The effects of reaction variables on the palladium-catalyzed reactions of butadiene with water

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Abstract

The effects of reaction variables on the reactions of butadiene with water in the presence of homogeneous palladium catalysts were investigated. The reactions in the presence of palladium, a phosphine ligand and carbon dioxide comprized telomerization, linear dimerization and cyclodimerization. The rate of reaction and the selectivity to 2,7-octadien-1-ol, 1,3,7-octatriene and 1-methylene 2-vinyl cyclopentane depended strongly upon the ratio of water to butadiene, the ratio of phosphine to palladium, the amount of carbon dioxide and the reaction time. 2,7-Octadien-1-ol that formed initially was subsequently converted to a mixture of 1,7-octadien-3-ol, 1,3,7-octatriene and 1-methylene-2-vinyl cyclopentane, the degree of which depended on the reaction conditions. A possible reaction pathway for the reaction of butadiene with water has been proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Butadiene; Water; Octadienol; Telomerization; Cyclodimerization; Palladium catalysts; Reaction variables

1. Introduction

The telomerization of butadiene with water into 2,7-octadien-1-ol is a very interesting reaction. 2,7-Octadien-1-ol can be easily hydrogenated to 1-octanol, a valuable plasticizer alcohol. Also, 1,9-nonanediol can be derived from 2,7-octadien-1-ol. The palladium complex-catalyzed reaction of butadiene with water to octadienols was reported first by Atkins et al. [1]. Thereafter, it has been studied by industrial research groups such as Kuraray, BASF, Elf Atochem and Mitsubishi [2–14]. In contrast to telomerization with alcohols, phenols and amines, the telomerization of butadiene with water requires the

presence of carbon dioxide and a solvent. However, Kuntz et al. claimed the efficient telomerization of butadiene into 2,7-octadien-1-ol in the presence of additives like Na_2CO_3 or K_2CO_3 instead of solvent and carbon dioxide [15–17]. Recently, Monflier et al. have reported that this telomerization could also be carried out without a solvent but in the presence of a cationic surfactant [18–20]. In a study of telomerization of butadiene with water in the presence of carbon dioxide, Bergamini et al. found for the first time that the palladium-catalyzed cyclodimerization of butadiene to 1-methylene-2-vinyl cyclopentane occurred [21]. The role of carbon dioxide or additives has not been established yet, although some hypotheses have been suggested.

This paper is focused on the effects of various reaction variables that include the ratio of water to butadiene, the ratio of phosphine to palladium, the

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amount of carbon dioxide, the reaction time and solvent. These reaction variables have an influence on the selective synthesis of 1-methylene 2-vinyl cyclopentane, 2,7-octadien-1-ol and 1,3,7-octatriene. From these results, we wish to describe the reaction pathway available for the reaction of butadiene with water.

2. Experimental

The reaction of butadiene with water was performed in a 100 ml stainless steel autoclave reactor (Autoclave Engineers). Typically, a palladium catalyst (Pd content 0.5 mmol), triphenylphosphine (1.5 mmol), water (0.5 mol) and solvent (40 ml) were introduced under nitrogen atmosphere and then 1,3-butadiene (0.25 mol) was charged. The reactor was pressurized with carbon dioxide to 200 psi at room temperature, and the contents were heated to 363 K and kept at this temperature for the desired reaction time with vigorous stirring. During the reaction, the reaction mixture was sampled and analyzed by a gas chromatograph (GC, HP 6890) with a 60 m AT-1 capillary column and a flame ionization detector. Products were identified through both GC-mass spectroscopy (HP 5972 MSD) and NMR analyses.

3. Results and discussion

3.1. Effects of reaction variables: a possible reaction pathway

Table 1 shows the results obtained under various reaction conditions. The products obtained

in the reaction of butadiene with water were 2,7-octadien-1-ol, 1,7-octadien-3-ol, 1,3,7-octatriene, 1-methylene-2-vinyl cyclopentane, 4-vinyl cyclohexene, heavy oligomers and a trace of 3-buten-2-ol. In the absence of catalyst, butadiene slowly dimerized to 4-vinyl cyclohexene. With palladium acetate present, the major product was still 4-vinyl cyclohexene without phosphine ligand under nitrogen or carbon dioxide atmosphere (Run 1 and 2). Thus, the cyclodimerization of butadiene is dominant under these conditions without phosphine ligand [22]. However, when butadiene reacts in the presence of palladium acetate and Ph_3P, but without water, 1,3,7-octatriene was formed predominantly (Run 3). This indicates the formation of a palladium–phosphine complex that catalyzes the linear dimerization of butadiene. With both palladium and the phosphine ligand present, the reaction of butadiene with water still produced 1,3,7-octatriene under nitrogen atmosphere (Run 4), but produced mainly octadienols under carbon dioxide atmosphere (Run 5). From these results, it appears that carbon dioxide assists OH group of water to combine itself with a reaction intermediate to form octadienols. During the reaction of butadiene with water in the presence of palladium and phosphine ligand, we could obtain 1-methylene-2-vinyl cyclopentane as a side product (Run 4 and 5). As mentioned above, the cyclodimerization of butadiene to form 1-methylene-2-vinyl cyclopentane in the presence of carbon dioxide and water was reported first in 1995 by Bergamini [21]. Table 1 shows that 1-methylene 2-vinyl cyclopentane is formed under nitrogen as well as carbon dioxide atmosphere.

Table 1
The reaction of butadiene with water: effects of reagents[a]

Run	Reactant	Ph_3P (mmol)	CO_2 (psi)	N_2 (psi)	C_4H_6 conversion (%)	Selectivity (%)					
						2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene	Heavy oligomers
1	$C_4H_6 + H_2O$	0	0	200	4.7	0	0	0	0	61.4	38.6
2	$C_4H_6 + H_2O$	0	200	0	12.4	0	0	0	0	88.0	12.0
3[b]	C_4H_6	1.5	200	0	68.9	0	0	63.5	0	0.5	36.0
4	$C_4H_6 + H_2O$	1.5	0	200	33.7	5.8	0	68.1	11.2	4.7	10.3
5	$C_4H_6 + H_2O$	1.5	200	0	77.6	74.8	7.2	8.1	6.6	0	3.3
6[c]	2,7-Octadien-1-ol	1.5	200	0	92.8	–	0.2	73.8	18.1	0	8.0

[a] The following procedure was used unless otherwise stated: butadiene = 0.25 mol, H_2O = 0.5 mol, Pd acetate = 0.5 mmol, acetone = 40 ml, temperature = 363 K, time = 1.5 h.

[b] H_2O = 0 mol, DMF = 40 ml instead of acetone.

[c] 2, 7-Octadien-1-ol = 0.1 mol, DMF = 40 ml instead of acetone, time = 13 h.
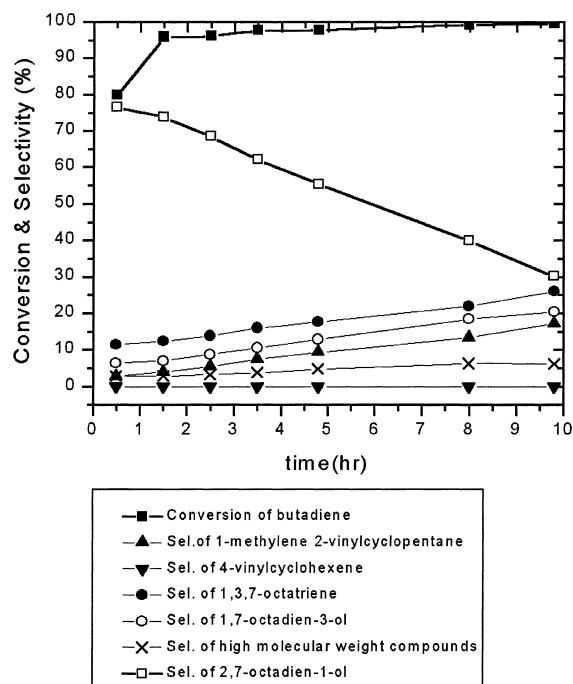
Fig. 1. Change in butadiene conversion and selectivity to various products with time in the reaction of butadiene with water: butadiene = 0.25 mol, water = 0.5 mol, Pd(II)acetate = 0.5 mmol, Ph$_3$P = 1.5 mmol, DMF = 40 g, CO$_2$ = 200 psi, temperature = 363 K.

In Fig. 1, it is shown that the change in product distribution with time for catalytic run carried out in the presence of palladium–triphenylphosphine catalyst and under carbon dioxide atmosphere. 2,7-Octadien-1-ol appeared to be the main product initially, which was subsequently converted to a mixture of 1,7-octadien-3-ol, 1,3,7-octatriene and 1-methylene-2-vinyl cyclopentane. To confirm this reaction scheme, 2,7-octadien-1-ol was separated after the reaction of butadiene with water and then the reaction of 2,7-octadien-1-ol itself was performed in the presence of the palladium–phosphine catalyst and carbon dioxide (Run 6 in Table 1). As expected, 2,7-octadien-1-ol was converted mostly to 1,3,7-octatriene and 1-methylene-2-vinyl cyclopentane.

The results obtained from the reaction of butadiene with water under various conditions, as described above, provide information on the cat-alytic reaction pathway of butadiene and water with palladium–phosphine complex. The proposed reaction pathway is shown in Scheme 1. A π-allyl palladium complex coordinated with phosphine is well known as an intermediate in the dimerization of butadiene [23,24]. The intermediate is involved in the formation of octadienols, octatriene and cyclodimer in the following manner. First, carbon dioxide reacts with water to give carbonates and then the carbonate ions attack the intermediate to give rise to mono acid octadienyl carbonates. These mono acid octadienyl carbonates are unstable in the reaction medium and decompose into octadienols and carbon dioxide [18–20]. 2,7-Octadien-1-ol is formed via 1,6-addition of carbonic acid to the intermediate and 1,7-octadien-3-ol via 3,6-addition. Away from this cycle, 1,3,7-octatriene is formed from the same π-allyl palladium intermediate by the migration of hydrogen from C4 to C6 positions [24], and the formation of a bond between C2 and C6 gives 1-methylene 2-vinyl cyclopentane. 3-Buten-2-ol as a trace product comes from a butenyl palladium intermediate involving a single butadiene molecule that reacts with water.

The fact that 2,7-octadien-1-ol is the primary product at early reaction times suggests that the addition of water to the intermediate occurs more rapidly than the hydrogen migration or the formation of cyclodimer. But, 2,7-octadien-1-ol formed initially is unstable and converts to a mixture of 1,7-octadien-3-ol, 1,3,7-octatriene and 1-methylene-2-vinyl cyclopentane via a reversible path through carbonate and π-allyl palladium intermediates. Though, 1,7-octadien-3-ol was also converted to 1,3,7-octatriene and 1-methylene-2-vinyl cyclopentane in the presence of the excess amount of phosphine as discussed later, it was more stable than 2,7-octadien-1-ol. The formation of 1,3,7-octatriene and 1-methylene 2-vinyl cylcopentane was regarded to go through irreversible paths. This is not consistent with what Bergamini has proposed [21]. However, under reaction conditions employed in this study 1,3,7-octatriene and 1-methylene 2-vinyl cylcopentane, once formed, remained stable. As shown below, the relative extent of reaction by each pathway depended on the relative amounts of reagents and catalysts including water, phosphine and carbon dioxide.
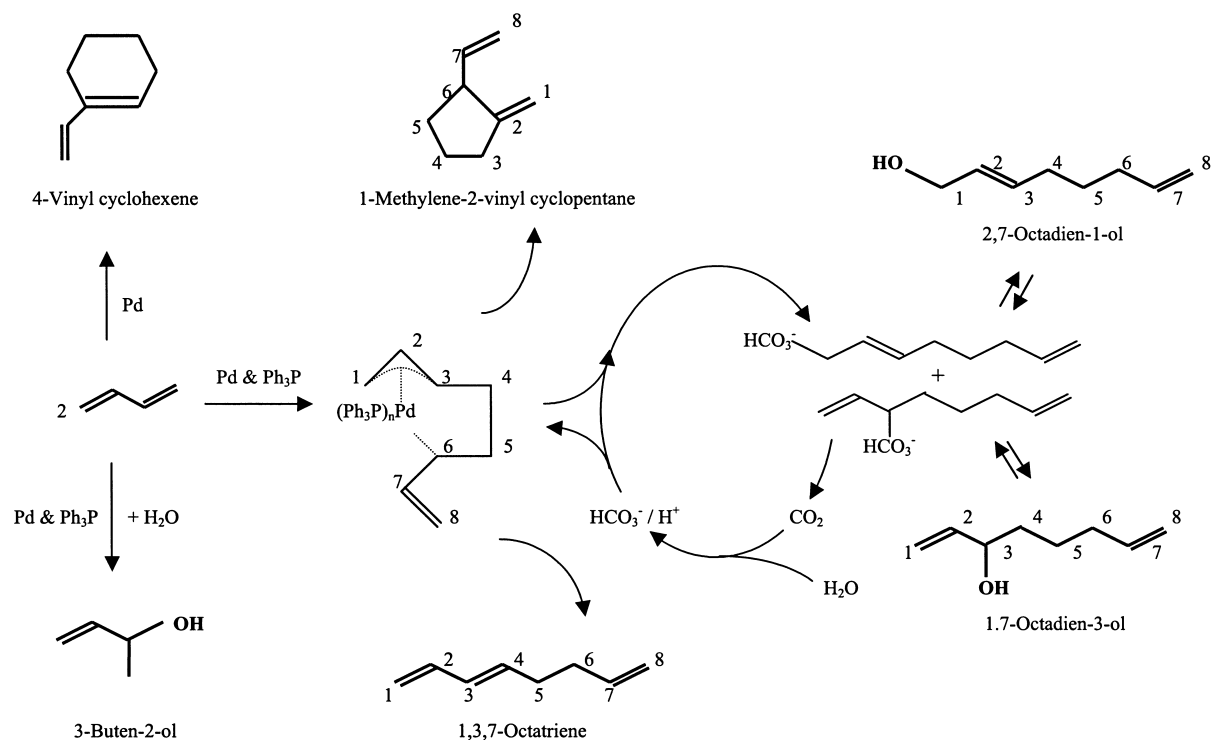
Scheme 1. A reaction pathway proposed for the reaction of butadiene with water.

3.2. Effect of palladium precursor

Typical results for the reaction of butadiene with water over various palladium precursors are presented in Table 2. As well known, palladium acetate and palladium acetyl acetonate showed high activity and selectivity to 2,7-octadien-1-ol (Run 5 and 7) [1]. Inorganic precursors such as palladium nitrate (Run 9), palladium oxide (Run 10) and palladium chloride (Run 11) gave lower activities than the organic precursors. Furthermore, the reaction of butadiene with water using inorganic palladium precursors produced mainly 4-vinyl cyclohexene. As mentioned above, 4-vinyl cyclohexene was not formed in the presence of palladium–phosphine complex. Thus, inorganic ions appear to block free coordination sites at palladium and inhibit palladium from coordination to phosphine [24]. Bis(acetonitrille)chloronitropalladium(II) containing chloride ions also gave a low activity and 4-vinyl cyclohexene as the main product (Run 12). Palladium metal catalyst does not seem to form palladium–phosphine complex either as seen from its low activity (Run 13).

When preformed palladium complexes were employed, the activity of $(Ph_3P)_4Pd(0)$ (Run 15) with four phosphine ligand per one palladium atom was much higher than that of $(Ph_3P)_2Pd(II)(O_2CCH_3)_2$ with two phosphine per one palladium (Run 14). This is consistent with the observation that the increase of Ph_3P/Pd molar ratio improves the reaction rate and the selectivity to octadienols. The fact that the zero-valent palladium compound such as trisdibenzyldeneacetonedipalladium(0) (Run 8) was as active as divalent palladium compounds (Run 5 and 7) in this reaction system indicates that the difference in oxidation states of palladium is not responsible for the difference in activity among palladium precursors.

3.3. Effect of solvent

The present reaction system can be divided into two parts, one is the water-soluble components of water

Table 2
The reaction of butadiene with water: effects of palladium precursors[a]

Run	Catalyst	C_4H_6 conversion (%)	Selectivity (%)						1-ol/Σ ol[b]
			2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene	Heavy oligomers	
5	$Pd(II)(CH_3CO_2)_2$	77.6	74.8	7.2	8.1	6.6	0	3.3	91.2
7	$Pd(II)(CH_3COCH=COCH_3)_2$	85.0	76.7	11.0	5.6	2.8	3.2	0.7	87.5
8	$(C_6H_5CH=CHCOCH=CHC_6H_5)_3Pd_2(0)$	81.1	69.2	10.2	5.6	3.7	3.9	7.3	87.2
9	$Pd(II)(NO_3)_2$	12.4	0	0	47.9	36.1	5.8	10.2	–
10	$Pd(II)O$	2.4	0	0	0	0	30.6	69.4	–
11	$Pd(II)Cl_2$	3.0	0	0	19.3	0	22.8	58.0	–
12	$(CH_3CN)_2Pd(II)(NO_2)Cl$	0.8	0	0	49.7	0	50.3	0	–
13	$Pd(0)$	3.1	0	0	0	0	17.0	83.0	–
14[c]	$(Ph_3P)_2Pd(II)(O_2CCH_3)_2$	6.7	54.7	3.9	21.6	13.2	2.8	3.8	93.3
15[d]	$(Ph_3P)_4Pd(0)$	81.1	69.1	12.1	10.7	3.7	0	4.3	85.0

[a] The following procedure was used unless otherwise stated: butadiene = 0.25 mol, H_2O = 0.5 mol, Pd = 0.5 mmol, Ph_3P = 1.5 mmol, acetone = 40 ml, CO_2 = 200 psi, temperature = 363 K, time = 1.5 h.

[b] 1-ol/Σ ol = 2,7-octadien-1-ol/(2,7-octadien-1-ol + 1,7-octadien-3-ol).

[c] Ph_3P = 0 mmol.

[d] Ph_3P = 0 mmol.

Table 3
The reaction of butadiene with water: effects of solvents[a]

Run	Solvent	Volume (ml)	Solubility in water	Polarity index[b]	C_4H_6 conversion (%)	2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene	Heavy oligomers	1-ol/Σ ol
16	Heptane	40	No	0	14.9	9.0	6.4	68.0	10.5	2.7	3.4	58.4
17	3-Pentanone	40	No	4.5	10.9	53.1	7.0	30.3	4.0	0	5.6	88.4
18	THF	40	Yes	4.2	83.1	74.6	8.9	16.5	0	0	0	89.3
19	1,4-Dioxane	40	Yes	4.8	85.8	77.8	8.6	9.9	2.5	0	1.2	90.0
20	Sulfolane	40	Yes	–	73.7	66.3	6.2	14.8	10.8	0.5	1.4	91.4
5	Acetone	40	Yes	5.4	77.6	74.8	7.2	8.1	6.6	0	3.3	91.2
21	DMSO	40	Yes	6.5	80.0	80.1	10.2	2.2	1.8	0	5.7	87.1
22	DMF	11	Yes	6.4	37.1	36.6	5.5	34.6	17.4	3.4	2.5	86.9
23	DMF	22	Yes	6.4	95.0	76.0	7.6	9.0	3.9	0.3	3.3	90.9
24	DMF	40	Yes	6.4	95.9	73.8	7.0	12.4	4.0	0	2.8	91.3
25	DMF	64	Yes	6.4	88.4	70.5	6.7	17.4	3.8	0	1.6	91.3
26	DMF	123	Yes	6.4	25.3	45.2	2.7	39.7	2.7	5.0	4.8	94.3

[a] Reaction conditions: butadiene = 0.25 mol (= 22 ml), H_2O = 0.5 mole (= 9 ml), Pd(II)acetate = 0.5 mmol, Ph_3P = 1.5 mmol, CO_2 = 200 psi, temperature = 363 K, time = 1.5 h.

[b] Adapted from: Norman B. Godfrey, Solvent selection via miscibility number, CHEMTECH (1972) 359–363.

and carbon dioxide and the other is the water-insoluble components of butadiene, palladium acetate and triphenylphosphine, Therefore, it is important to use the solvent to mix all reaction mediums. Table 3 shows the effect of different organic solvents on catalytic activity. The reaction progressed little without a solvent. But, with solvent, octadienols were formed regardless of the kind of solvent. We found that carbon dioxide was much more soluble in water-solvent system than in water by itself. Thus, solvents in the present system may play an important role by dissolving carbon dioxide to give carbonates.

The reaction of butadiene with water in heptane or 3-pentanone as water-insoluble solvents gave low conversions of butadiene since they made a clear phase separation between aqueous and organic phases (Run 16 and 17). Thus, mainly 1,3,7-octatriene was formed by the linear dimerization occurring in the organic phase. But, the selectivity to 2,7-octadine-1-ol was much higher in 3-pentanone than in heptane. This indicates that the insertion of OH group into an intermediate could be favorable in 3-pentanone with polarity. When the reaction was carried out in the presence of water-soluble solvents such as THF (tetrahydrofuran), 1,4-dioxane, sulfolane, acetone, DMSO (dimethylsulfoxide) and DMF (dimethylformamide), a remarkable increase in the rate of the reaction and selectivity to 2,7-octadien-1-ol was obtained (Run 5, 18–21, 24). The product profiles had little changed by the nature of water-soluble solvents, but the catalytic activity was higher in DMF than in any other solvents (Run 24). DMF is more basic than other used solvents. The high activity in DMF may correlate with the fact that carbon dioxide is easy to form carbonate ions in the basic solution such as DMF.

The amount of employed DMF solvent revealed a significant influence on the reaction rate as shown in Runs 22–26. When the volume of solvent was 11 ml (the volume ratio of solvent/butadiene = 0.5), the catalytic activity was low and the selectivity to 1,3,7-octatriene was as high as that of 2,7-octadien-1-ol (Run 22). This indicates that the amount of solvent was not sufficient enough for the reactants to be fully mixed. As the amount of DMF was increased, the reaction rate and the selectivity to 2,7-octadien-1-ol were increased and showed a maximum activity at 40 ml (the volume ratio of solvent/butadiene = 1.8) (Run 23 and 24). But, further excess amounts of DMF sharply decreased the reaction rate and the selectivity of 2,7-octadien-1-ol (Run 25 and 26). This suggests that both the reaction rate and the selectivity to each product are dependent on the concentration of reactants and catalytic components in the reaction mixture since the amount of the solvent could change the concentration of the involved species.

3.4. Effect of water/butadiene ratio

Table 4 shows the effect of water/butadiene molar ratio on the catalytic activity. When butadiene reacted without water in the palladium–phosphine catalyst, mainly 1,3,7-octatriene via linear dimerization was formed as mentioned above (Run 3). Though, the stoichiometric molar ratio of water/butadiene is 0.5 in the telomerization of butadiene with water, the rate of reaction and the selectivity to 2,7-octadien-1-ol increased as the water/butadiene molar ratio increased up to 2 (Run 24, 27 and 28). But, with the ratio above 2, the reaction rate and the selectivity of

Table 4
The reaction of butadiene with water: effects of water/butadiene molar ratios[a]

Run	Molar ratio of H_2O/C_4H_6	C_4H_6 conversion (%)	Selectivity (%)							1-ol/Σ ol
			2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene	Heavy oligomers	
3	0	68.9 (100)	0 (0)	0 (0)	63.5 (62.8)	0 (0)	0.5 (0.4)	36.0 (36.7)	–
27	0.5	84.4 (100)	61.3 (0)	11.0 (14.4)	22.4 (79.6)	0.6 (1.0)	0 (0)	4.7 (5.0)	84.8 (0)
28	1	94.3 (100)	65.1 (0)	9.7 (23.8)	19.4 (53.4)	2.5 (18.0)	0 (0)	3.3 (4.8)	87.0 (0)
24	2	95.9 (100)	73.8 (0)	7.0 (24.1)	12.4 (37.0)	4.0 (32.2)	0 (0)	2.8 (6.7)	91.3 (0)
29	4	83.7 (100)	51.5 (0)	10.6 (6.6)	20.2 (26.9)	15.6 (54.8)	0 (0)	2.0 (11.6)	82.9 (0)

[a] Reaction conditions: butadiene = 0.25 mol, Pd acetate = 0.5 mmol, Ph$_3$P = 1.5 mmol, DMF = 40 ml, CO$_2$ = 200 psi, temperature = 363 K, time = 1.5 h (20 h).

2,7-octadien-1-ol decreased, while the selectivity of 1,3,7-octatriene and 1-methlyene 2-vinyl cyclopentane increased (Run 29). The excess water relative to solvent could make the phase separation between aqueous and organic phases in the reaction medium and thus, the catalytic activity was suppressed.

The selectivity to 1-methylene-2-vinyl cyclopentane shows a strong dependence on the molar ratio of water to butadiene. The formation of 1-methylene-2-vinyl cyclopentane increased monotonously with the amount of water. When the water/butadiene molar ratio was 4, 2,7-octadien-1-ol formed initially was subsequently converted mainly to 1-methylene-2-vinyl cyclopentane. This is reasonable because a hydrogen atom of water could participate in the formation of 1-methylene-2-vinyl cyclopentane [21]. The water concentration in the reaction mixture must be controlled in a suitable range because it is a predominant factor that governs the reaction rate and the selective synthesis of 2,7-octadien-1-ol and/or 1-methylene-2-vinyl cyclopentane.

3.5. Effect of triphenylphosphine/palladium ratio

Triphenylphosphine is most commonly used as the ligand for homogeneous metal catalysts including palladium. The effect of Ph_3P/Pd molar ratio on the reaction of butadiene with water was studied as shown in Table 5. The reaction without triphenylphosphine gave a low conversion of butadiene and a high selectivity of 4-vinyl cyclohexene after 1.5 h at 363 K

(Run 30). The use of triphenylphosphine as the ligand suppressed the formation of 4-vinyl cyclohexene and gave high yields of 2,7-octadien-1-ol. As the Ph_3P/Pd molar ratio increased up to 3, both the rate of reaction and the selectivity of 2,7-octadien-1-ol increased (Run 24, 31 and 32). Varying the Ph_3P/Pd ratio from 3 to 10 had little influence on the initial rate of the reaction, but the ratio of 2,7-octadien-1-ol:1,7-octadien-3-ol in the reaction mixture changed from 74:7 to 62:17 (Run 24, 33 and 34). Octadienols, once formed early, converted to a mixture of 1,3,7-octatriene and 1-methylene 2-vinyl cyclopentane as the reaction time was prolonged. By increasing the amount of triphenylphosphine, the formation of 1,3,7-octatriene from 2,7-octadien-1-ol increased while the formation of 1-methylene 2-vinyl cyclopentane decreased after 20 h of the reaction. This indicates that triphenylphosphine added in excess accelerates the conversion of 2,7-octadien-1-ol into 1,3,7-octatriene, while suppresses its conversion into 1-methylene-2-vinyl cyclopentane.

Recently, the water-soluble phosphine ligands such as $(C_6H_4SO_3Na)_3P$ (TPPTS, trisodium salt of tri(*m*-sulfophenyl)phosphine) have been used in two-phase reactions [15–17]. When TPPTS instead of triphenylphosphine was used in the present reaction system, the activity was low initially but 1-methylene 2-vinyl cyclopentane was obtained selectively after 20 h (Run 35). These results show that 1-methylene 2-vinyl cyclopentaene could be formed with a high selectively under excess water and TPPTS.

Table 5
The reaction of butadiene with water: effects of Ph_3P/Pd molar ratios[a]

Run	Molar ratio of Ph_3P/Pd	C_4H_6 conversion (%)	Selectivity (%)						1-ol/Σ ol
			2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene	Heavy oligomers	
30	0	9.2 (10.4)	0 (0)	0 (0)	13.0 (12.8)	0 (0)	55.7 (51.9)	31.3 (35.3)	–
31	1	69.5 (100)	59.5 (20.7)	4.4 (13.8)	23.4 (34.5)	3.6 (21.2)	1.8 (1.4)	7.3 (8.4)	93.1 (0.6)
32	2	75.4 (100)	61.1 (15.4)	8.6 (19.7)	22.8 (33.1)	5.4 (25.6)	0 (0)	2.2 (6.2)	87.7 (0.4)
24	3	95.9 (100)	73.8 (0)	7.0 (24.1)	12.4 (37.0)	4.0 (32.2)	0 (0)	2.8 (6.7)	91.3 (0)
33	5	95.9 (100)	68.1 (0)	19.6 (15.0)	12.9 (67.0)	2.0 (10.1)	0 (0)	2.4 (7.9)	77.7 (0)
34	10	94.6 (100)	61.6 (0)	17.0 (14.8)	12.4 (72.1)	0.6 (2.4)	0 (0.6)	8.5 (10.1)	78.4 (0)
35[b]	3	40.6 (100)	40.9 (0)	3.0 (1.0)	33.8 (22.8)	22.3 (69.2)	0 (0)	0 (7.0)	93.0 (0)

[a] The following procedure was used unless otherwise stated: butadiene = 0.25 mol, H_2O = 0.5 mol, Pd acetate = 0.5 mmol, Ph_3P, DMF = 40 ml, CO_2 = 200 psi, temperature = 363 K, time = 1.5 h (20 h).
[b] $(C_6H_4SO_3Na)_3P$ instead of Ph_3P.

Table 6
The effect of carbon dioxide on the reaction of butadiene with water[a]

Run	CO_2 (mol)	C_4H_6 conversion (%)	Selectivity (%)							1-ol/Σ ol
			2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene	Heavy oligomers	
36	0	27.0 (52.2)	16.2 (6.3)	1.1 (2.2)	64.1 (42.8)	5.9 (25.9)	4.9 (2.7)	7.9 (20.1)	93.6 (74.1)
37	0.0015	86.2 (100)	34.8 (20.1)	5.2 (6.4)	27.5 (44.0)	3.6 (17.2)	0 (0)	28.8 (12.3)	87.0 (75.8)
38	0.01	92.4 (100)	63.6 (18.2)	8.3 (12.3)	16.1 (41.6)	3.5 (15.0)	0 (0)	8.4 (12.9)	88.5 (59.7)
39	0.1	95.1 (100)	74.5 (15.0)	9.4 (19.1)	10.0 (39.0)	3.2 (15.8)	0 (0)	2.9 (11.1)	88.8 (44.0)
40	0.2	96.7 (100)	71.6 (12.7)	10.8 (16.6)	10.2 (36.6)	3.9 (24.5)	0 (0)	3.5 (9.0)	86.9 (43.3)
41	0.37	95.5 (100)	60.2 (12.9)	18.9 (17.7)	13.1 (34.7)	5.5 (20.3)	0 (0)	2.3 (14.5)	76.1 (42.2)

[a] Reaction conditions: butadiene = 0.25 mol, H_2O = 0.5 mol, Pd(II)acetate = 0.5 mmol, Ph_3P = 1.5 mmol, DMF = 40 ml, temperature = 363 K, time = 1.5 h (15 h).

3.6. Effect of carbon dioxide

It is already well known that the rate of formation of octadienols can be increased by adding carbon dioxide to the above reaction system [1]. Our study was focused on the effect of the amount of carbon dioxide in the reaction of butadiene with water and the results after 1.5 and 15 h of the reaction were summarized in Table 6. Without carbon dioxide, butadiene dimerized to form 1,3,7-octatriene (Run 36). However, with carbon dioxide present, palladium–phosphine complex converted butadiene mainly to octadienols (Run 37–41). As the amount of carbon dioxide increased, both the reaction rate and the selectivity of 1,7-octadien-3-ol increased. When the same mole of carbon dioxide (1.5 mmol) as that of phosphine ligand was added, the catalytic activity was high but the selectivity of 2,7-octadien-1-ol was still low (Run 37). However, as the mole of carbon dioxide as much as those of reactants was added, both the catalytic activity and the selectivity of 2,7-octadien-1-ol were high (Run 39–41). This supports indirectly the role of carbon dioxide as a reagent that forms carbonate ions in water. That is, carbon dioxide reacts with water to give carbonates, which react with a palladium–phosphine complex to form mono acid octadienyl carbonates which are unstable in the reaction medium, and decompose into octadienols and carbon dioxide [18–20]. The increase of acidity in the DMF solution after addition of carbon dioxide shows indirectly the formation of carbonic acid from carbon dioxide and water. The pH value in the DMF solution was 9.89 before addition of carbon

dioxide, and became 6.61 after the addition of carbon dioxide.

The ratio of 1,3,7-octatriene to 1-methylene-2-vinyl cyclopentane formed from 2,7-octadien-1-ol was hardly influenced by the amount of carbon dioxide. The excess amount of carbon dioxide compared to reactants induced the rapid reaction rate, and yet decreased the selectivity to 2,7-octadien-1-ol. Therefore, the amount of carbon dioxide should be controlled properly to obtain the maximum yield of 2,7-octadien-1-ol.

4. Conclusions

The reaction of butadiene with water in the presence of palladium, a phosphine ligand and carbon dioxide consists of three main reactions, i.e. telomerization, linear dimerization and cyclodimerization. To obtain the maximum yield of 2,7-octadien-1-ol, the reaction time and the amount of water, palladium, phosphine, solvent and carbon dioxide should be controlled. In the choice of solvent, three important factors should be considered: the solubility of water, the solubility of carbon dioxide and basicity.

1,3,7-Octatriene and 1-methylene-2-vinyl cyclopentatne could be formed from octadienols in consecutive reactions as well as from butadiene and water directly. The formation of 1,3,7-octatriene from 2,7-octadien-1-ol increases as the amount of water decreases and that of phosphine ligand increases. 1-Methylene-2-vinyl cyclopentane is not formed without water or in large excess of triphenlyphosphine. The

water/butadiene molar ratio plays a decisive role in the case of the selective synthesis of 1-methylene-2-vinyl cyclopentane. The formation of 1-methylene-2-vinyl cyclopentane increases as the amount of water increases. 1-Methylene-2-vinyl cyclopentane could be formed with a higher selectively in the presence of TPPTS instead of triphenylphosphine. Also, it has been found that 1-methylene-2-vinyl cyclopentane is produced under nitrogen as well as carbon dioxide atmosphere.

Acknowledgements

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