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Reactivity of a Simplest Conjugated Diolefin in Liquid-Phase Oxidation: Mechanisms and Products

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Additional information is available at the end of the chapter

Abstract

Ethylene is the simplest member of olefin series, but butadiene-1,3 (BD) is the simplest conjugated diolefin. In this chapter, we describe liquid-phase oxidations of BD with an emphasis on comparison of the diolefin with monoolefins. BD interacts with oxygen to form polyperoxide, whose thermal decomposition or hydrogenation leads to the formation of 2-butene-1,4-diol, 3-butene-1,2-diol, or butanediols together with furan and acrolein. BD can be oxidized in polar solvents by radical chain route to form directly the dioxygenates. Metal catalysts are able to control the oxidation by promoting formation of 2-butene-1,4-diol, 4-hydroxybut-2-enal, and furan. PdTe/C catalyst is applied in industry to produce 2-butene-1,4-diol diacetates with selectivity of 98%. The outstanding selectivity of the catalyst is caused by combined action of components in nonradical route and esterification of final product in acetic acid. Similar reaction in methyl alcohol yields 1,4-dimethoxy-2-butene, but with lower efficiency. The nonradical mechanism is firmly established for epoxidation of BD with hydrogen peroxide catalyzed by phosphotungstates. The selectivity of BD and hydrogen peroxide conversion to 3,4-epoxy-1-butene around 100% is attained. Analysis of published information and our own studies show many similarities in oxidation of BD and light olefins, which are very useful for understanding the mechanisms.

Keywords: butadiene-1,3, olefin, oxygen, hydrogen peroxide, homogeneous catalyst, heterogeneous catalyst, liquid-phase oxidation, oxidation products, mechanism

1. Introduction

Butadiene-1,3 (BD) is diolefin containing two conjugated double bonds. In oxidation, BD exhibits properties inherent to all olefins, but higher reactivity was compared to but-1-ene and

but-2-ene. Both BD and C$_4$-olefins can be a feedstock for producing valuable chemicals by gas-phase oxidation [1, 2]. The oxidation on oxide catalysts in gas phase results in the formation of maleic anhydride together with crotonaldehyde and 2,5-dihydrofuran. Centy and Trifiro suggested a simple consecutive pathway for BD oxidation over V-P-oxide catalysts [3, 4], whereas Honicke et al. proposed multiple pathways from BD to crotonaldehyde, 2,5-dihydro-furan, 2-butene-1,4-dial, 2(5H)-furanone and furan, and finally to maleic anhydride over V$_2$O$_5$ catalysts [5]. Schroeder specified the oxidation pathway on V-Mo-oxide catalysts, including 3,4-epoxy-1-butene as a primary oxidation product [6]. Epoxidation of BD occurs over Ag catalysts [7–10] used in industry for the production of ethylene oxide and intensively investi-gated in the oxidation of other olefins (e.g., [11, 12]). 3,4-Epoxy-1-butene is further converted into 2,3-dihydrofuran followed by hydrolysis to form 4-hydroxybutyraldehyde. The second-ary transformations occur directly under epoxidation conditions on Ag catalysts promoted with B-P [13], Mo [14], and Mo-P-Sb [15] or by subsequent treatments of 3,4-epoxy-1-butene.

In the early 1980s, oxidation of n-butane has become the preferred method for manufacturing maleic anhydride [16, 17]. The invented synthesis of maleic anhydride from butane creates a competition for the gas-phase oxidation of BD since hydrogenation of maleic anhydride opens a possibility of producing various oxygenates, which produced from BD earlier. At the same time, the gas-phase oxidation of BD still suffers from formation of polymer resins, which leads to excessive consumption of raw materials and catalyst deactivation. This prob-lem and large power consumption inherent to all gas-phase reactions are absent in the liquid-phase oxidation since the low temperature and application of appropriate solvents prevent the formation of the resins. The liquid-phase low-temperature oxidative reactions, in particu-lar the oxidation of olefins, were intensively studied at the end of the last century [18–23]. A renewed interest in this area is growing now [24–27] and can be expected to be strengthened in the nearest future as a response to modern requirements of green chemistry to minimize power and materials consumption. In addition, the liquid-phase reactions are well applicable for the oxidation of various olefins and BD because of high reactivity of these hydrocarbons that allows the oxidation at low temperature. At the same time, BD becomes more affordable owing to permanent improvements in its manufacturing.

The title of this chapter concerns the application of green oxygen (air and hydrogen perox-ide) in liquid-phase conditions. The liquid-phase oxidative reactions are an important part in chemistry of all olefins and, in particular, of the simplest representative of conjugated diole-fins as they open many routes for the conversion of the hydrocarbons. We represent here an analysis of literature information concerning the oxidation of BD in liquids and references to the related reactions of olefins. In detail, we described the catalytic systems in the study of which we acquired our own experience.

2. Radical chain reactions of BD with oxygen

Olefins readily interact with radical species. The most susceptible to radical attack is allyl position to produce allyl oxygenates [28, 29]. In the absence of an allylic carbon atom,

one of the double bonds of BD is involved in the oxidation. Neat or dissolved in a nonpolar solvent, BD interacts with oxygen at moderate temperature according to radical chain mechanism to form oligomeric butadiene polyperoxide, $C_4H_6O_2$ [30]. The reaction is accelerated by increasing the temperature or adding free radical initiators and inhibited by adding acids. From the NMR analysis, molecular structure of the polyperoxide formed at 50°C in the presence of 37 Torr of oxygen was composed of equal amounts of 1,4- and 1,2-butadiene units separated by peroxide units [31]. The structure of the polyperoxide (the ratio of 1,4- to 1,2-butadiene units) does not depend on the reaction temperature, whereas the content of bound oxygen in the polyperoxide varies with oxygen pressure. The ratio of peroxide to hydrocarbon units is below 1 at a low oxygen partial pressure. Thermal decomposition as well as hydrogenation of polyperoxide leads to the formation of 3-butene-1,2-diol and 2-butene-1,4-diol or corresponding saturated diols, preferably 1,4-derivatives (**Scheme 1**) [30, 32–35].

Decomposition of the polyperoxide forms not only 3-butene-1,2-diol and 2-butene-1,4-diol but also side products such as formaldehyde, acrolein (from 1,2-units), and resinous insoluble material (presumably resulting from the reaction of the 1,4-units with aldehydes) [31]. Therefore, the preferred formation of 1,4-oxygenates from the thermal decomposition of polyperoxide is not a strong support of predominance of 1,4-units in the polyperoxide structure.

The rate of decomposition of the polyperoxide increases with increasing temperature, addition of bases (amines) [36], or metal ions as radical initiators. Butadienyl polyperoxide is readily decomposed in the presence of metal ions of variable oxidation state. Therefore, the transition metal compounds participate as catalysts in the radical chain oxidation of BD with oxygen. The oxidation products are similar to those obtained under the decomposition of the polyperoxide. 3-Butene-1,2-diol and 2-butene-1,4-diol can be obtained with the selectivity sufficiently high for the chain radical process, especially if one considers the low stability of these products with respect to secondary oxidation. Thus, a mixture of 3-butene-1,2-diol and 2-butene-1,4-diol has been prepared by oxidative dihydroxylation of BD with oxygen in acetic acid solution of $Pd(OAc)_2$. From a practical point of view, the most valuable 2-butene-1,4-diol has been formed with selectivity of 25% [37].

We tested Pd and Au catalysts in the radical chain oxidation of BD in polar media. Both soluble palladium acetate and insoluble supported metals caused the formation of the products,
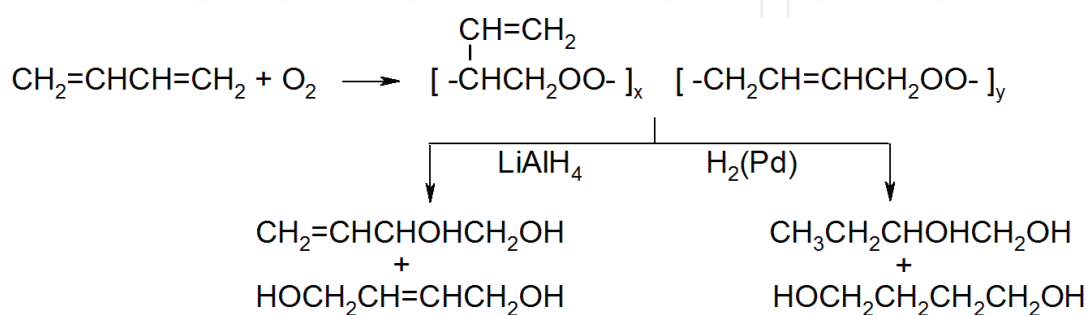

Scheme 1. Formation and reductive decomposition of the polyperoxide [30].

the most part of which appeared from decomposition of the intermediate butadienyl polyperoxide [32] (**Scheme 2**). The main products are 3-butene-1,2-diol and 2-butene-1,4-diol. 4-Hydroxybut-2-enal can be formed in the decomposition of polyperoxide and in oxidation of 2-butene-1,4-diol. Oxidative dehydration of 2-butene-1,4-diol produces furan. Both butanediols can be esterified to form corresponding diacetates, but only 2-butene-1,4-diol diacetate has been found in the reaction solution. Acrolein occurs from breaking C—C bond under decomposition of polyperoxide or, possibly, from secondary conversion of 3-butene-1,2-diol. C8 oxygenates originate from polyperoxide fragments containing less than 1:1 ratio of butadiene to oxygen units. In addition, there are impurities of C6 cyclic oxygenates occurring from cyclodimerization of BD (Diels-Alder reaction) followed by oxidation of 4-vinylcyclohexene. The amount of the products is given in **Table 1**.

In addition to the stable compounds, a large amount of peroxide compounds have been iodometrically detected in acetic acid and acetic acid/dioxane solutions (**Table 1**). Peroxide oxygen refers to butadienyl polyperoxide since the addition of Ph$_3$P reducer to the solution results in disappearance of the peroxide and formation of 2-butene-1,4-diol together with minor amounts of furan and 3-butene-1,2-diol. The polyperoxide exhibited sufficient stability in several oxidation tests but almost completely decomposed with a large amount of Pd/C catalysts. As a result, enhanced formation of 2-butene-1,4-diol and 4-hydroxybut-2-enal is achieved in this case (fifth row in **Table 1**).

The addition of Te to Pd/C catalyst lowers the production of all oxidation products. Bottom row in **Table 1** shows the inhibitory effect of Te on the chain radical oxidation reaction. At the same time, more noticeable becomes formation of the oxidation products non typical for the chain radical mechanism. These are crotonaldehyde and methyl vinyl ketone, which show the possibility of a nonradical heterolytic mechanism of oxidation on the PdTe/C catalyst.
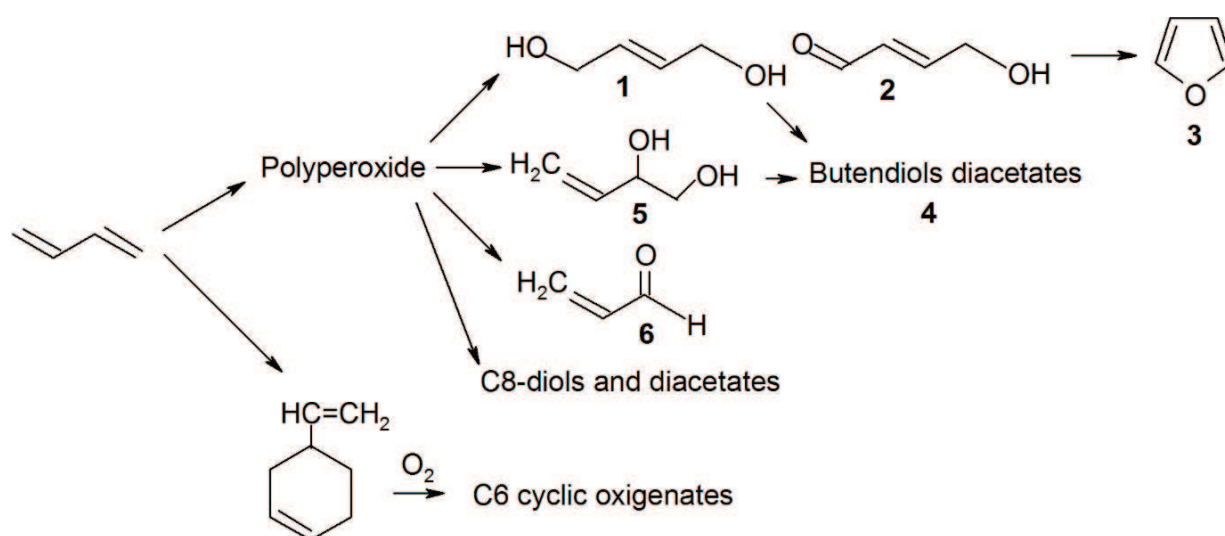
Scheme 2. GC-detected products of the radical chain oxidation of BD.

Catalyst (mg)	BD (mmol)	Solvent	T (°C)	Time (h)	Products (mmol)						
					1 + 2	3	4	5	6	Others[1]	Peroxide[2]
Pd(OAc)$_2$ 2.5	70	HOAc/H$_2$O 88/12	70	2	2.5	0.6	0.1	<0.1	1.3	0.2	8.5
Pd(OAc)$_2$ 2.5	70	HOAc/dioxane/H$_2$O 19/75/6	80	2	4.6	3.1	<0.1	0.4	7.8	0.1	9.4
0.5%Au/SiO$_2$ 120	70	HOAc/dioxane/H$_2$O 44/50/6	80	4	4.7	3.2	<0.1	0.1	8.9	2.0	9.1
0.5%Au/SiO$_2$ 120	70	HOAc/dioxane/H$_2$O 44/50/6	80	6	8.5	5.3	0.4	1.3	10.7	7.1	7.0
5%Pd/C 3000	100	DMA/H$_2$O 94/6	90	3	10.3	0.4	0	4.8	2.2	0.7[3]	0.8
5%Pd0.5%Te/C 3000	100	DMA/H$_2$O 94/6	90	3	0.5	0.1	0	0.1	0.1	0.8[4]	0.2

[1]C8 diols and acetates, and C6 cyclic oxygenates.

[2]Iodometric titration.

[3]0.1mmol crotonaldehyde and methyl vinyl ketone.

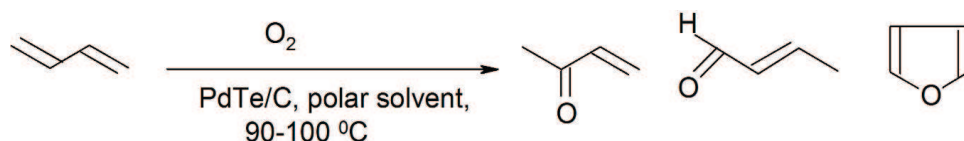[4]0.4 mmol crotonaldehyde and methyl vinyl ketone.

Table 1. GC detected products from oxidation of BD (70 mmol) by oxygen (O$_2$/N$_2$ = 10/90, 60 atm) in a solvent (100mL).

3. Oxidation of BD by a heterolytic mechanism involving palladium catalysts

Palladium catalysts are widely used in the liquid-phase heterolytic oxidation of olefins [38]. The most significant mechanisms for practice are acetoxylation of ethylene to vinyl acetate and Wacker oxidation of olefins converting ethylene to acetaldehyde and but-1-ene to methyl ethyl ketone. A mechanism of olefin oxygenation under the action of Pd(II) complexes established by Moiseev et al. and Henry et al. [39, 40] is now described in numerous publications (e.g., chapter by Reinhard Jira in book [24]). The mechanism includes the formation of Pd(II) complex with olefin and inner sphere transformations resulting in the reduction of Pd^{2+} to form carbonyl compound and Pd^0 black. Assisted by Cu(II) chloride or other intermediate oxidant, reoxidation of Pd^0 with oxygen closes the catalytic cycle, allowing the use of oxygen as a stoichiometric oxidant.

Analogous to light olefins, BD reacts under homogeneous conditions in an aqueous solution of $PdCl_2$ catalyst and $CuCl_2$ oxidant. The oxygenation is directed to one of the double bonds with the retention of the second double bond to produce crotonaldehyde [41, 42]. The oxidation conditions are identical to those applied for oxidation of ethylene to acetaldehyde and 1-butene to methyl ethyl ketone (Wacker-type oxidation), but the kinetics is different [43], in particular the order of reaction with respect to Cl^- and H^+ ions. Unlike the oxidation of ethylene and other olefins, the oxidation of BD is zero-order with respect to the hydrocarbon. The kinetic parameters of BD oxidation are determined by high reactivity of the conjugated π-bonds, in particular by a strong BD to Pd^{2+} bonding in the intermediate complex. Unlike propylene, the oxygenation of the BD double bond is directed at the terminal rather than inner carbon atom to form crotonaldehyde. This is probably due to the stabilizing effect of the second double bond. In the presence of Pd^{2+} ions and another strong oxidizing agents of P-Mo-V heteropolyacids, BD is converted to furan in the similar conditions [44]. It seems like crotonaldehyde was initially formed and then converted under oxidizing conditions to furan, as in a similar homogeneous system [45]. Oxygen is a final stoichiometric oxidant, but the strong intermediate oxidant (Cu^{2+} or heteropolyacid) is necessary for easy regeneration of the ionic palladium in the oxidation of BD and olefins, as well.

We have observed catalysis by $PdCl_2$ when the radical chain oxidation of BD to diols, furan, and acrolein proceeds along with nonradical oxidation to form mainly crotonaldehyde together with small amounts of methyl vinyl ketone and furan (**Scheme 3**) (first row in **Table 2**). It is interesting that the system does not contain an oxidizing agent, except oxygen. There is no need of any intermediate oxidant since reoxidation of Pd^0 to Pd^{2+} is provided by peroxide intermediates generated

Scheme 3. Nonradical reaction of BD on PdTe/C catalyst in polar solvents.

Catalyst (mg)	BD (mmol)	Time (h)	Products (mmol)						
			Furan	Acrolein	Methyl vinyl ketone	Croton-aldehyde	3-Butene-1,2-diol	2-Butene-1,4-diol, 4-hydroxybut-2-enal	Others
PdCl$_2$ 120	43	3	0.4	1.1	0.3	1.6	3.2	3.9	0.2
PdCl$_2$ 120, H$_6$TeO$_6$ 800	43	3	0.2	0.5	<0.1	0.4	<0.1	0.5	0.1
5% Pd 2% Te/C 2000	22	6	0.1	<0.1	0.8	0.6	—	0.2	0.3

Table 2. GC detected products from oxidation of BD by oxygen (O$_2$/N$_2$ = 10/90, 60 atm) in DMA (30 mL, 3% H$_2$O), T 90°C.

in a radical process. Telluric acid inhibits the radical process but does not operate as an oxidant for Pd^0 to maintain the nonradical oxidation by Pd^{2+}. As a result, the PdCl$_2$ with H$_6$TeO$_6$ solution is inactive in oxidation of BD (second row in **Table 2**). By contrast, the heterogeneous 5%Pd2%Te/C catalyst is able to provide nonradical oxidation, with the radical chain oxidation being inhibited by Te. As a result of inhibiting action of Te, the large amount of the catalyst and low concentration of BD appear unfavorable for the development of the chain process. The oxidation on the 5%Pd2%Te/C catalyst in aqueous dimethylacetamide (DMA) has been observed to give crotonaldehyde and methyl vinyl ketone as main products (third row in **Table 2**). Interestingly, crotonaldehyde is a predominant product of heterolytic oxidation with PdCl$_2$, but nearly equal amounts of crotonaldehyde and methyl vinyl ketone are produced on the 5%Pd2%Te/C catalyst in the same conditions.

Besides DMA, other polar solvents can be used in this oxidation. The presence of proton additive is required in the solvent (**Table 3**). No reaction has been observed in anhydrous acetonitrile.

Solvent (g)	Catalyst (g)	H$_2$O (%)	H$_2$SO$_4$ (mmol/L)	Time (h)	Products (mmol)		
					Furan	Methyl vinyl ketone	Croton aldehyde[1]
DMA	1	17	—	4	0.2	1.4	1.2
Dioxane	0.5	—	5	6	0.5	1.0	0.7
Acetonitrile	1	17	—	5	<0.1	1.0	0.8
Acetonitrile	1	17	8	5	0.3	1.7	0.9
Acetonitrile	0.5	—	2	4	0.8	2.0	1.2
Acetonitrile	0.5	—	—	3	0	0	0

[1]Crotonaldehyde can be partly subjected to further oxidation to crotonic acid.

Table 3. GC detected products from oxidation of BD (4.5 mmol) by oxygen (O$_2$/N$_2$ = 10/90, 40 atm) on 5% Pd 2%Te/C catalyst in a solvent (35 mL), T 100°C.
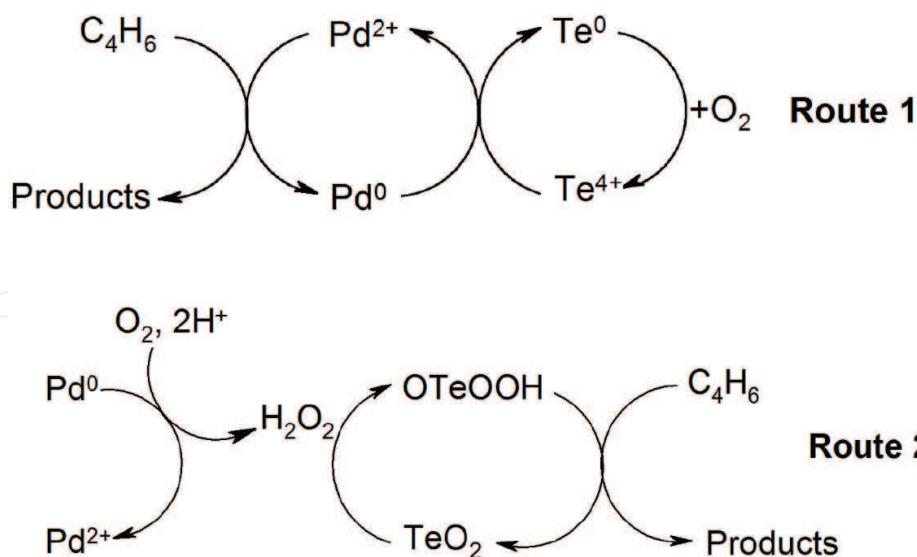
Scheme 4. Tentative routes for nonradical oxidation of BD on PdTe/C catalyst.

According to XPS analysis, the 5%Pd2%Te/C catalyst contains both reduced Pd^0 and ionic Pd^{2+}, and two oxidation states of tellurium Te^0 and Te^{4+} [46]. The Pd^{2+} to Pd^0 ratio on the catalyst surface becomes larger with an increase in tellurium content that indicates an oxidizing influence of TeO_2. It can be expected that the oxidation state of the surface is enhanced under the reaction conditions. Nevertheless, dissolution of Pd and Te during reaction does not exceed 1% of the content of both components in the solid catalyst, the solution exhibiting no catalytic activity. Therefore, activity of the catalyst refers to the active components on the surface of carrier and is associated with their reversible redox transformations. Based on the known mechanisms of homogeneous oxidation of olefin, one can propose two possibilities for oxidation of BD by oxygen on the PdTe species, both assuming a nonradical heterolytic interaction. Perhaps the mechanism is in general similar to that postulated for the oxidation of BD and olefins in the presence of Pd^{2+} complexes, oxygen, and intermediate oxidant (**Scheme 4**, Route 1). It involves surface Pd^{2+} ions and TeO_2 oxidant providing regeneration of Pd^{2+}.

However, there is a difference in products composition. Crotonaldehyde and furan are produced in above-mentioned oxidations of BD with homogeneous Pd^{2+} catalysts [41, 42], whereas methyl vinyl ketone is the second product formed in our oxidation on the PdTe catalyst. To explain this difference, one can consider an oxidation of BD by hydrogen peroxide as an alternative or parallel reaction (Route 2 in **Scheme 4**). Hydrogen peroxide is generated from oxygen on Pd^0 species. The high reactivity of olefins with respect to peroxide compounds is known [47]. It is known that hydrogen peroxide does not accumulate during reaction. But it is found in trace amounts in the reaction solution and can form a reactive peroxide compound of Te^{4+} on the surface of the catalyst. In both mechanisms proposed, Te serves as a carrier of molecular or peroxide oxygen, and the surface of Pd^{2+}/Pd^0 activates reagents due to the adsorption of O_2 and BD. Thus, the PdTe/C catalyst opens the possibility of oxidation of BD by a nonradical heterolytic mechanism due to the combined effect of the two active components.
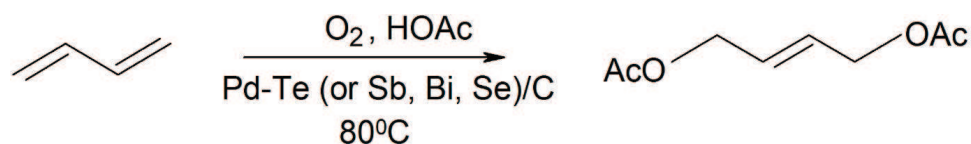
4. Heterolytic mechanism of 1,4-oxidative addition to BD

Wacker-type oxidation of olefins and analogous Pd-catalyzed nonradical oxidation of BD produce usually carbonyl compounds, but special additives are required for obtaining dioxygenates. Nevertheless, the oxidative 1,2-addition to olefins is known to occur under the action of Pd^{2+} complex and oxoanion strong oxidants, such as periodate [48] or nitrate anions, in acetic acid solution to form glycol derivatives [49–51]. Mechanism of the oxidation is based on a nonradical inner sphere interaction of olefin with oxidant in Pd^{2+} complex. Similar interaction is probably realized in oxidation of BD in the presence of palladium as the catalyst of nonradical heterolytic olefin oxidation and Sb, Bi, Te, or Se promoters. Heterogeneous catalysts containing these active components have shown unique catalytic properties in oxidation of BD selectively to 2-butene-1,4-diol diacetate (**Scheme 5**) [52, 53].

XPS analysis of the Pd and PdTe catalysts indicates that Te-oxide is able to increase positive charge on Pd surface [46], thus being an oxidation promoter for palladium. The ionic state of surface palladium is responsible for heterolytic oxidation. Acetic acid is used as a solvent for this reaction. The mechanism of formation of 2-butene-1,4-diol diacetate is proposed by Takehira et al. for PdTe catalyst (**Scheme 6**) [54], and fundamentally identical one is proposed for the RhTe catalyst [55]. The details in intermediate structures explain the preferential formation of trans-2-butene-1,4-diol in the case of Pd-containing catalyst and cis-isomer in the case of Rh.

Exceptionally high selectivity of BD to 2-butene-1,4-diol diacetate conversion is explained by a concert interaction of BD with surface Pd and with acetate anions. Adsorbed on Pd, BD forms π-allyl-type intermediate that undergoes acetoxylation on the terminal carbon atom. Resulting monoacetoxyl reacts with the second acetate to give 2-butene-1,4-diol diacetates and 3-butene-1,2-diol diacetate in amounts proportional to the reactivity of carbon atoms 1 and 2 (**Scheme 6**). In fact, only 2-butene-1,4-diol diacetates are produced. Analogous mechanisms are realized in homogeneous oxidation of various dienes in the presence of Pd complexes and p-benzoquinone oxidizing agent, instead of Te. Oxidation of diene alcohols [56] and substituted conjugated diolefins [57] proceed effectively, but BD reacts with low yield and selectivity.

As noted earlier, Te-oxide is able to inhibit radical chain oxidation of BD, the selectivity of which is lower than the selectivity of the heterolytic process. Besides, Te operates as an inhibitor of radical polymerization of BD and oxidation products, thus preventing the formation of side high-boiling products. Acetic acid (possibly, other carboxylic acids) also contributes to the achievement of high selectivity in BD oxidation. Being not only solvent but also reagent (OAc⁻ anions), it is involved in an intermediate interaction with olefin to form the surface Pd


Scheme 5. Oxidative 1,4-addition to BD.
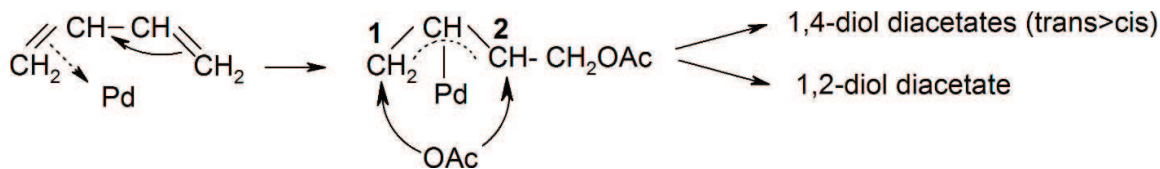
Scheme 6. Mechanism of 1,4-oxidative addition to BD [54].

intermediate, and finally stabilizes the product as ester, preventing its secondary transformations. Based on the unique properties of the PdTe/C-HOAc catalytic systems, the industrial process for the production of 2-butene-1,4-diol diacetate has been developed by Mitsubishi Chemical. BD is oxidized to 2-butene-1,4-diol diacetate with selectivity of 98%. Possible further improvements of the process can be connected with the application of other platinum metals (Pt, Rh, and Ir) combined with various promotors.

If acetic acid is replaced by alcohol, 1,4-dialkoxylation of conjugated dienes was developed in Pd(OAc)$_2$ solution. p-Benzoquinone was used as the oxidant and methanesulfonic acid as a promoter [58]. The oxidation is suggested to follow mechanism including the formation of the (π-allyl)palladium(benzoquinone) intermediate (**Scheme 7**).

In other case, dialkoxybutenes are prepared by reacting BD in the presence of carbon-supported Group VIII noble metals with Te or Se additives. Similar to diacetates, the formation of ethers in alcohol solvent increased the stability of dioxygenated products against secondary oxidation. However, the formation of 3,4-dimethoxy-1-butene and 1,4-dimethoxy-2-butene in comparable amounts is in contrast with **Scheme 6** and indicates a radical mechanism of BD oxidation, when 2-butene-1,4-diol and 3-butene-1,2-diol are formed as primary products and then converted to ethers in the alcohol medium [59].

We have prepared PdTe/C catalysts by hydrolytic deposition of palladium under the reductive conditions, followed by treatment with H$_6$TeO$_6$. The procedure is similar to one often described for the synthesis of PdTe catalysts. No evidences for the occurrence of binary Pd–Te phases have been provided by XRD, and XPS analysis evidences Pd^0, PdO, Te^0, and TeO$_2$ [60]. The absence of the Pd-Te phase and the partially oxidized state of the active metals have also been reported by Takehira [54] for Pd-Te-C catalysts. As assumed, Te is located in the
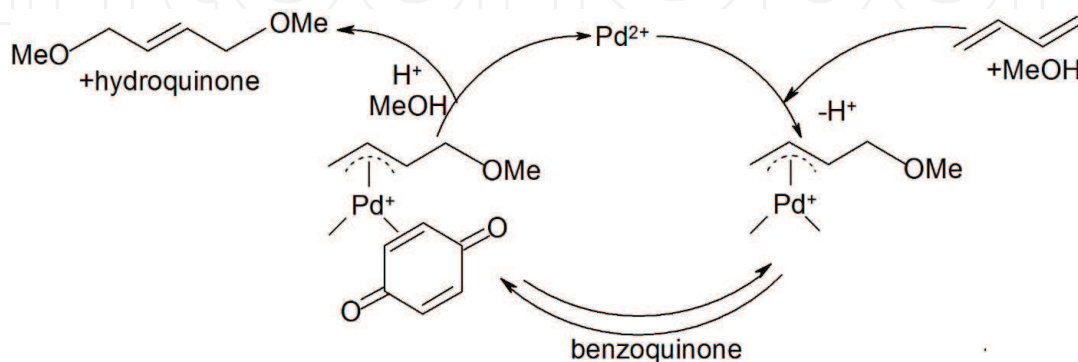

Scheme 7. 1,4-Dialkoxylation of conjugated dienes [38].

outer layer of supported particles. The characteristics of the PdTe/C catalysts were detailed by HAADF-STEM analysis of the surface and line EDX analysis of composition of the supported particles [60]. The results represent an unusual distribution of components on the surface, where Te does not form an individual crystalline phase but is located on the surface of Pd particles in a highly dispersed state. These data explain properties of the PdTe catalysts. In particular, the ability of Te to inhibit the radical reactions is in part due to the coverage of the palladium surface, which normally tends to initiate radical chains.

The primary products in BD oxidation on PdTe/C catalyst in methanol and further conversion of them under the oxidation conditions are shown in **Scheme 8**, and the amounts are given in **Table 4**.

As well as in DMA, nonradical heterolytic oxidation of BD in alcohol medium leads to the formation of crotonaldehyde (1) and methyl vinyl ketone (4). Besides, 1,4-dimethoxy-2-butene (6) is produced analogously to 2-butene-1,4-diol diacetate in acetic acid. The primary products undergo further transformations depending on the reaction conditions. Sulfuric acid promotes oxidation, especially toward 1,4-oxidative addition (comparison of first and second rows in **Table 4**). An increase in Te content lowers the reaction rate but increases proportion of products formed through 1,4-addition (third row in **Table 4**). Composition of oxidation products obtained in the presence of the Pd0.5Te/C catalyst and H_2SO_4 is differed from the one in the radical chain oxidation (compare data given in **Tables 1** and **4**). 3,4-Dimethoxy-1-butene and acrolein that indicate nonradical oxidation do not appear. Peroxide compounds were also not detected in the solution after the reaction. The chain process does not develop due to the presence of Te and low concentration of BD used to eliminate the formation of the radical chains. Moreover, the radical products do not appear even at increased concentration of BD (fourth row in **Table 4**). Similarly to acetic acid, methyl alcohol in a mixture with sulfuric acid converts the oxidation products to methyl esters. However, oxidation in the alcohol medium is slower than in acetic acid, and further improvement of the selectivity of the formation of 1,4-addition products is required.
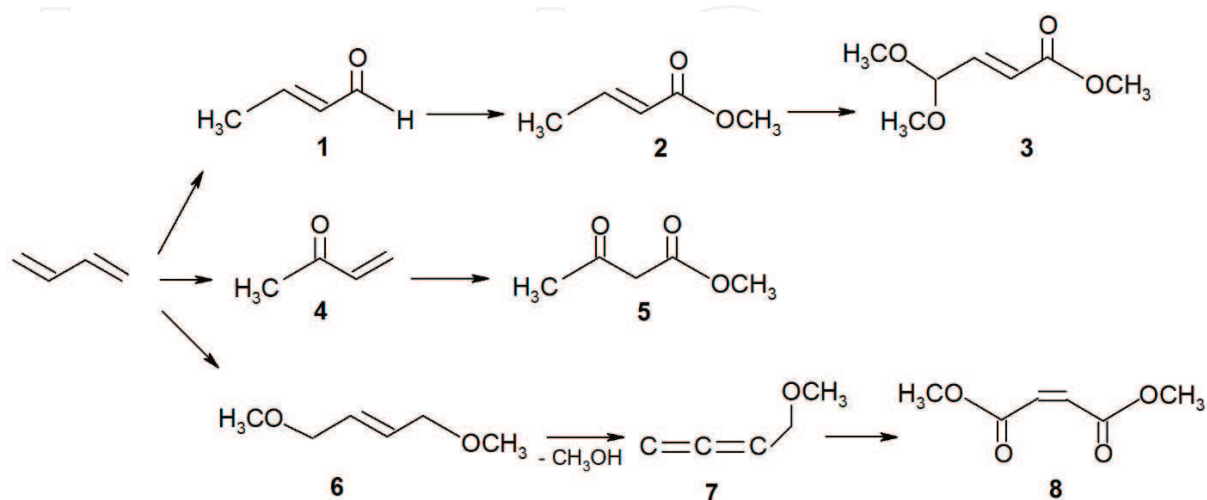
Scheme 8. Products of BD oxidation on PdTe/C catalyst in methyl alcohol.

| Catalyst, conditions	Products (mmol)							
	1	2	3	4	5	6	7	8
5%Pd0.5%Te/C, 10 mmol BD, 100°C, 3 h	0.54	1.16	0.35	1.58	0.17	1.48	0	0.73
5%Pd0.5%Te/C, H$_2$SO$_4$, 10 mmol BD, 100°C, 3 h	0.45	2.02	0.08	0.12	1.42	2.30	0	1.81
5%Pd2.7Te/C, H$_2$SO$_4$, 10 mmol BD, 120°C, 2 h	0.24	0.06	0	0.06	0.66	2.80	2.0	0
5%Pd2.7Te/C, H$_2$SO$_4$, 40 mmol BD, 120°C, 2 h	0.23	0.06	0	0.07	0.78	6.70	3.90	0

Table 4. Products of BD oxidation in solvent CH$_3$OH (10% H$_2$O) (30 mL), H$_2$SO$_4$ (0.1 mmol where indicated).

5. Synthesis of 3,4-epoxy-1-butene in liquid phase

Two competitive methods for direct epoxidation of olefins are gas-phase oxidation with oxygen over silver catalyst and liquid-phase reactions with organic hydroperoxides or hydrogen peroxide in the presence of soluble or supported W, Mo, Ti complexes. The gas-phase epoxidation is typical for obtaining light epoxides, whereas epoxidation with peroxide compounds in liquid is applicable for a wide range of substrates containing double bonds. Both type reactions are based on interaction of olefin with electrophilic oxygen species. Under liquid-phase epoxidation, catalytically active metal complexes react with peroxides to attach the reactive oxygen as ligand which attack the double bond of olefin. Hydrogen peroxide is effective oxygen donor and has an advantage of low-temperature reaction giving environmentally benign water as a by-product [61, 62].

The liquid-phase epoxidation of BD with H$_2$O$_2$ is known to occur over titanium silicates in CH$_3$OH [63] and in CH$_3$CN solution of heteropoly compounds [64, 65]. The data for these reactions are given in **Table 5**.

Both catalysts are activators of hydrogen peroxide, capable of forming peroxide complexes. Thoroughly investigated for various olefins, the mechanism of epoxidation is realized for the conversion of BD to 3,4-epoxy-1-butene. Coordinated on metal ion, the electrophilic oxygen interacts with one of the equivalent double bonds of BD leaving intact the second C=C bond. Oxygen transfer from peroxide ligand to double bond of olefin has been proved using isotopic reagents [64]. The addition of oxygen to the second bond of BD is more difficult; therefore, the formation of a diepoxide is not detected in reactions with hydrogen peroxide.
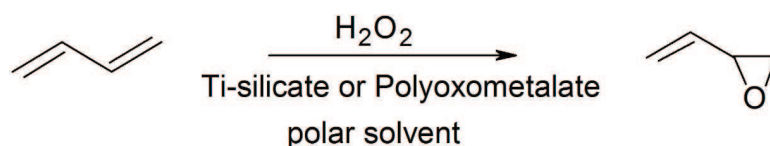
Lacunary polyoxotungstates are effective catalysts for epoxidation of olefins with H$_2$O$_2$ [66]. Besides olefins, [HPW$_{11}$O$_{39}$]$^{6-}$ and [γ-SiW$_{10}$O$_{34}$(H$_2$O)$_2$]$^{4-}$ anions catalyze epoxidation of BD with

| Catalyst[1]	H_2O_2[1] (mmol)	BD (bar)	Time (h)	Epoxide (mmol)	Sel.BD (%)	H_2O_2 efficiency (%)	Reference
TS-1(6 mg)[2]	0.5	1.5	1	0.25	n.d.	52	[63]
TBA4[γ-SiW$_{10}$O$_{34}$(H$_2$O)$_2$] (3 μmol)[3]	0.3	2.5	9	0.30	99	99	[64]
TBA-PW$_{11}$(10 μmol)[4]	0.9	1	5.5	0.51	88	88	[65]
EMIm-PW$_{11}$(10 μmol)[4]	0.9	1	5	0.65	91	90	[65]
EMIm-PW$_{11}$(2.3 μmol)[5]	1.0	1	5	0.20	97	100	[65]

[1]Catalyst, H_2O_2 and epoxide produced were normalized to 2 mL of the reaction mixture.
[2]CH$_3$OH solvent, room temperature.
[3]CH$_3$CN solvent, room temperature.
[4]CH$_3$CN solvent, 60 °C.
[5]CH$_3$CN solvent, 50 °C.

Table 5. Epoxidation of BD with H_2O_2 in solvents.

diluted aqueous H_2O_2 in acetonitrile solution. Epoxidation of BD has been shown to proceed with high selectivity for 3,4-epoxy-1-butene. Appearance of small admixtures of furan, 3-butene-1,2-diol, and 2-butene-1,4-oxygenates is associated with isomerization and hydrolysis of 3,4-epoxy-1-butene. The unproductive radical decomposition of H_2O_2 is minimal or absent when the reaction is carried out at a low temperature and at a low concentration of hydrogen peroxide. This is favorable for maintaining high selectivity for 3,4-epoxy-1-butene, because the secondary oxidation of 3,4-epoxy-1-butene by radical intermediates is prevented. As a result, only negligible amount of acrolein appears in the product. Moreover, small additives of EMImBr have been found to inhibit radical decomposition of H_2O_2, thus increasing the selectivity of BD to 3,4-epoxy-1-butene conversion and efficiency of H_2O_2 consumption. As a result, the efficiency of H_2O_2 consumption for producing 3,4-epoxy-1-butene is extremely high, it approaches to 100% under favorable conditions. Both Si- and P-centered heteropolytungstates exhibit equally effective catalysis.

Under reaction conditions, the catalytically active anions are generated from starting lacunary polyoxotungstate anion. It has been shown by NMR that [HPW$_{11}$O$_{39}$]$^{6-}$ anion is a precursor of tungsten-depleted anions [PW$_4$] and [PW$_2$], which operate as the most effective activators of hydrogen peroxide and are responsible for epoxidation (**Scheme 9**) [65]. This is confirmed by the high reactivity of a specially synthesized anion {PO$_4$[WO(O$_2$)$_2$]$_4$}$^{3-}$ in epoxidation of olefins [67].

Despite the limited use of 3,4-epoxy-1-butene itself, it is nevertheless a raw material for the synthesis of various C4-oxygenates such as 1,4-butanediol [68], 3-butene-1,2-diol and 2-butene-1,4-diol [69–71], and 2,5-dihydrofuran [72]. Therefore, low-temperature and selective epoxidation of BD can be considered as a principal stage of alternative synthesis of demanded and valuable chemicals.
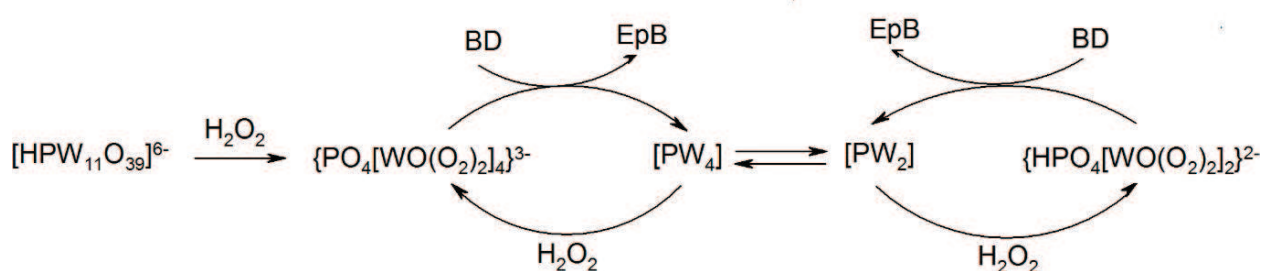
Scheme 9. Transformations of heteropolytungstates in oxidation of BD to 3,4-epoxy-1-butene (EpB) [65].

6. Conclusion

Close nature of BD and light olefins is manifested in similar reaction properties, so that liquid-phase oxidation reactions of BD and olefins have similar mechanisms in many features. The oxidation of olefins and BD in liquid medium enables realization of several routes and obtaining a wide range of products, which are more diverse if compared with gas-phase oxidation. We have considered here the radical chain oxidative conversion of BD realized through the stable polyperoxide intermediate, the formation of which is, to a certain extent, inherent to many olefins. Palladium is able to catalyze homolytic (radical) and heterolytic (Wacker-type) oxidation of olefins. Very close to olefins, the properties of BD are manifested in reactions assisted by homogeneous and more often heterogeneous Pd-containing catalysts. (Note that the tendency to heterogenization of soluble catalysts is observed in liquid-phase reactions.) We observe an interesting phenomenon when the mechanism and products of the Pd-catalyzed oxidation are controlled by promoters. In dependence on other components, the catalytic action of Pd is switched from radical oxidation to nonradical oxygenation directed to one carbon atom or 1,4-position of BD when Pd is promoted with Te or related metals. The effect of Te as an oxidation promoter of palladium and a radical inhibitor allows PdTe catalysts to show substantial efficiency in the well-known industrial synthesis of 1,4-diacetoxybutene in acetic acid and also in other oxidations of BD such as formation of crotonaldehyde and methyl ethyl ketone in aqueous media. The reaction medium and concentration of reagents are also important factors to vary the mechanism of oxidation. Low concentration of BD in the reaction mixture reduces the development of the chain process and makes it possible to realize the oxidation by the heterolytic mechanism. Polar organics are conventional solvents for various oxidations, but acetic acid and methanol exhibit special properties creating conditions for preferable formation of esters of 1,4-butanediol. The identity in mechanisms is also observed in epoxidation of olefins and BD with hydrogen peroxide, where the same catalytically active Ti silicates and polyoxometalates are successfully used to attain highly selective conversion of hydrocarbon and H_2O_2. All this shows that liquid-phase oxidation have a great potential in converting the BD into valuable oxygenates. To develop this area, extremely productive can be appeal to analogy in chemistry of BD and olefins. A large body of information relating to the oxidation of olefins can be productively applied to understand the mechanisms in oxidation of BD and to develop a strategy for synthesis of purposed oxidation products.

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