heat of formation to model fuel combustion processes (Chung et al., 1999), we are presenting a thorough computational investigation using quantum mechanical methods to reliably estimate the heat of formation for *exo*-DCPD at 298.15 K and 1 atm.

2. Computational methods

A variety of methods were used in this work including semi-empirical (AM1) (Dewar et al., 1985), post-SCF methods (MP2, MP3, MP4, CCSD, CCSD(T)) (Møller and Plesset, 1934; Pople et al., 1976; Krishnan and Pople, 1978; Purvis and Bartlett, 1982; Pople et al., 1987), density functional theory (B3LYP, M06-2X, M06-HF, M06-L) (Becke, 1993; Zhao and Truhlar, 2006, 2008), double-hybrid density functionals (B2PLYP, mPW2PLYP) (Grimme, 2006; Schwabe and Grimme, 2006) and composite methods (G3, G3 variants, G4, CBS-APNO, CBS-QB3, CBS-4M) (Curtiss et al., 1998, 2007; Baboul et al., 1999; Ochterski et al., 1996; Montgomery et al., 1999, 2000). In addition, the Grimme's empirical dispersion correction (D3) with Becke-Johnson damping function (Schwabe and Grimme, 2007) was used with the following density functional (BLYP, B3LYP) and double hybrid density functional (B2PLYP and mPW2PLYP), and wB97xD (Chai and Head-Gordon, 2008) and B97D3 (Grimme et al., 2011) density functional incorporated with the empirical damping density functional were used as well. All calculations were performed using Gaussian 09 (Frisch et al., 2009). Calculations were performed using the following basis sets: the triple ζ quality Pople-style basis sets with diffuse and polarization functions on both the hydrogen and carbon atoms (6-311++G(d,p)) (Krishnan et al., 1980), Dunning's correlation consistent basis sets cc-pVTZ and aug-cc-pVTZ (Dunning, 1989; Kendall et al., 1992). The geometry optimization and frequency calculations for all species involved in the reaction were performed using DFT methods, MP2 and double hybrid density functionals to calculate the thermodynamic partition functions. Single Point Energy (SPE) calculations were performed on the MP2 optimized geometry using MP3, MP4, CCSD and CCSD (T) methods.

There are various approaches to calculate the standard heat of formation for a desired compound. The two main approaches are using atomization energies directly from molecular simulations and the other is constructing a scheme that results in cancellation of errors systematically arising from the calculations. Calculation of thermochemical quantities from atomization reactions involves very high order calculations and corrections to other terms such as post Born-Oppenheimer effects and anharmonicity corrections for zero point energies which involve very rigorous calculations not feasible for large systems. To minimize the systematic errors in calculation of atomization energies, an approach was adopted via construction of a balanced reaction scheme for cancellation of systematic errors present in atomization energies. To calculate the heat of formation, a homodesmotic reaction was constructed per the hierarchy suggested by Wheeler (Wheeler et al., 2009). For closed shell hydrocarbons, the homodesmotic reaction (HD-4) is defined as a reaction in which the number of each type of carbon-carbon bonds is equal and an equal number of hydrogen attached to each carbon type (sp^2, sp^3) in the reactants and products. Using this methodology, the cancellation of the systematic errors in the electronic energies is achieved quite well and the need to calculate at very high computational levels of theory is minimal. Homodesmotic reactions do not work as well for cyclic compounds as

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