Liquid-Phase Cyclodimerization of 1,3-Butadiene in a Closed Batch System

Daolai Sun, Fumiya Sato, Shin-ichi Yamauchi, Yasuhiro Yamada, and Satoshi Sato*

Graduate School of Engineering, Chiba University, Yayoi, Inage-ku, Chiba 263-8522

Received December 6, 2012; E-mail: satoshi@faculty.chiba-u.jp

Dimerization of 1,3-butadiene was investigated in a closed batch system under high-pressure conditions. 4-Vinylcyclohexene was mainly produced without using any solvents or catalysts at temperatures of 150–215 °C. The conversion of 1,3-butadiene was significantly dependent on the temperature and pressure. 1,3-Butadiene was converted to 4-vinylcyclohexene at selectivity higher than 90 mol % with by-products of 1,5-cyclooctadiene and 1,2-divinylcyclobutane. Large charges of reactant are efficient in achieving high conversions of 1,3-butadiene. Use of solvents, which dilute the reactant and absorb the reaction heat, is not favorable in the present dimerization of 1,3-butadiene under pressured conditions.

Dimerization and polymerization of typical conjugated dienes, such as 1,3-butadiene, have been investigated for more than 50 years. 1,3-Butadiene is an important industrial chemical used as a monomer in the production of synthetic rubber. Many products, which contain cyclic products, linear chain oligomers, and polymers, can be produced by the dimerization, trimerization, and polymerization of 1.3-butadiene. 4-Vinvlcvclohexene (VCH), which is an intermediate in an industrially important styrene,¹⁻³ can be produced by Diels-Alder reaction of 1,3butadiene. Different reaction conditions always gave different products. The photochemical cycloaddition of 1,3-butadiene mainly generates four-membered ring products such as 1,2-divinylcyclobutane (DVCB).^{4,5} Under very high-pressure conditions, reaction of 1,3-butadiene has been studied at room temperature, with VCH produced from 1,3-butadiene as an only liquid product at 700 MPa.⁶ A variety of homogeneous catalysts have also been investigated in the reaction. Fe catalysts are favorable for the formation of VCH from 1,3-butadiene.^{7,8} Nickel catalysts are favorable for the formation of eight-membered ring products such as cyclooctadienes depending on the kinds and the amount of the ligands used,⁹ while palladium catalysts are favorable for the formation of linear chain products.¹⁰

It is known that Diels–Alder reactions are accelerated under pressurized conditions.^{11–17} Rao et al. investigated the reaction of 3-methylsulfanylfuran and 3-phenylsulfanylfuran with various cycloalkenones under pressurized conditions, and almost all the reactions proceeded at 50 °C under a pressure of 1.1 to 1.5 GPa.¹⁴ Intermolecular Diels–Alder reactions of methyl 2methyl-5-vinyl-3-furoate with various dienophiles under high pressure were investigated by Drew et al.¹⁵ The yields were higher than 90% at 1.9 GPa, 25 °C for 1 day when maleic anhydride or *N*-methylmaleimide was used as the dienophile in the reaction. Hetero Diels–Alder reactions, such as the reaction of 2,3-dimethyl-1,3-butadiene with perfluorooctanonitrile, also proceed at 50 °C and 150 MPa without using solvents and catalysts.¹² However, there are few studies on Diels–Alder reactions of conjugated dienes themselves under pressure at high temperature. Recently, we reported solvent-free Diels-Alder reactions in a closed batch system.¹⁸ Typical dienes, such as 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and isoprene, were used in the reactions and high vields of Diels-Alder products were obtained within short reaction time under solvent-free conditions. The use of solvent, which dilutes the reactants and absorbs the reaction heat, was found inefficient in achieving high conversions. In the reaction of 1,3-butadiene with methyl vinyl ketone at 125 °C, a small amount of VCH was generated as a by-product. Thus, at much higher temperatures, the possibility that VCH will selectively be produced under pressured conditions attracted our interests. We preliminarily found that Diels-Alder reaction of conjugated dienes themselves proceeded under pressure at 200 °C. In this study, we investigated the reaction behavior of 1,3-butadiene under pressure at high temperatures and discussed the optimum reaction conditions for yielding VCH.

Results

Dimerization of 1,3-Butadiene. Table 1 shows the effect of reaction temperature in the reaction of 1,3-butadiene, and Figure 1 shows the main products. Three cyclic dimers were the main products. Catalysts and solvents were not used dur-

 Table 1. Closed Batch Reaction of 1,3-Butadiene at Different Temperatures^{a)}

Temperature	Conversion	Selectivity/mol %			
/°C	/%	VCH	COD	DVCB	Others
215	75.3	88.8	7.7	0	3.6
200	64.5	90.6	6.5	0.7	2.2
175	48.0	82.2	3.8	4.9	9.1
150 ^{b)}	43.5	81.5	2.4	5.3	10.7
125 ^{c)}	36.6	83.7	2.1	6.3	7.9

a) The volume of the reaction vessel is 20 cm^3 . Reaction conditions: 1,3-butadiene charge, 5.5 g; reaction time, 2 h. b) Reaction time, 6 h. c) Reaction time, 40 h.



Figure 1. Main products derived in the dimerization of 1,3-butadiene.

Table 2. Change in the Reaction of 1,3-Butadiene with Reaction Time^{a)}

Temperature	Reaction	Conversion /%	Selectivity/mol %				
/°C	time /h		VCH	COD	DVCB	Others	
175	2	48.0	82.0	3.8	4.9	9.1	
	4	64.3	89.3	4.9	3.2	2.6	
	6	68.3	90.2	4.8	2.1	2.9	
200	2	64.5	90.6	6.5	0.7	2.2	
	4	72.9	90.5	6.6	0.0	2.8	
	6	75.1	91.2	6.1	0.0	2.7	

1,3-Butadiene	Conversion	Selectivity/mol %				
/g	/%	VCH	COD	DVCB	Others	
1.1	21.5	87.3	5.4	1.7	5.5	
1.7	23.2	90.8	5.6	2.5	1.1	
3.0	56.6	90.6	5.8	2.0	1.6	
5.5	64.5	90.6	6.5	0.7	2.2	
8.0	73.3	90.0	7.3	0.1	2.5	

Table 3. Effect of Charge of 1,3-Butadiene at 200 °C^{a)}

a) Reaction conditions: reaction time, 2 h.

a) Reaction conditions: 1,3-butadiene charge, 5.5 g.

Table 4. Effect of Solvents in the Closed Batch Reaction of 1,3-Butadiene at 200 °Ca)

1,3-Butadiene Solvent		Time	Conv.	Selectivity/mol %			
/cm ³	/cm ³	/h	/%	VCH	COD	DVCB	Others
4.7 (3.0 g)	0	1	26.4	90.3	4.7	4.0	1.0
4.7 (3.0 g)	3.9 (THF)	1	19.8	90.5	5.1	3.2	1.3
8.6 (5.5 g)	0	2	64.5	90.6	6.5	0.7	2.2
4.7 (3.0 g)	0	2	56.6	90.6	5.8	2.0	1.6
4.7 (3.0 g)	3.9 (THF)	2	54.1	93.0	5.2	1.3	0.6
4.7 (3.0 g)	3.9 (cyclohexane)	2	54.9	92.0	5.6	1.3	1.1
12.5 (8.0 g)	0	2	73.3	90.0	7.3	0.1	2.5
4.7 (3.0 g)	7.8 (THF)	2	52.9	91.3	5.7	1.3	1.7

a) The volume of the reaction vessel is 20 cm^3 .

ing the reaction. Since the vessel made of poly(tetrafluoroethylene) begins to deteriorate at about 230 °C, the reaction was conducted at temperatures up to 215 °C. The conversion of 1,3butadiene increased with increasing temperature. The selectivity to VCH, which was the only product generated through Diels–Alder reaction, was high and even exceeded 90% at 200 °C. The reaction proceeded with difficulty at temperatures lower than 150 °C: the conversion was 36.6% at 125 °C for 40 h. The selectivity to 1,5-cyclooctadiene (COD) increased with increasing temperature while the selectivity to 1,2-divinylcyclobutane (DVCB) decreased. DVCB was not detected in the reaction at 215 °C for 2 h. A small amount, lower than 0.03 g per 5.5 g of reactant, of polymer was observed at temperatures higher than 200 °C.

Table 2 shows the effect of reaction time at 175 and 200 °C. The conversion of 1,3-butadiene increased with increasing the reaction time. Selectivity to VCH was almost constant irrespective of the reaction time, while the selectivity to COD tended to increase with increasing reaction time, and the selectivity to DVCB tended to decrease.

Table 3 shows the effect of the charge of 1,3-butadiene at 200 °C. The conversion of 1,3-butadiene was low at amounts less than 1.7 g in a vessel with a volume of 20 cm^3 , while it

steeply increased with increasing the charge of 1,3-butadiene to more than 3.0 g. The conversion increased to 73.3% at a charge of 8 g. The selectivity to VCH was nearly unchanged while the selectivity to COD increased with increasing the charge of 1,3-butadiene and the selectivity to DVCB decreased.

Table 4 shows the effect of solvents in the closed batch reaction of 1,3-butadiene at 200 °C. THF and cyclohexane were used as polar and nonpolar solvents, respectively. For 4.7 cm³ of 1,3-butadiene without using solvent, the conversion was 26.4% for 1 h, which was higher than that of 19.8% with THF solvent. However, the conversion without using solvent was 56.6% for 2 h, which was slightly higher than those with THF and cyclohexane solvents. When 3.9 cm³ of THF and cyclohexane was added to 4.7 cm³ of 1,3-butadiene at 200 °C for 2 h, the conversion was 54.1% and 54.9%, respectively. In contrast, the solvent-free reaction showed a higher conversion of 64.5% at the 1,3-butadiene charge volume of 8.6 cm³ (Entry 3). In the same void space of the reactor, this clearly indicates that solvents decrease the reaction rate. The conversion was 73.3% at a charge of 12.5 cm³ 1,3-butadiene at 200 °C (Entry 7), which was much higher than that of 52.9% in THF at the same reactant volume. Namely, small void space in the reactor increases the conversion.



Figure 2. Changes of pressure with reaction time at different temperatures in the reaction of 1,3-butadiene. 1,3-Butadiene charge, 5.5 g; reaction temperature: (a) 125, (b) 150, (c) 175, and (d) 200 °C.

The pressures were measured in the reaction of 1,3-butadiene at different temperatures. Figure 2 shows the changes of the pressures with the reaction time. The maximum pressure of 2.20 MPa was observed after 80 min from the start of the reaction and remained almost unchanged with the reaction time at 125 °C. It required 80, 70, and 50 min to reach the maximum pressures at 150, 175, and 200 °C, respectively, and after that the pressure decreased with the reaction time. The maximum observed pressure was 4.78, 4.16, 3.35, and 2.20 MPa at 200, 175, 150, and 125 °C, respectively. The pressure at 6 h was 2.32, 1.40, and 1.98 MPa at 150, 175, and 200 °C, corresponding with the conversion of 1,3-butadiene at 43.5, 68.3, and 75.1%, respectively.

The pressure during the reaction time at different charges of 1,3-butadiene was measured at $175 \,^{\circ}\text{C}$ (Figure 3). The maximum pressure of 4.16 MPa was observed at ca. 70 min at a charge of 5.5 g (Figure 3c). The maximum pressure of 4.20 MPa was observed at ca. 55 min at a charge of 8.0 g (Figure 3b), and the decrease of pressure was faster than that at a charge of 5.5 g. For the reaction in THF solvent (Figure 3a), the maximum pressure was 2.78 MPa at ca. 70 min, and the decrease of pressure was slower than that without solvent.

Discussion

Effect of Reaction Temperature and Pressure. Since the dienes have vapor pressures higher than those of the dimers produced at the same temperature, the pressure decreases as the reaction proceeds. The changes in pressures measured in the reaction of 1,3-butadiene at different temperatures are shown in Figure 2. For the reaction at $125 \,^{\circ}$ C, it took ca. 80 min to reach the maximum pressure, which indicates that the reaction of 1,3-butadiene hardly proceeds at $125 \,^{\circ}$ C and ca. 80 min are required for the reactant to reach $125 \,^{\circ}$ C. After 80 min, the pressure starts to plateau, which must contribute to the low conversion (Table 1). It took less time to reach maximum pressures at high temperatures than those at low temperatures, which is possibly contributed to that the reaction has proceeded before reaching the set temperature at high temperatures.



Figure 3. Changes of pressure with reaction time at different charges in the reaction of 1,3-butadiene. Reaction temperature, $175 \,^{\circ}$ C. 1,3-Butadiene charge was 5.5 (a), 8.0 (b), and 5.5 g (c); 3.9 cm³ of THF was used as solvent in (a).

It is known that the dimerization of 1,3-butadeiene to VCH is through Diels–Alder reaction. Many Diels–Alder reactions proceed in both thermal and high-pressure conditions,^{19–25} which indicate that high temperature and pressure are efficient for Diels–Alder reaction. Minuti et al. investigated the Diels–Alder reactions of 5-nitro[2.2]paracyclophanepyran-6-one with 1,2-dihydro-3-vinylnaphthalene under both thermal and high-pressure conditions, and the yields were 70 and 75% at 50 °C, 800 MPa for 24 h and at 110 °C, 0.1 MPa for 40 h, respective-ly.²³ In the reaction of 2-vinyl-2-benzo[*b*]furan with 2-inden-1-one, the Diels–Alder yield was 80% at 50 °C and 1000 MPa for 3 days, while it was 68% at 76.8 °C and 0.1 MPa for 3 days.²⁰ In our reaction conditions, high pressure was also obtained at high temperatures, and it is reasonable that the high temperature and pressure result in the high conversions of dienes.

The temperature also affects the selectivity of dimers produced from dienes. The favorable temperature for yielding VCH is 200 °C. It is interesting that the changes in the selectivities to COD and DVCB are always opposite in the reaction of 1,3-butadiene. Since COD can be produced by *cis*-DVCB (*cis*-1,2-divinylcyclobutane) under thermal conditions,^{4,5} *cis*-DVCB generated is possibly converted to COD at high temperatures.

The mechanism of Diels–Alder dimerization of 1,3-butadiene had been studied by several groups. Benson estimated the heats of formation for the transition state and concluded that the reaction is not a concerted process but a two-step process.²⁶ However, Doering et al. by a careful thermochemical analysis showed that the mechanism of the reaction is likely to be concerted, but not two-step.²⁷ Li et al. also investigated the mechanism of 1,3-butadiene dimerization by MCSCF calculations.²⁸ Since the formation of *trans–trans* divinyltetramethylene biradicals, which lead to DVCB, was the most favorable process, the stepwise biradical pathway was found slightly more favorable than the concerted pathway, which is explained to be simultaneous σ -bond formation. In our conditions, DVCB is generated by a small amount, which does not agree with the calculation results of Li and supports the concerted pathway.

Effect of Charge of Dienes. The high conversion achieved by using high charges attracted our interest. To understand the effect of charge, the pressure during the reaction was measured. As shown in Figure 3, the changes of pressure are different at different charges. It took less time to reach to the maximum pressure at a charge of 8.0 g of 1,3-butadiene than at a charge of 5.5 g. In our recent paper, the temperature during the reaction was measured in the solvent-free Diels-Alder reaction of 1,3butadiene with methyl vinyl ketone.¹⁸ The maximum temperature was found to be 15 °C higher than the set temperature of 125 °C, which contributed to the accumulation of reaction heat, the increased temperature was found to accelerate the reaction. The change in temperature was not measured in this work since the equipment for measuring temperature could not be used higher than 150 °C. However, the enthalpy change of the dimerization of 1,3-butadiene to VCH was calculated using B3LYP/6-31g(d) of Gaussian 03. The enthalpy change was -41.6 kcal mol⁻¹ at 200 °C, 4 MPa, which is close to that of -35.4 kcal mol⁻¹ at 25 °C, and 0.1 MPa calculated by Janz.²⁹ The enthalpy change of dimerization of 1.3-butadiene to VCH was lower than those in the Diels-Alder reaction of 1,3butadiene with methyl vinyl ketone and methyl acrylate, which was -150.1 and -163.4 kcal mol⁻¹, respectively, calculated at 125 °C, 0.1 MPa.¹⁸ It can be also understood that 1,3-butadiene, as a dienophile, is less reactive than methyl vinyl ketone and methyl acrylate, since 1.3-butadiene is not substituted with electron-withdrawing group(s).²⁴ However, it is also reasonable that the reaction heat increases the temperature and affects the rate.

It was found that the increase of pressure at a charge of 8.0 g (Figure 3b) was faster than that of 5.5 g (Figure 3c), which indicated that more reaction heat was generated at higher charge and the increase in temperature and pressure was accelerated. Moreover, the temperature and pressure increased quickly as the reaction proceeded, and resulted in the quick decrease of the pressure at high charge. High charge also leads to high percentage of liquid-phase 1,3-butadiene, which is more reactive than gas-phase 1,3-butadiene because of high concentration. Thus, the high charge of reactant 1,3-butadiene is efficient for achieving high conversions.

Effect of Solvents. Under pressure, the use of solvents resulted in lower conversions than without solvents at the same reactant volume. It can be shown that use of solvents affects the pressure of a reaction system through Raoult's law:

$$P_{\text{total}} = \sum_{i} P_i^* X_i \tag{1}$$

where P_i^* is the partial pressure of the component *i* in the solution, and X_i is the mole fraction of the component *i* in the solution. Since the solvents used in this work have vapor pressures lower than 1,3-butadiene, the pressure of the mixture would be lower than that without solvents at the same temperature.

The pressure was measured in the reaction of 1,3-butadiene using THF as a solvent (Figure 3a). The maximum pressure was much lower than that without solvents, as expected from Raoult's law. It should be noted that the solvent also absorbs the reaction heat, which decreases the temperature. The use of solvent caused the decrease of both temperature and pressure, which resulted in low conversion. Moreover, use of solvents dilutes the reactant, which is another reason for low conversions.

As we have demonstrated in Table 4, large void space in the reactor decreases conversion. Although the use of solvent and solvent-free conditions seem to give similar conversions (Entries 4–6 in Table 4), the time profiles of the pressures are much different (Figure 3). The initial pressure was different between the solvent-used and solvent-free reactions (Figures 3a and 3c), while the conversion for 1 h (Entries 1 and 2 in Table 4) is correlated with vapor pressure. It is, however, difficult to discuss the relation between changes in the reaction rate and the pressure with reaction time. It can be claimed that small void space leads to a high conversion because of small volume for 1,3-butadiene vapor in the reactor.

Conclusion

Dimerization of 1,3-buadiene was studied in a closed batch system under pressure at high temperature. VCH was obtained at a high yield from 1,3-butadiene without using solvents or catalysts. High temperature and pressure are necessary for the dimerization of 1,3-butadiene. Large charges of substrate leads to high percentage of liquid 1,3-butadiene, which is efficient for the reaction. The reaction without solvent proceeds more rapidly than the solvent-used reaction, since the solvent decreases the concentration of reactant. In addition, it is convenient that pressure is controlled only by changing the substrate charge and the temperature. Furthermore, the solventfree system has a significant advantage that there is no need to separate solvents from the products, which has less impact on the environment.

Experimental

1,3-Butadiene was purchased from Tokyo Chemical Industries Co., Ltd. THF and cyclohexane were purchased from Wako Pure Chemical Industries Ltd. The dimerization of 1,3butadiene was performed in a pressure vessel made of poly-(tetrafluoroethylene) with a volume of 20 cm³. A prescribed amount of reactant diene was poured into the vessel. Residual space in the vessel contained ambient air. The vessel with reactant diene was set in a stainless steel jacket and placed in an oven controlled at 200 °C. After 2 h, the vessel was cooled at 0 °C in ice bath. The recovered reaction mixture was diluted with *n*-decane and analyzed on a gas chromatograph (FID-GC, Shimadzu GC-14A) using a 60-m capillary column (Inertcap-1, GL Science, Japan). The temperature program for analyzing the products of 1,3-butadiene was 60 to 250 °C at a heating rate of 10 °C min⁻¹. A gas chromatograph with a mass spectrometer (GCMS-QP-5050A, Shimadzu, Japan) and a 30-m capillary column (DB-WAX, Agilent Technologies, USA) was used for identification of recovered compounds. The pressure was independently measured by using another vessel with a volume of 22.7 cm³ and with a pressure gauge ranging from 0.1 MPa to 6.1 MPa. The volume of 1,3-butadiene was calculated from weight of liquid 1,3-butadiene poured into the vessel divided by the density of 0.64 g cm⁻³ at -6 °C.

Enthalpy change of reaction was calculated using $B3LYP^{30}/6-31g(d)$ of Gaussian 03,³¹ which is based on density functional theory. The calculation was done without consideration

of scaling factor. Depending on the experimental reaction conditions, temperature was set at $200 \,^{\circ}\text{C}$ and a pressure of $4 \,\text{MPa}$.

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