Oxygenation of Butadiene Catalyzed by Low-Valent Group 8 Metal Complexes

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Butadiene complexes of Ir(I) and Rh(I) induce efficient oxygenation of butadiene at 55 °C and a pressure of 1–15 atm. The products are oligomeric peroxides resulting from free radical chain addition of oxygen in the 1,2 and 1,4 positions. It is postulated that molecular oxygen reacts with diene bonded to the low valent group 8 metal, forming a metal-bonded alkylperoxy radical which initiates the radical chain. Coordinated oxygen species are not involved.

Low-valent transition-metal complexes are known to form peroxo complexes when exposed to oxygen. At present, only one such complex is known which contains both dioxygen and ethylene in the coordination sphere of the metal.[1] Recently, the oxygenation of coordinated long-chain olefins was postulated[2] in the oxidation of terminal olefins to 2-alkanones promoted by $RhCl(PPh_3)_3$. Surprisingly, no effort has been made to study oxygenation of conjugated dienes in the presence of low-valent metal complexes. The complexes containing only dienes in the coordination sphere would be of special interest since cooxidation[2] of other ligands could be avoided. If a diene and dioxygen could be assembled in the coordination sphere, 1,4 addition of oxygen to the diene might be accomplished. For these reasons our effort has been devoted to a study of oxygenation of butadiene in the presence of iridium(I)– and rhodium(I)–butadiene complexes.

Results

The oxygenation of butadiene promoted by butadiene complexes of low-valent metals such as $IrCl(butadiene)_2$ and $RhCl(butadiene)L$, where L = PPh_3 and $AsPh_3$, leads to oligomeric peroxides. The structure of the peroxides corresponds to 1,4- and 1,2-dioxygen adducts of butadiene. Molecular weight measurements indicate an average value of 723. Titration of active oxygen gives a peroxidic oxygen value of 1.17/mol of oligomer suggesting some chains are terminated by hydroperoxy functions. The products obtained via Ir(I) or Rh(I) catalysis exhibit the same characteristics as those obtained by AIBN initiation and match those described by Mayo et al.[3] for the 1,2- and 1,4-mixed oxygenation product containing some butadiene oligomeric units. A small amount of aldehyde is present as evidenced by ^{1}H-NMR and IR analysis. The structure of the product is further confirmed by lithium aluminum hydride reduction; subsequent acetylation of the crude product yields diacetates of the two isomeric butenediols.

In our studies, summarized in Table I, we have found that the most effective catalyst for the oxygenation is $Ir(butadiene)_2Cl$. Although it has been claimed that initiators are not necessary[4] for oxygenation of butadiene, we have found that under the mild reaction conditions used, oxygenation of butadiene is extremely slow, giving only a trace of the product. Temperatures in excess of 80 °C are necessary for appreciable oxidation in the absence of catalyst. Even using AIBN as initiator, we find that the reaction is slower by a factor of 100 than the Ir complex catalyzed reaction. At the higher temperatures necessary for AIBN initiated oxygenation, undesirable and extensive decomposition of peroxidic units results. Using known free-radical inhibitors such as 2,6-di-*tert*-butyl-*p*-cresol the oxidation reaction catalyzed by Ir(butadiene)$_2$Cl is quenched.

There are subtle ligand effects in the oxygenation reaction as evidenced by the difference in the reactivity of $RhCl(C_4H_6)PPh_3$ and $RhCl(C_4H_6)AsPh_3$. The phosphine complex is slower than $Ir(butadiene)_2Cl$ in catalyzing the reaction, but it is about five times faster than the arsine complex. These two complexes can be readily generated from butadiene and $RhClL_3$ which, therefore, should be effective catalysts as well. The corresponding cobalt complex, $CoCl(PPh_3)_3$, is ineffective. Rapid oxidation of Co(I) to Co(II) was observed.

Most solvents do not seem to influence the character of butadiene oxygenation. Thus, in acetic acid, acetonitrile, and benzene, the same ratio of the oligomeric peroxide isomers is obtained. However, the reaction is very slow in methanol.

Discussion

Oxygenation of olefins promoted by transition metal complexes follows two pathways. Olefins which readily form hydroperoxides usually undergo autocatalytic oxidation characterized by the Haber–Weiss mechanism.[5] Allylic oxidation is usually the end result. Another type of olefin oxygenation promoted by metal complexes is exemplified by the oxidation of terminal olefins to the corresponding methyl ketones.[2] The complex is postulated to serve as a center for the coordination of both reacting species allowing an orderly transfer of "activated oxygen" to the ligated substrate[6] without intervention of free radicals in the process. However, the initiation step of the observed butadiene oxygenation cannot be adequately described by either mechanism. Control experiments revealed that oligomerization of butadiene in the presence of the Rh and Ir complexes is much slower than the corresponding oxygenation. It is, therefore, reasonable to assume that the oxygenation is initiated by the interaction of molecular oxygen with either the metal of the complex forming superoxo radical I or the complexed butadiene forming a metal-bonded alkylperoxy radical II.
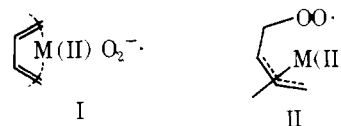
Reaction of butadiene with either I or II would then start the radical chain.[8] Rh(I) and Ir(I) complexes, which are the most active catalysts, are known to form peroxo species[7] by a formally two-electron transfer rather than superoxo species by a one-electron transfer. In addition, Co(II) complexes, which are known to form superoxo complexes[7] on contact with molecular oxygen, are inactive as catalysts for oxygenation of butadiene. We, therefore, favor chain initiation by species II.

With high butadiene concentration, such as the conditions used, the formation of the oligomeric butadiene units reflects a competition between butadiene and oxygen for the radical center. One can also appreciate the formation of small amounts of $C_4H_6O_2$, $C_8H_{12}O_2$, and $C_8H_{12}O_4$, products from short chain terminations. The small amount of terminating

Table I. Butadiene Oxygenation to Oligomeric Peroxides

catalyst[a] (mmol)	registry no.	reaction time, h	conversion,[b] %	solvent
Ir(C$_4$H$_6$)$_2$Cl (0.30)	39732-20-2	6	66	C$_6$H$_6$
Ir(C$_4$H$_6$)$_2$Cl (0.30)		18	50	CH$_3$OH
Ir(C$_4$H$_6$)$_2$Cl (0.30)		4	60	CH$_3$CN
Ir(C$_4$H$_6$)$_2$Cl (0.30)		4	63	CH$_3$CO$_2$H
Ir(C$_4$H$_6$)$_2$Cl (0.39)		48	38[c]	C$_6$H$_6$
none		45	4	C$_6$H$_6$
AIBN (3.3)		63	66	C$_6$H$_6$
Ir(C$_4$H$_6$)$_2$Cl (1.5) and di-*tert*-butyl-*p*-cresol (0.5)		30	0[d]	C$_6$H$_6$
Rh(C$_4$H$_6$)ClPPh$_3$ (0.13)	33568-90-0	24	71	C$_6$H$_6$
Rh(C$_4$H$_6$)ClAs-Ph$_3$ (0.12)	67761-62-0	60	47	C$_6$H$_6$
CoCl(PPh$_3$)$_3$ (0.20)		16	0	CH$_3$CN

^{a} Standard conditions are: 3 g of C$_4$H$_6$, 4 mL of solvent, 200 psi of initial O$_2$ pressure, and 55 °C. ^{b} The yields of the peroxides based on the consumed butadiene are $\geq$90%. ^{c} Large-scale reaction carried out at 60 °C using 20 g of butadiene in 50 mL of C$_6$H$_6$. ^{d} Reaction carried out at 60 °C.

aldehyde and hydroxy groups results from decomposition of the peroxy radicals[5] (eq 1 and 2) or from decomposition of the dimer of the peroxy radical via the Russell mechanism.[9]

$$2RCH_2OO\cdot \rightarrow O_2 + 2RCH_2O\cdot \qquad (1)$$

$$2RCH_2O\cdot \rightarrow RCH{=}O + RCH_2OH \qquad (2)$$
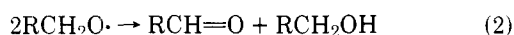
Hydrogen abstraction by the peroxy radical gives the terminating hydroperoxy groups. Hydroxy groups were observed in the IR spectra. The presence of the hydroperoxy group is reflected also in the number of peroxidic oxygens per oligomeric unit.

Experimental Section

General. The synthesis and isolation of the metal complexes were performed under vacuum or in an Ar atmosphere with degassed or Ar-saturated solvents. Magnetic resonance spectra (reported in δ, relative to Me$_4$Si in CDCl$_3$) were recorded on a Varian T-60 spectrometer. Infrared spectra (reported in microns) were obtained on a Model 283 Perkin-Elmer spectrometer. GC–MS results were obtained with a Finnigan Model 3200 GC–MS instrument.

Ir(butadiene)$_2$Cl. This complex was prepared according to the method of Onderdelinden and Van der Ent[10] starting from Ir(C$_8$H$_{14}$)$_2$Cl dimer. The butadiene complex can also be prepared directly from the corresponding ethylene complex.

Rh(butadiene)ClL. The complexes where L = triphenylphosphine and arsine were prepared according to the method of Roundhill et al.[11] An alternative method starting with the olefin chloride dimer of Rh(I), excess butadiene, and an equivalent of the ligand gave a quantitative yield of the product.

Butadiene Oxygenation. In a typical procedure for the oxygenation of 1,3-butadiene, the catalyst, Ir(C$_4$H$_6$)$_2$Cl (ca. 0.1 g), solvent (ca. 4 mL, usually benzene), and a magnetic stir bar were introduced into a glass insert and the insert placed inside a stainless steel reactor with ca. 250 mL of total capacity. The portion of the reactor containing the solvent was chilled to −179 °C and then evacuated. A volume of butadiene, usually 3 g, was condensed into the reactor. The reactor was then connected to a source of oxygen. While the bomb was still cold, ca. −78 °C, O$_2$ was added to the desired pressure (up to 200 psi).[12]

The reactor was then placed in a thermostatted bath and stirred. The reaction could be terminated at any time by lowering the temperature. The workup consisted of releasing the pressure, filtering precipitated catalyst, and vacuum transfer of the solvent and small amounts of low-boiling materials. The residue was composed of ca. equal molar amounts of the oligomers of 1,2- and 1,4-peroxides of butadiene to the extent of about 90%, the rest being oligomerized butadiene; H-NMR spectra corresponded to those reported:[2] 1,4 isomer, 4.3–4.6 (m, 4 H), 5.8–6.1 (m, 2 H); 1,2 isomer 3.8–4.1 (m, 2 H), 4.6–4.9 (m, 1 H), 5.0–5.8 (m, 3 H); IR 2.8 (s), 3.4 (s), 5.8 (s), 7.0 (s), 7.4 (s), 10.0 (broad); average mol wt 723. Active oxygen analysis showed 2.67 equiv per 100 g of oligomeric material. The aldehyde impurity exhibited H-NMR 9.64 (doublet, 8 Hz) and IR 5.8 (s); the hydroxy group had IR 2.8 (s).

The results obtained with different catalysts and solvents are summarized in Table I.

Lithium Aluminum Hydride Reduction. Preformed butadiene peroxide oligomer (2.5 g, 29.0 mmol) dissolved in 20 mL of ether was added dropwise to an ice-cooled suspension of LiAlH$_4$ (5.0 g, 130 mmol) in 100 mL of ether. The resulting mixture was refluxed for 3 h. Acetic anhydride (20 mL) in ether was then slowly added to the mixture. After an aqueous workup and neutralization, the solution was continuously extracted with ether to obtain the crude product in 45% yield. By comparison with authentic samples, GC–MS analysis indicated it to be a mixture of the diacetates of isomeric butene-diol.

References and Notes

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(5) R. A. Sheldon and J. K. Kochi in "Oxidation and Combustion Reviews", C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1973, p 135.
(6) There are well-documented cases of metal-catalyzed ligand oxygenation via oxygen atom transfer in the literature, e.g., phosphine oxide from phosphine[7] and isocyanate from isocyanide.[7]
(7) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976); M. M. T. Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Vol. 1, Academic Press, New York, 1974; J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973).
(8) Regardless of the identity of the active species in the initiation, an odd electron change is required on the metal. In accordance with the IR complex in CH$_2$Cl$_2$ under a diluted oxygen atmosphere, a paramagnetic metal species with $\langle g \rangle$ = 2.4 together with a weak, perhaps organic, radical species with $\langle g \rangle$ = 2.0 were observed by ESR. However, the possible danger of explosion (see ref 12) during the ESR measurements precluded mimicking of actual experimental conditions for oxygenation. Therefore, no further delineation of these paramagnetic species can be obtained.
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(12) *Caution:* Even though no difficulty was experienced, these compositions are within the flammable range. In addition, the oligomeric peroxides are shock and heat sensitive, see: D. G. Hendry, F. R. Mayo, D. A. Jones, and D. Schuetzle, *Ind. Eng. Chem., Prod. Res. Dev.*, **7**, 145 (1968).