Insights into the Diels−Alder Reactions between Cyclopentadiene and 1,3−Butadiene with High Temperature and High Pressure

6 AUTHORS, INCLUDING:

Kun Cao
University of Bristol
51 PUBLICATIONS   298 CITATIONS

SEE PROFILE

Jiale Shi
Tsinghua University
7 PUBLICATIONS   7 CITATIONS

SEE PROFILE

Zhen Yao
Fudan University
49 PUBLICATIONS   248 CITATIONS

SEE PROFILE

Insights into the Diels−Alder Reactions between Cyclopentadiene and 1,3-Butadiene with High Temperature and High Pressure

Kun Cao, Xue Liu, Yan Zhang, Jia-le Shi, Yue-xiao Song, and Zhen Yao*

State Key Laboratory of Chemical Engineering, Institute of Polymerization and Polymer Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

S *Supporting Information*

ABSTRACT: Synthesis of 5-vinyl-2-norbornene based on the Diels−Alder reactions of cyclopentadiene (CPD) generated from dicyclopentadiene (DCPD) and 1,3-Butadiene (BD) have been investigated in a continuous tube reactor under high temperature and high pressure. The experimental results show that the concentration of main product 5-vinyl-2-norbornene (VNB) increases with the increasing of reaction time at low reaction temperature. The elevated temperature greatly promotes the synthesis rate of both product VNB and its isomer *cis*-3a,4,7,7a-tetrahydroindene (THI) and tricyclopentadiene, resulting in a mountain-shaped curve of VNB concentration versus the reaction time. Particularly, it has been confirmed that the trimer (4,4a,4b,5,8,8a,9,9a-octahydro-1H-1,4-methanofluorene should be prepared by direct reaction of BD with DCPD rather than by the reaction of CPD with VNB or THI. This comprehensive study can lay a solid foundation for the process optimization of VNB synthesis.

1. INTRODUCTION

Since its discovery in 1928 by Diels and Alder, the Diels−Alder (D−A) reaction involving a conjugated diene and a dienophile has been used for the diastereo- and regioselective generation of six-membered rings. Many industrial applications have been known to utilize D−A addition for the synthesis of pharmacologically active ingredients, agrochemicals, flavors, and fragrances.[1] However, in light of the new state of knowledge, mechanistic aspects of D−A reactions are much more complex than previously thought. The recent studies continue to provide new data in this area, which can be divided into nonpolar mechanisms and polar mechanisms. Beno et al.[2] had examined the existence of both concerted and diradical mechanisms for the retro-Diels−Alder reaction of norbornene. Firestone[3] demonstrated that a stepwise-diradical mechanism occurred in the presence of heavy atoms in diene or dienophile. Singleton et al.[4] probed a variety of Diels−Alder reactions to distinguish synchronous, asynchronous, and stepwise pathways. Jasiński et al.[5,6] considered the existence of the polar mechanisms (one step−two stage mechanism and stepwise mechanism) by adopting both experimental and theoretical study.

Synthesis of 5-vinyl-2-norbornene (VNB) is also a typical D−A addition, which consists of two steps: thermal cracking of dicyclopentadiene (DCPD) into cyclopentadiene (CPD) via retro-DA scheme, and the D−A reaction between CPD and 1,3-Butadiene (BD).[7] Although the electron withdrawing group on the C atom of ethylene can lower the activation barriers considerably,[8−11] the negative inductive effect of C═C on ethylene is so weak that the matching energy gap between the orbits of CPD is still large. The global electrophilicity of cyclopentadiene (CPD) is equal to 0.83 eV,[12] whereas the global electrophilicity of butadiene is equal to 1.17 eV.[13] As a consequence, the interactions between CPD and BD have practically nonpolar character. Next, the small difference between global eletrophilicities is a source of weak reaction

drive power, which results in the reaction conditions that require both high temperature and high pressure.[14−16] Besides, the initiation of DCPD cracking requires temperatures beyond 140 °C, at which several exothermic reactions can be initiated as well.[17] The thermal runaway in these reactions can not only increase the temperature of the reaction mixture by several hundred degrees, but also can result in a considerable pressure increase,[18,19] which further highlights the extreme danger of the VNB synthesis process. In 1973, the Japan Petroleum Chemical was forced off production of VNB, due to the explosion of a stirred tank reactor.[20]

The VNB preparation process was mainly carried out in the liquid phase in a stirred tank reactor. Jiang et al.[7] studied the production of VNB in a batch reactor with a small "dead" volume for gas and a built-in high-speed stirrer. Just et al.[14] and Fehrmann et al.[15] studied the kinetic model and obtained the kinetic parameters of the principal reactions pertaining to VNB synthesis, respectively. However, both of them ignored two kinds of trimers,4, 4a,4b,5,8,8a,9,9a-octahydro-1H-1,4-methanofluorene (OMF) and 2-vinly-1,2,3,4,4a,5,8,8a-octahydro-1,4-methanonaphthalene (VOMN), shown as byproducts 9 and 10 in Scheme 1, respectively. These byproducts can greatly affect the reaction selectivity and may play a decisive role in the choice of technology. Titova et al.[16] indicated OMF was synthesized by DCPD and BD, and obtained the kinetic parameter. However, Kimura et al.[21] proposed the relatively comprehensive reaction mechanism and considered that OMF was produced by CPD reacted with VNB or its isomer *cis*-3a,4,7,7a-tetrahydroindene(THI). Osokin[22] reviewed almost all the possible chemical transformations for preparation of VNB. But of the above, both works lack experimental verification.

Scheme 1. Summary of Both Main Reactions and Side Reactions

Main Reactions
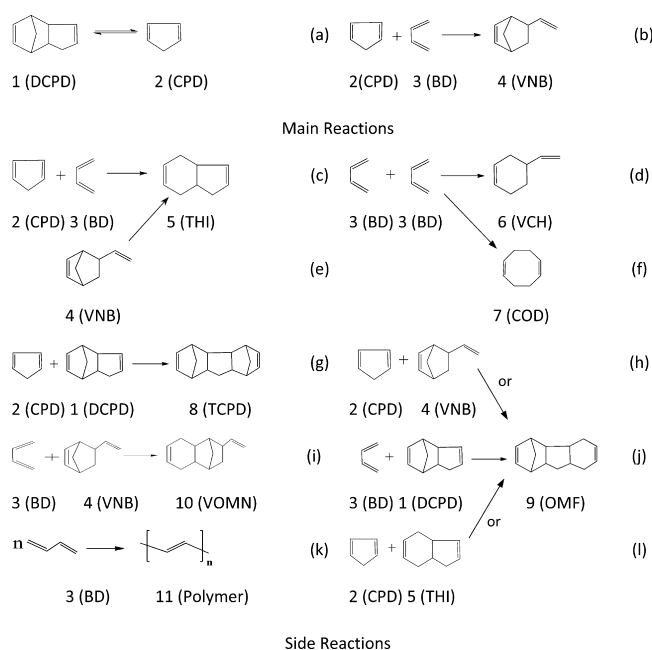
Side Reactions

Previous studies make it possible to describe the process as a set of the following parallel and consecutive reactions as shown in Scheme 1.[7,14−16,23] It should be noted that the reaction pathways of the trimer OMF as byproduct 9 proposed in those literatures were not consistent with each other, which can be summarized in three possible ways as shown in Scheme 1. In this work, a series of the designed experiments with various ratio of BD/DCPD, DCPD concentration, reaction temperature, and pressure were carried out to study the influences of process conditions on main reactions and side reactions in a continuous tube reactor. Additionally, the synthesis pathway of

the trimer OMF, of which there existed controversy in previous literature, has been confirmed.

2. EXPERIMENTAL SECTION

2.1. Materials. The two major reaction reagents DCPD and BD were kindly provided by Sinopec Shanghai Petrochemical Company Limited. In the process, in order to make the reaction heat release more smoothly, toluene (analytical reagent) was used as a solvent, supplied by Shanghai Lingfeng Chemical Reagent Co, Ltd. The other reagents and chemicals, unless otherwise noted, were purchased from J&K Scientific Ltd.

2.2. Experimental Setup. All experiments were conducted in a specially designed continuous tube reactor with a length of 50 m and a nominal outer diameter of 20 mm. Four sampling ports were installed along the flowing direction, as shown in Scheme 2. It was possible to simultaneously obtain samples with four different residence times in one experiment. The system included an independent BD feed system and DCPD solution feed system with a real-time flow monitor control system.

Samples were collected at steady state and cooled rapidly with ice water to stop the reaction for analysis. To ensure the reliability of the data, at least three samples at each sampling site were analyzed for each experimental run.

2.3. GC−MS/GC Analysis. GC−MS analyses were performed using an Agilent 6890−5973 GC/MS spectrometer (Agilent, Co., Ltd., U.S.A.) equipped with an HP-1 ms copper capillary column (50 m × 0.2 mm × 0.5 μm). The electron ionization positive mode ionization energy of 70 eV, mass range of m/z 10−500, column temperature of 70−300 °C at a rate of 10 °C/min, GC injector temperature of 250 °C, MS transfer line temperature of 280 °C, split ratio of 100:1, carrier gas (helium gas) of 0.5 mL/min and injection volume of 0.4 μL were adopted. Essential compounds were identified by their retention times and mass fragmentation patterns using NIST05

Scheme 2. Schematic Illustration of the Experimental Setup
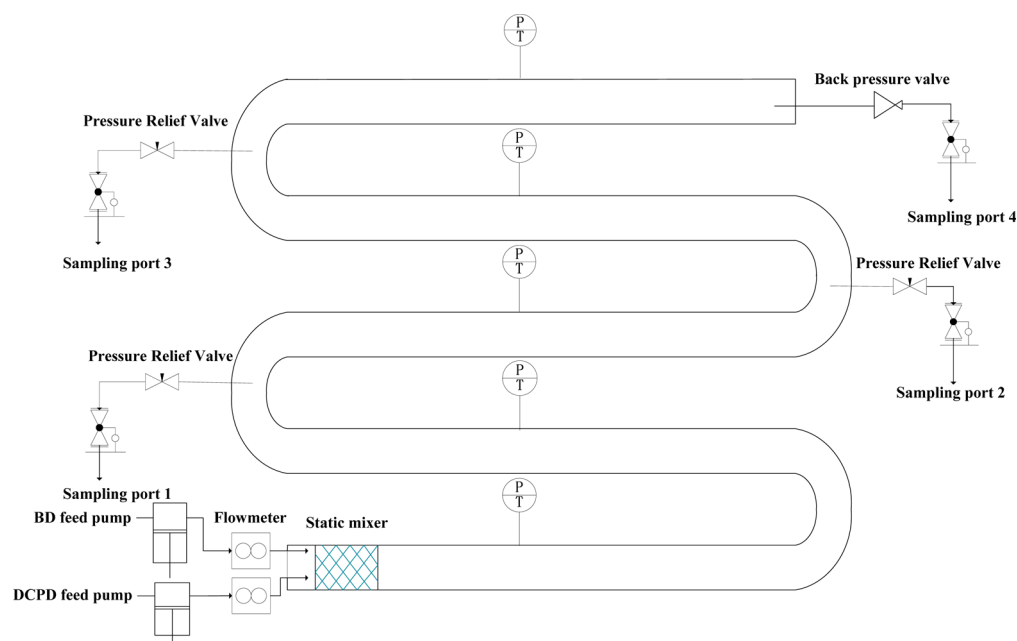
standard data. The typical results can be found in the Supporting Information (SI).

3. RESULTS AND DISCUSSION

The other industrial common reagents such as retardant or inhibitor were not added in this work based on the purpose to study the variation rules of the main reactions and side reactions under different process conditions. Reagents addition would further complicate the reaction system.

Table 1 lists the summary of experiments with various operating conditions, including the ratio of BD/DCPD, DCPD concentration, reaction temperature, and pressure.

Table 1. Summary of the Experimental Conditions

run	1	2	3	4	5
pressure (MPa)	5	5	5	5	15
temperature (°C)	180	160	160	160	160
BD/DCPD molar ratio	0.8	0.8	1.6	0.8	1.6
DCPD concentration (wt %)	30	30	30	60	30

The weight percentage of all of the starting materials (DCPD, CPD, BD), products, and byproducts were measured at four residence times in each experiment, as shown in Figure 1. Figure 1(a)−(c) shows the effect of different experimental conditions on the DCPD, CPD, and BD. Figure 1(d) shows the variation trend of VNB as the main product under different process conditions. The rest are the overall byproducts, as shown in Figure 1(e)−(k).

The conversion and selectivity, determined with DCPD and BD as raw materials, are shown in Figure 2, which can be a reference for the process selection. The selectivity based on DCPD or BD is the mass fraction of the consumed raw material (DCPD or BD) converted into target product (VNB). The conversion based on DCPD or BD is the mass fraction of the consumed raw material (DCPD or BD) accounted for the total initial amount of raw material (DCPD or BD).

3.1. Effect of Reaction Temperature. To study the effect of reaction temperature, we conducted the comparative experiments 1 and 2. The effect of reaction temperature was investigated from 160 to 180 °C with other conditions unchanged, as shown in Table 1. According to the reaction kinetics and practical experience, the elevated temperature can greatly accelerate the consumption rate of CPD, DCPD, and BD, shown in Figure 1(a)−(c). Although the elevated temperature can boost the cracking of DCPD into CPD, the consumption rate of CPD is greatly accelerated as well, which leads to the reduction of CPD concentration. Particularly, Figure 1(d) displays a unique phenomenon at 180 °C that with the increase of the residence time, the content of VNB increases at first and then decreases subsequently, which differs from the other four experiments. This phenomenon can be well explained by the dynamic derivation. The main product VNB is the intermediate in the consecutive reaction, which can be simplified into a sequential model as follows:[24]

$$A + B \xrightarrow{K_1} C(\text{Objective}) \xrightarrow{K_2} D$$
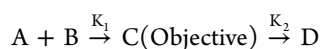
Through the derivation of dynamic equations, the concentration of intermediate product C_C can be expressed as follows:

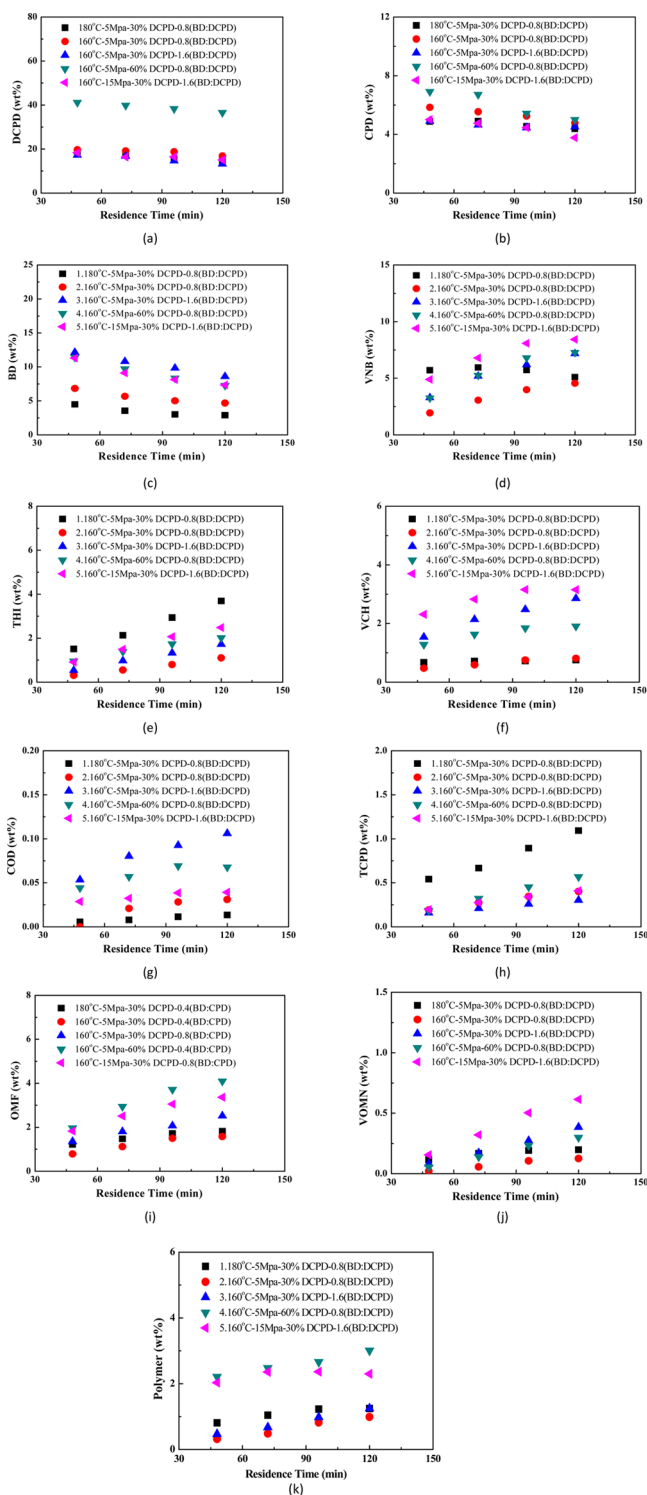
Figure 1. Effect of different reaction conditions on the reactants and products.

$$C_C = \frac{K_1 C_{A,0} C_{B,0}}{K_2 - K_1}(e^{-K_1 t} - e^{-K_2 t}) \tag{1}$$

where $C_{A,0}$ and $C_{B,0}$ denote, respectively, the initial concentration of A and B, and t is the reaction time.

When the reaction temperature is low, the kinetic parameter $K_1 > K_2$. According to eq 1, the concentration of intermediate C_c is increased with increasing reaction time. This can be a good explanation for the continuous growth of the concen-
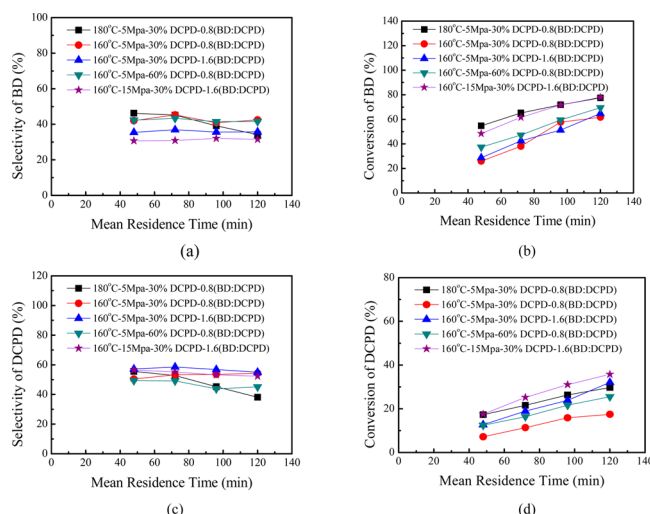
Figure 2. Effect of different reaction conditions on the conversion and selectivity of both DCPD and BD.

tration VNB, as shown in the experiments, with the exception of Run 1. With the temperature increasing, the elevated temperature can greatly accelerate the isomerization rate of VNB to its isomer THI. In this case, the kinetic parameter K_2 cannot be neglected compared with K_1. On the basis of eq 1, with the increasing of reaction time t, the concentration of intermediate C increases to a maximum value and then decreases subsequently.

Besides, the comparison with Figure 1(c), (f), (g), and (k) indicates that VCH is the principal BD dimer and the content of COD is small. Moreover, the elevated temperature is favorable to the formation of VCH and butadiene oligomer rather than COD. Figure 1(h)−(j) shows that the elevated temperature speeds up the synthesis rate of the three kinds of trimmers, especially the formation rate of TCPD.

Although the elevated temperature can boost the formation rate of VNB, the production rates of all the byproducts are increased as well. Figure 2(b) and (d) shows that the elevated temperature can improve the conversion of both DCPD and BD, but the selectivity encounters a decrease, as shown in Figure 2(a) and (c). Further increase in the operating temperature is undesired in commercial processes, in which the residual BD and DCPD can be recycled. Besides, the range of the reaction temperature in most of the literature[7,14,15] is below 180 °C.

3.2. Effect of BD/DCPD Molar Ratio. To assess the effect of the BD/DCPD molar ratio, we designed experiments 2 and 3 with the BD/DPD molar ratio rising from 0.8 to 1.6 and the other conditions unchanged. The concentration of BD in liquid phase can be enhanced with the increase of both the BD/DCPD molar ratio and the reaction pressure. The increasing BD/DCPD molar ratio can greatly promote the formation rate of the main product VNB and its isomer THI, as shown in Figure 1(d) and (e), due to the significant improvement of the BD "starvation" condition. It can be seen from Figure 1(a) and (b) that the enrichment of BD can accelerate the consumption of the other two starting materials (DCPD and CPD), which suppresses the formation of TCPD, as shown in Figure 1(h). Besides, on the basis of the reaction equation, the increasing of BD greatly increases the synthesis rate of VCH and COD, which is displayed clearly in Figure 1(f) and (g). It should be noted that the synthesis rate of the trimer VOMN was

significantly faster than the trimer OMF, which can be attributed to both increasing VNB content and decreasing DCPD content.

Figure 2(c) and (d) shows that the increase of the BD/DCPD molar ratio can improve the conversion and selectivity of DCPD. However, the selectivity of BD encounters a great loss, as shown in Figure 2(a). Figure 2(b) displays that the BD/DCPD molar ratio has an insignificant influence on the BD conversion.

3.3. Effect of DCPD Concentration. The comparative experiments 2, 3, and 4 were carried out to study the effect of DCPD concentration. As shown in Table 1, the concentration of DCPD in Run 4 is 100% higher than that in Run 2. To maintain the same BD/DCPD molar ratio in Runs 2 and 4, the mass flow rate of BD in Run 4 was also twice as much as that in Run 2. However, the mass flow rate of BD in Runs 3 and 4 were identical, while the concentration of DCPD in Run 3 was only half of that in Run 4. Therefore, the BD/DCPD molar ratio in Run 3 was two times that in Run 4.

Figure 1(a) demonstrates that the concentration of DCPD in Run 4 is greater than that in Run 3 throughout the whole experimental process, while the CPD concentration falls rapidly with the increase in reaction time in Run 4 and finally approaches the same level with that in Run 3 (Figure 1(b)). There is no doubt that the synthesis rate of TCPD is accelerated, as shown in Figure 1(h). Figure 1(d) and (e) indicates that the increase in concentration of DCPD has a minor impact on the synthesis rate of VNB and THI. The content of VCH and COD in Run 3 are obviously higher than those in Run 4, as shown in Figure 1(f) and (g), due to the higher BD content in Run 3, which directly demonstrates that the BD content contributes significantly to formation of its isomer as discussed in the above Section 3.2.

In Figure 1(a)−(e), the concentrations of DCPD, CPD, BD, VNB, and THI in experiment 2 are lower than those in experiment 4. It seems that the three reaction pathways of the trimer OMF, as shown in Scheme 1, are all reasonable. The contradiction of the reaction mechanism about the trimer OMF still exists. However, the comparison of experiment 3 and 4 can provide the direct valid evidence for the reaction mechanism of trimer OMF. Figure 1(i) indicates that the trimer OMF greatly increases with the increase of DCPD concentration in Run 4, while the content of VNB, THI, and BD, as shown in Figure 1(c)−(e), shows no obvious difference compared with Run 3, which directly proves that the trimer OMF should be mainly produced by BD reacted with DCPD.

Figure 2 shows that the increase of DCPD concentration can enhance both the conversion of BD and DCPD at the cost of a sharp decline of the selectivity of DCPD. The BD selectivity is not affected by the change in DCPD concentration.

3.4. Effect of Reaction Pressure. To study the effect of reaction pressure, we conducted the comparative experiments 3 and 5 with the reaction pressure rising from 5 to 15 MPa and other conditions unchanged.

1,3-Butadiene concentration in toluene can be calculated according to Henry's law:

$$C_B = P_B \times H_0 \exp\left(\frac{\Delta H_L}{RT}\right) \tag{2}$$

where C_B = BD concentration (mol·L^{-1}); P_B = BD pressure (atm); H_o = Henry coefficient (mol·L^{-1}·atm^{-1}); ΔH_L =

enthalpy of solvatation of BD in toluene (cal·mol⁻¹); and $R = 1.989$ (cal·mol⁻¹·K⁻¹).

On the basis of the Henry's law, the BD concentration in toluene increases with increasing pressure. This provides a reasonable explanation to the inexplicable phenomenon that there is no visible difference in the starting materials' (DCPD, CPD, BD) concentration shown in Figure 1(a)−(c), but results in a significant difference in both main product VNB and the byproducts. Apparently, the synthesis rates of VNB, its isomer THI and COD, trimer OMF as byproduct 9, VOMN as byproduct 10, and polymer are greatly accelerated, while the TCPD concentration is basically unchanged, which implies that the elevated pressure is an effective method to improve the synthesis rate of main product VNB, but is not necessarily a suitable way to improve the selectivity of BD in a Diels−Alder reaction.

Although the elevation of pressure can increase the conversion of both DCPD and BD, the concentration of the byproducts, such as THI, COD, OMF, VOMN, and BD polymer, are greatly increased as well. Figure 2(a) and (c) shows that the selectivity of DCPD and BD are both reduced with the increasing reaction pressure, especially the selectivity of BD. Therefore, further increase in pressure would not be preferred.

4. CONCLUSIONS

In this paper, influences of condition parameters such as the ratio of BD/DCPD, DCPD concentration, reaction temperature, and pressure, have been investigated in a continuous tube reactor for the synthesis of VNB. On the basis of the experimental data and theoretical analysis, the following conclusions have been reached:

(1) In the low temperature, the concentration of main product VNB increases with the increase of reaction time. However, prolonging reaction time is not an effective way to improve the VNB concentration in the elevated temperature due to the greatly enhanced of the synthesis rate of VNB isomerization to THI.

(2) Although increasing the BD/DCPD molar ratio can increase the production rate of VNB, the synthesis rate of its trimer COD, VCH, and butadiene polymer greatly increases as well.

(3) Increasing both the DCPD and BD can improve the producing rate of VNB. However, only increasing the DCPD concentration has no effect on the yield of VNB when BD/DCPD molar ratio is less than 2. Instead, the concentration of trimer OMF is significantly improved. It can be confirmed that the trimer OMF is mainly synthesized by direct reaction of BD with DCPD rather than by reaction of CPD with VNB or THI.

(4) By increasing the reaction pressure, the concentration of BD in liquid phase can be greatly enhanced in liquid phase, where the reactions mainly take place. All the reactions are accelerated except the production of TCPD.

ASSOCIATED CONTENT

S **Supporting Information**
Identification of the reaction products were measured by GC-MS analysis; (Figure S1) gas chromatogram of the typical sample for VNB synthesis; (Figure S2) mass spectra of the substance (BD) at 4.444 min retention time in gas chromato-

gram; (Figure S3) mass spectra of the substance (CPD) at 4.671 min retention time in gas chromatogram; (Figure S4) mass spectra of the substance (toluene) at 5.821 min retention time in gas chromatogram; (Figure S5) mass spectra of the substance (VCH) at 6.463 min retention time in gas chromatogram; (Figure S6) mass spectra of the substance (VNB) at 7.032 min retention time in gas chromatogram; (Figure S7) mass spectra of the substance (THI) at 8.213 min retention time in gas chromatogram; (Figure S8) mass spectra of the substance (DCPD) at 9.055 min retention time in gas chromatogram; (Figure S9) mass spectra of the substance (VOMN) at 13.598 min retention time in gas chromatogram; and (Figure S10) mass spectra of the substance (OMF) at 15.834 min retention time in gas chromatogram. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b01054.

AUTHOR INFORMATION

Corresponding Author
*E-mail: yaozhen@zju.edu.cn (Z.Y.).
Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Funel, J.; Abele, S. Industrial Applications of the Diels-Alder Reaction. *Angew. Chem., Int. Ed.* **2013**, *52*, 3822−3863.
(2) Beno, B. R.; Wilsey, S.; Houk, K. N. The C₇H₁₀ Potential Energy Landscape: Concerted Transition States and Diradical Intermediates for the Retro-Diels-Alder Reaction and [1,3] Sigmatropic Shifts of Norbornene. *J. Am. Chem. Soc.* **1999**, *121*, 4816−4826.
(3) Firestone, R. A. Volume of Concert and Heavy Atom Effects in Diels-Alder Reaction Mechanisms. *Tetrahedron* **1996**, *52*, 14459−14468.
(4) Singleton, D. A.; Schulmeier, B. E.; Hang, C.; Thomas, A. A.; Leung, S.; Merrigan, S. R. Isotope Effects and the Distinction Between Synchronous, Asynchronous, and Stepwise Diels-Alder Reactions. *Tetrahedron* **2001**, *57*, 5149−5160.
(5) Jasiński, R.; Kubik, M.; Lapczuk-Krygier, A.; Kacka, A.; Dresler, E.; Boguszewska-Czubara, A. An Experimental and Theoretical Study of the Hetero Diels-Alder Reactions between (E)-2-Aryl-1-Cyano-1-Nitroethenes and Ethyl Vinyl Ether: One-step or Zwitterionic, Two-step Mechanism? *React. Kinet., Mech. Catal.* **2014**, *113*, 333−345.
(6) Jasiński, R. Searching for Zwitterionic Intermediates in Hetero Diels-Alder Reactions between Methyl α,p-Dinitrocinnamate and Vinyl-Alkyl Ethers. *Comput. Theor. Chem.* **2014**, *1046*, 93−98.
(7) Jiang, Z. X.; Guo, S. Z.; Yang, Z. B.; Ma, H. X. Sequential Experimentation of Synthesis of Vinyl Norbornene. *Chinese Petrochemical Technology.* **2003**, *32*, 847−852.
(8) Wang, Y.; Fang, D. C.; Liu, R. Z. Theoretical Study of the Diels-Alder Reactions of Lewis Base-Stabilized Borabenzenes with Dienophiles. *Chem. J. Chinese. U.* **2008**, *29*, 1005−1010.
(9) Zhang, Z.; Peng, Z. W.; Hao, M. F.; Gao, J. G. Mechanochemical Diels-Alder Cycloaddition Reactions for Straightforward Synthesis of endo-Norbornene Derivatives. *Synlett* **2010**, *19*, 2895−2898.
(10) Lee, S.; Cho, S.; Park, Y.; Rhee, H. Kinetics of Norbornene Synthesis and Continuous Reactor Modeling Study. *Stud. Surf. Sci. Catal.* **2006**, *159*, 709−712.
(11) Molina-Espíritu, M.; Esquivel, R. O.; Kohout, M.; Angulo, J. C.; Dobado, J. A.; LÓpezRosa, S.; Soriano-Correa, C. Insight into the Informational-Structure Behavior of the Diels-Alder Reaction of Cyclopentadiene and Maleic Anhydride. *J. Mol. Model.* **2014**, *20*, 2361−2373.

(12) Jasiński, R.; Kwiatkowska, M.; Barański, A. Stereoselectivity and Kinetics of [4 + 2] Cycloaddition Reaction of Cyclopentadiene to para-Substituted E-2-Arylnitroethenes. *J. Phys. Org. Chem.* **2011**, *24*, 843−853.

(13) Perez, P.; Chamorro, E. Theoretical Analysis of Substituted Diels-Alder Reagents to Determine the Polar or non-Polar Character of the Reaction. *Lett. Org. Chem.* **2011**, *8*, 88−94.

(14) Just, V. G.; Lindner, U.; Pritzkow, W.; RÖllig, M. Diels-Alder-reactions. V. Kinetic Modelling of the Reactions Taking Place. *J. Prakt. Chem.* **1975**, *S*, 979−989.

(15) Fehrmann, V. W.; Hampet, M.; Pritzkow, W.; RÖllig, M. Untersuchungen Uber die Mischdimerisierung yon Cyclopentadien mit Butadien-(1,3). *J. Prakt. Chem.* **1975**, *S*, 966−978.

(16) Titova, L. F.; Bazhanow, Y. V.; Basner, M. E.; Nefedova, A. I.; Chaplits, D. N.; Belikova, N. A. Thermal-Reaction Kinetics of Butadiene with Dimers and Codimers of 1-Methylcyclopentadiene, 2-Methycyclopentadiene and Cyclopentadiene. *Zhurnal Organicheskoi Khimii.* **1982**, *18*, 710−716.

(17) Zhang, X. W.; Jiang, Q.; Xiong, Z. Q.; Zou, J. J.; Wang, L.; Mi, Z. T. Diels-Alder Addition of Dicyclopentadiene with Cyclopentadiene in Polar Solvents. *Chem. Res. Chin. Univ.* **2008**, *24*, 175−179.

(18) Ahmed, M.; Lavin, M. Exothermic Reactions of DCPD and Protection against Them. *Plant/Oper. Prog.* **1991**, *10*, 143−153.

(19) Lenz, T. G.; Vaughan, J. D. Employing Force-Field Calculations to Predict Equilibrium Constants and Other Thermodynamic Properties for the Dimerization of 1,3-Cyclopentadiene. *J. Phys. Chem.* **1989**, *93*, 1592−1596.

(20) Kanagawa Labor Standards Bureau. The Fire Accident Investigation Report of the Ethylidenenorbornene Manufacturing Equipment. *High Pressure Mashgas* **1974**, *2*, 528−541.

(21) Kimura, K.; Usui, M.; Suzukamo, G.; Fukao, M.; Yamamoto, S. Development and Industrialization of the Process for Ethylene Norbornene Production. *Sumitomo Kagaku* **1990**, *2*, 4−11.

(22) Osokin, Y. G. Vinylnorbornene: Preparation, Chemical Transformations, and Use in Organic Synthesis and Polymer Chemistry. Vinylnorbornene Synthesis and Isomerization to Ethyl-idenenorbornene (Review). *Pet. Chem.* **2007**, *47*, 1−11.

(23) Nakia, N.; Iwase, S.; Ishii, Y.; Ogawa, M. Trimers Derived From Diels-Alder Reactions of Cyclopentadiede with Butadiene and Their Carbon-13 Nuclear Magnetic Resonance Spectra. *Sekiyu Gakkaishi* **1978**, *6*, 415−419.

(24) Fogler, H. S. *Elements of Chemical Reaction Engineering*, 4th ed.; Prentice Hall Professional Technical Reference: Upper Saddle River, New Jersey, 2009, pp 320−327.