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Product distribution of tricyclopentadiene from cycloaddition of dicyclopentadiene and cyclopentadiene: A theoretical and experimental study

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ABSTRACT

Tricyclopentadiene (TCPD), product of dicyclopentadiene (DCPD)/cyclopentadiene (CPD) cycloaddition, is a promising candidate as high-energy–density fuel. Thermal [4 + 2] cycloaddition of DCPD and CPD was simulated using M05-2X/6-311G(d,p) to predict the product distribution. There are four concerted but slightly asynchronous pathways leading to four adducts for endo-DCPD/CPD and exo-DCPD/CPD additions, respectively. The pathways connecting endo-adduct are kinetically preferred compared with those connecting exo-adduct. NB-adducts show higher stability than corresponding CP-adducts. Moreover, exo-isomers are more stable for CP-adducts, but the tendency is inverse for NB-adducts. The predicted product preference is NB-endo > CP-endo > CP-exo > NB-exo. Experiment shows product composition of NB-endo:CP-endo = 7.32:1 and NB-endo:CP-endo:CP-exo = 3.79:1:0.1 for thermal endo-DCPD/CPD and exo-DCPD/CPD additions, respectively, consistent with the predicted result. However, catalytic reaction gives completely different distribution, in which [4 + 2] NB-exo and CP-exo, along with at least 21.6% [2 + 2] adducts, are formed.

1. Introduction

High-energy–density fuel has attracted considerable attention due to their advantages such as high volumetric energy content and good stability. Compared with refined aviation fuels, combusting equal volume of high-energy–density fuel can generate more propulsion. This is specifically attractive for volume-limited aircrafts such as missile and rocket because the utilization of high-energy–density fuel significantly increases the flight range and payload.

Multi-cyclic hydrocarbons are ideal high-energy–density candidate because their compact structure generates high density and additional strain energy. Among them, tetrahydrotricyclopentadiene (THTCPD) based compounds are very promising. Burdette and Schneider reported exo-THTCPD has volumetric energy of 39.4 MJ/L, which is 12% higher than JP-5 (34.8 MJ/L) [1]. Cheng et al. disclosed that THTCPD isomerized by trifluorochloromethanesulfonic acid has energy density of 41.3 MJ/L [2]. Boulton and Kremer presented that THTCPD catalytically synthesized using zeolites shows even higher energy of 43.1 MJ/L [3]. Actually, THTCPD has been used as the component of high-energy–density fuel RJ-7 [4,5]. We also studied the hydrogenation of TCPD and isomerization of THTCPD [6–8]. In general, this fuel is synthesized through three steps. First, tricyclopentadiene (TCPD) is prepared from the cycloaddition of dicyclopentadiene (DCPD) and cyclopentadiene (CPD). Then TCPD is saturated into THTCPD to obtain stability for long-term storage. Finally THTCPD is treated, often by acid-catalytic isomerization, to reduce its freezing point and viscosity. The cycloaddition of DCPD and CPD is a crucial procedure because different reaction conditions may lead to various TCPD compositions, which ultimately influences the property of synthesized fuel.

Several experimental investigations as to the DCPD/CPD cycloaddition have been taken by researchers, but the result continues to be controversial. Originally, Alder and Stein showed the reaction is typical Diels–Alder [4 + 2] addition occurring between the norbornyl ring of DCPD and CPD [9]. Then Тереньева observed that CPD molecule could also be fused to cyclopentyl ring of DCPD [10]. DCPD has two isomers, namely endo- and exo-DCPD, with the weight of former as about 99%. Nakagawa revealed that endo-DCPD/CPD addition generates some exo-DCPD/CPD adducts [11]. Ramhold also reported similar result [12], indicative of the occurrence of endo- to exo-isomerization during the reaction. In addition, Behr and Keim reported that novel [2 + 2] cycloaddition occurs with the presence of homogeneous bifunctional Pd–acid catalyst [13]. Boulton and Kremer showed that, with the presence of zeolite, the adduct becomes very complex [3]. It indicates that the DCPD/CPD cycloaddition may proceed through many pathways leading to various adducts, which is much more complicated than as expected.

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As for fuel synthesis, exo-adducts are desired because they have relatively low freezing point and viscosity after hydrogenation [1,2,8]. The complex cycloaddition pathways make some difficulties in composition and quality control. One has to clarify the product profile before taking any measurement to improve the selectivity of desired adducts. Quantum chemical calculation has become an advantageous tool to study cycloaddition reactions. In this work, we first conducted a DFT simulation on the Diels–Alder [4 + 2] addition of DCPD and CPD in gas phase to describe possible reaction pathways and predict the product distribution. Then we carried out thermal and catalytic cycloadditions to analyze the actual product composition.

2. Computational and experimental methods

2.1. Computational methods

All reactants and products concerned were geometrically optimized to minima by M05-2X/6-311G(d,p) in Gaussian 03 package [14]. The presence of no imaginary vibrational frequency was checked for the optimization configurations based on the same level.

In search of the transition states (TSs), the linear synchronous transit-guided quasi-Newton method was first used to identify initial TS structures. Then the quadratic synchronous transit-guided quasi-Newton method was used to refine the transition structures. Frequency analysis was performed to prove the optimized transition structure was the first-order saddle point with only one imaginary frequency. Finally, the determined transition structures were verified using intrinsic reaction coordinate (IRC) calculation. Moreover, natural bonding orbital analysis was carried out to quantify the natural charge populated on the optimized structures [15,16].

2.2. Experimental methods

Commercial endo-DCPD was purified to 99% by vacuum distillation. exo-DCPD was prepared and purified according to published procedure [17]. HY zeolite was calcined at 500 °C for 5 h to remove the template residues.

The cycloaddition reaction was conducted in a 250 mL mechanically agitated reactor equipped with an external band heater. To conduct the reaction, 100 mL reactant was introduced into the autoclave, sealed and flushed with nitrogen to exclude air. Then it was heated to 160 °C at low agitation speed (100 rpm). Finally the agitation speed was quickly increased to 720 rpm and the reaction lasted for 12 h. endo-DCPD, mixture of equal molar exo-DCPD and endo-DCPD, and endo-DCPD with 10% zeolite were used as the feedstock, respectively. At the reaction temperature, part of endo-DCPD will dissociate into CPD which further reacts with other DCPD molecules. So endo-DCPD also served as the CPD precursor [18].

After reaction, the product was purified by vacuum distillation (120–130 °C/5 mm Hg). Their composition was analyzed using GC–MS (HP5890) with a HP-5 capillary column (30 m × 0.5 mm). MS analysis confirmed these products were TCPD($C_{15}H_{18}$) with molecular weight of 198. The product component of thermal cycloaddition was identified according to literature [11,12]. ^{1}H-NMR spectra of product were recorded at 25 °C in $CDCl_3$ on a Varian Unity INOVA spectrometer at 500 MHz, with TMS as internal reference.

3. Results and discussion

3.1. General considerations for DFT simulation

DCPD has two isomers, namely endo- and exo-DCPD. In each stereoisomer, there are two C=C bonds, one in the norbornyl (hereafter referred as NB) ring and the other in the cyclopentyl (hereafter referred as CP) ring. During [4 + 2] cycloaddition reaction, CPD may be fused to NB or CP bond of DCPD (hereafter referred as NB- or CP-addition). Moreover, the subsequently formed bicyclo[2.2.1] hept-2-ene fragment may be orientated in endo or exo position (hereafter referred as endo- or exo-addition). Therefore, the [4 + 2] cycloaddition of DCPD and CPD may produce eight TCPD stereoisomers, as shown in Fig. 1. TCPDs generated from NB- or CP-addition are denoted as NB- or CP-adduct, and those from endo- or exo-addition as endo- or exo-adduct, respectively. Thus, TCPD formed from NB- and endo-addition is referred to as NB-endo-adduct. TS corresponding to each adduct is also given the same prefix.

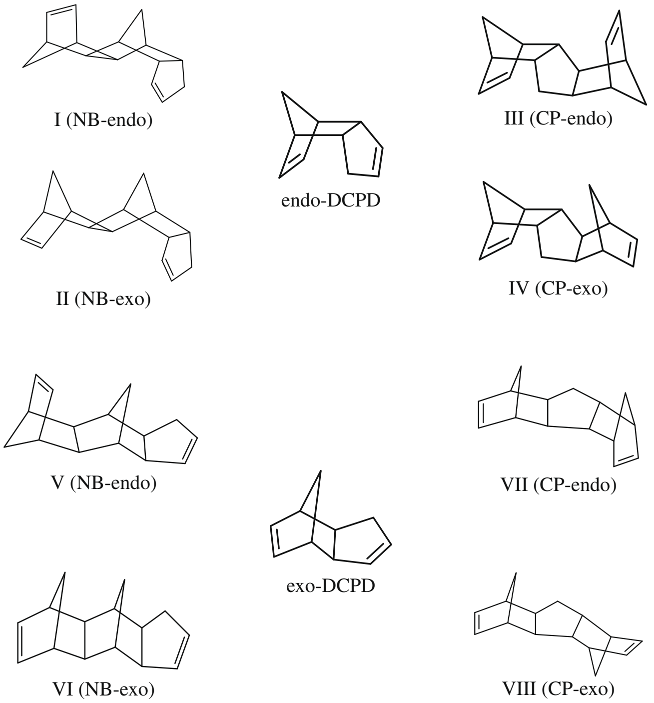

Fig. 1. TCPD stereoisomers formed from the [4 + 2] cycloaddition of DCPD and CPD.

Table 1
Total energy of TCPD I calculated using M05-2X method with deferent basis sets.

Basis set	6-31G(d)	6-31G(d,p)	6-311G(d,p)	6-311+G(d,p)
Total energy (kJ/mol)	−1533958.4	−1534031.1	−1534328.0	−1534334.7

Prior to the simulation, the calculation method was validated. Recently, density functional M05-2X has been used by many researchers [19–21]. Zhao and Truhlar pointed out that, for the [4 + 4] cycloaddition reaction of anthracene, M05-2X may give more correct result [22,23]. They also reckoned that M05-2X can effectively estimate complicated steric hindrance. Thus M05-2X was used in this work. As for the basis set, Table 1 shows there is little energy discrepancy when the basis set is increased from 6-311G(d,p) to 6-311 + G(d,p). Actually, diffused function is negligible for nonpolar molecules such as CPD, DCPD and TCPD. Therefore, the basis set 6-311G(d,p) was employed in the simulation. The zero-point vibration energy was scaled with a scaling factor of 0.964 [24]. In the following sections, if not mentioned, the energy of TSs and products is relative value respected to reactants.

3.2. Reaction mechanism

Fig. 2 shows the relative energies of reactants and adducts. One can see the reaction is exothermic, and the reaction heat ranges