

# Activation of Molecular Oxygen: Rhodium-Catalyzed Oxidation of Olefins

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**Abstract:** Several new aspects of the rhodium-catalyzed oxidation of olefins by molecular oxygen are presented. The best catalysts are comprised of combinations of rhodium trichloride and cupric perchlorate or nitrate and are most efficient in alcoholic solvents. The reactivity of the olefins strongly depends on the nature of the rhodium-olefin interaction. Linear terminal olefins are quantitatively oxidized to the corresponding methyl ketones. This reaction is inhibited by the presence of free water and accelerated when a dehydrating agent such as 2,2-dimethoxypropane (DMP) is introduced into the reaction medium. Internal acyclic olefins oxidized either very slowly or not at all. In the case of cycloolefins, cyclopentene [which is found to form a  $\pi$  allylic complex of rhodium(III)] gives mainly 3-alkoxy- and 4-alkoxycyclopentene, resulting from the oxidative substitution of alcohols on the saturated positions of this olefin. Small amounts of cyclopentanone are also detected. Addition of water or DMP has the opposite effect on this reaction compared to that observed in the case of terminal olefins. Cycloheptene (which forms a rhodium(I)  $\pi$  complex) gives mainly cycloheptanone. Rhodium perchlorate is a good catalyst for the oxidation of terminal olefins to methyl ketones and is active in the absence of free water, chloride, or copper ions. A new mechanism involving the coupling of an oxygen activation path with a Wacker-type oxidation path is proposed for the oxidation of terminal olefins. For the oxidation of cyclopentene, we propose a different mechanism involving the nucleophilic attack of the alkoxide group on the coordinated  $\pi$  allylic group in competition with a classical Wacker cycle. Finally, we attribute the oxidative cleavage of olefins to a rhodium-oxo intermediate complex and tentatively suggest a mechanism involving the transient formation of metal-carbenic species.

## Introduction

The use of oxygenated complexes of group 8 transition metals as catalysts for oxidation of olefins by molecular oxygen has until recently led only to products which are commonly obtained in free-radical chain oxidation.<sup>2-6</sup> However, Read et al. have recently shown that rhodium(I) complexes such as  $\text{RhCl}(\text{PPh}_3)_3$  can promote the cooxygenation of terminal olefins to methyl ketones and triphenylphosphine to triphenylphosphine oxide.<sup>7-9</sup> They suggested the formation of a five-membered peroxometalloycle as an intermediate following the complexation of both olefin and dioxygen on the same metal center, i.e., rhodium(I). Likewise, Milner et al. concluded that a metal centered mechanism was operative in the autoxidation of styrene and cyclooctene catalyzed by rhodium species.<sup>10-11</sup>

Ketones are also produced from terminal olefins in the Wacker oxidation by palladium(II) in the presence of water.<sup>12-15</sup> James et al. have proposed a Wacker-type mechanism for the oxidation of ethylene to acetaldehyde by rhodium trichloride whether associated with ferric chloride or not.<sup>16</sup> In this case, a water molecule coordinated to rhodium(III) is the source of the oxygen atom incorporated into the olefin. It is therefore important to know whether rhodium either activates dioxygen or uses water in a Wacker-type oxidation. In fact, activation of molecular oxygen and Wacker-type oxidation involve two antagonistic mechanisms. In the former case, which is analogous in several aspects to *in vivo* monooxygenases,<sup>17</sup> dioxygen and substrate are bonded to the metal in a lower oxidation state; one oxygen atom is then incorporated into the substrate and the other one remains on the metal, which thus becomes oxidized. In order to be catalytic, this reaction requires the presence of a coreducing agent (e.g., phosphines) to bring the metal back to its initial reduced state. In the Wacker process, the nucleophilic attack of the hydroxide anion on the olefin coordinated to the metal in its higher oxidation state gives both the carbonyl compound and the reduced metal, which has to be reoxidized by a cooxidative agent [e.g., copper(II)] to make the reaction catalytic.

This paper describes three main aspects of the rhodium-catalyzed oxidation of olefins: Part 1 describes the catalytic oxidation of terminal olefins to methyl ketones by dioxygen

catalyzed by rhodium-copper systems in anhydrous alcoholic solvents. Part 2 involves the study of catalytic oxidation of internal linear olefins and cycloolefins, in the presence of alcohols, to allylic ethers and ketones. Finally, part 3 discusses the oxidative cleavage of olefins to aldehydes, which also occurs when rhodium complexes are used without cocatalysts.

## Results

**Part 1. Selective Oxidation of Terminal Olefins to Methyl Ketones. (a) The Catalyst System.** Table I lists some representative results obtained when 1-hexene is oxidized in ethanol at 40 °C by molecular oxygen in the presence of several catalytic systems formed by the coupling of a rhodium complex with a copper or iron cocatalyst. Rhodium trichloride alone was a very inefficient and nonspecific catalyst for converting 1-hexene to 2-hexanone (expt 1). Addition of copper(II) nitrate or perchlorate<sup>19</sup> furnished a very efficient oxidation catalyst which gave 2-hexanone almost quantitatively from 1-hexene. The absorbed  $\text{O}_2$  corresponded to the 1-hexene consumed and to the 2-hexanone produced (expt 2-3). Under these conditions, more than 100 mol of 2-hexanone was produced per mol of rhodium in 4 h. Replacing cupric perchlorate or nitrate by copper(II) chloride (expt 4) caused a large decrease in the reactivity of the catalyst. This is presumably due to the presence of the chloride anion which inhibits the dissociation of  $\text{RhCl}_3$  into less chlorinated species (*vide infra*). The use of copper(II) bromide or iodide with  $\text{RhCl}_3$  gave inactive catalysts. Addition of ligands such as pyridine, bipyridine, phosphines, or arsines resulted in a decrease in the activity of the catalyst, presumably by blocking the vacant sites necessary for the coordination of the olefin. Addition of 1,5-cyclooctadiene inhibited the catalytic activity of the  $\text{RhCl}_3\text{-Cu}(\text{ClO}_4)_2$  (HMPA)<sub>4</sub> system. Active catalysts were also obtained when iron(III) nitrate was associated with rhodium trichloride (expt 5). Again use of iron(III) chloride or bromide gave markedly inferior results. The combination of rhodium(III) and copper(II) perchlorate gave inactive catalysts (expt 7), but replacing the latter with copper(II) chloride restored the activity of the catalyst (expt 6). Coupled with copper(I) perchlorate, the dimeric complex  $[\text{RhCl}(\text{cyclooctene})_2]_2$  could act as a catalyst (expt 8), but addition of a twofold excess of hydro-

**Table I.** Oxidation of 1-Hexene Catalyzed by Rhodium-Copper or Iron Systems<sup>a</sup>

expt	complex, 0.02 M	cocatalyst, 0.04 M	total O <sub>2</sub> uptake, M	1-hexene consumed, M	2-hexanone produced, M	select., <sup>b</sup> %	turn. <sup>c</sup> no.
1	RhCl <sub>3</sub> ·3H <sub>2</sub> O	none	0.08	0.58	0.034	6	2
2	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Cu(NO <sub>3</sub> ) <sub>2</sub> (HMPA) <sub>4</sub> <sup>d</sup>	1.16	2.35	2.32	≥98	116
3	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Cu(ClO <sub>4</sub> ) <sub>2</sub> (HMPA) <sub>4</sub> <sup>d</sup>	1.05	2.13	2.09	≥98	105
4	RhCl <sub>3</sub> ·3H <sub>2</sub> O	CuCl <sub>2</sub>	0.11	0.22	0.21	≥97	10
5	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Fe(NO <sub>3</sub> ) <sub>3</sub> (HMPA) <sub>4</sub> <sup>d</sup>	0.7	1.37	1.35	≥98	67
6	Rh(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	CuCl <sub>2</sub>	0.7	1.4	1.38	≥98	70
7	Rh(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Cu(ClO <sub>4</sub> ) <sub>2</sub> (HMPA) <sub>4</sub> <sup>d</sup>	0.02		0.03		1
8	[RhCl(C <sub>8</sub> H <sub>14</sub> ) <sub>2</sub> ] <sub>2</sub>	Cu <sup>I</sup> (ClO <sub>4</sub> ) <sup>e</sup>	0.16	0.35	0.33	≥94	16
9	[RhCl(C <sub>8</sub> H <sub>14</sub> ) <sub>2</sub> ] <sub>2</sub>	Cu <sup>I</sup> (ClO <sub>4</sub> ) <sup>e</sup> + HCl <sup>f</sup>	0.64	1.30	1.28	≥98	64

<sup>a</sup> Reaction conditions: temp, 40 °C; P(O<sub>2</sub>), 860 mmHg; reaction time, 4 h; 1-hexene, 3.94 M (50% vol); solvent, absolute ethanol; water (coming from hydrated salts and solvent), 0.25 M (0.5%, w/w). <sup>b</sup> Selectivity based on consumed olefin. <sup>c</sup> Turnover: moles of 2-hexanone produced per mole of rhodium in 4 h. <sup>d</sup> HMPA: hexamethylphosphorotriamide. The complexes were prepared according to Donoghue and Drago.<sup>18</sup> <sup>e</sup> Anhydrous cuprous perchlorate was prepared from the reaction of cupric perchlorate with excess metallic copper powder in ethanolic solution containing 20% of DMP as dehydrating agent. <sup>f</sup> Anhydrous ethanolic solution of gaseous hydrochloric acid. HCl concentration was 0.04 M.

**Table II.** Oxidation of Terminal Olefins Catalyzed by RhCl<sub>3</sub>·3H<sub>2</sub>O-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub><sup>a</sup>

expt	olefin	O <sub>2</sub> uptake, M	product	select. <sup>b</sup> %	turn. no.
10	1-hexene	0.6	2-hexanone	≥98	60
11	1-octene	0.52	2-octanone	≥98	52
12	1-dodecene	0.4	2-dodecanone	≥98	40
13	4-methyl-1-pentene	0.3	4-methyl-2-pentanone	≥97	30
14	styrene	0.3	acetophenone <sup>c</sup>	≥97	30
15	1,7-octadiene <sup>d</sup>	0.46	1-octen-7-one	≥95	46
16	2-ethyl-1-hexene	0.01			

<sup>a</sup> Reaction conditions: temp, 40 °C; reaction time, 4 h; olefin, 2.5 M; solvent, absolute ethanol; RhCl<sub>3</sub>·3H<sub>2</sub>O, 0.02 M; Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub>, 0.04 M; water (coming from reactants), 0.25 M; P(O<sub>2</sub>), 860 mmHg. <sup>b</sup> Calculated on consumed olefin. <sup>c</sup> Traces of benzaldehyde were also detected. <sup>d</sup> Concentration, 1.25 M.

chloric acid caused a fourfold increase in the turnover number under the same conditions (expt 9). Thus, presumably, the presence of small amounts of free hydrochloric acid is beneficial for high catalytic activity of the rhodium-copper system.

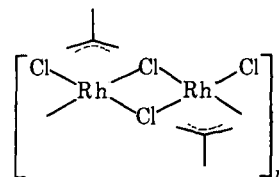
The activities of the RhCl<sub>3</sub>·3H<sub>2</sub>O-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub> catalyst in several different solvents follow the order: ethanol ~ isopropyl alcohol > CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH > methanol > 2-octanol > *tert*-butyl alcohol >> acetone. Alcohols do not directly participate in the reaction but probably aid in the formation of the catalytic species. Thus, when the catalytic reaction was carried out in ethanol, small amounts of acetaldehyde, roughly equimolar with respect to the rhodium present in solution, were formed at the beginning of the reaction. However, this then remained constant during the rest of the oxidation. The catalyst was less active with ketones such as acetone and methyl ethyl ketone as solvents and inactive in chlorinated solvents, acetonitrile, DMF, ethylene glycol, and THF. In the presence of small amounts of ethanol, the catalyst was active in nitrobenzene, esters (e.g., ethyl acetate), or hydrocarbons (e.g., benzene or toluene).

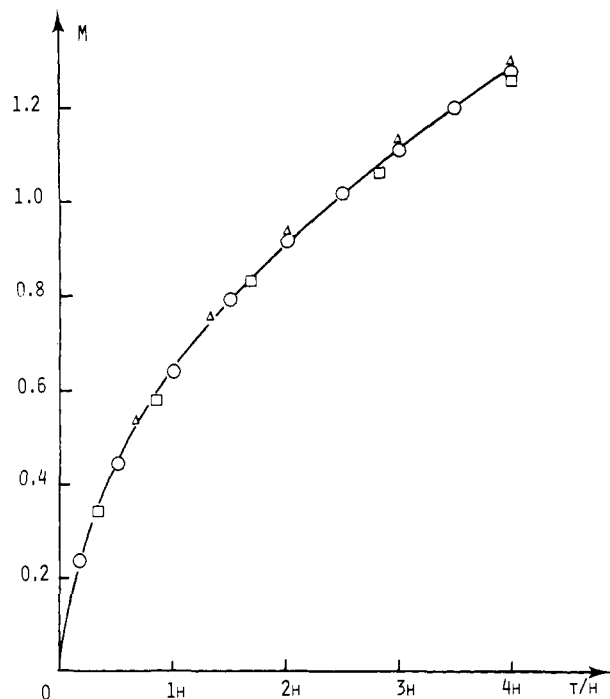
Note that palladium- and rhodium-based catalysts differ in their behavior in various solvents. Whereas the palladium catalysts are active in donor solvents like DMF, ketones or diols,<sup>20-22</sup> the rhodium complexes are mostly inactive in such solvents.

(b) **Oxidation of Terminal Olefins.** Table II shows that the use of the catalytic system RhCl<sub>3</sub>-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub> affords a general procedure for the selective oxidation of terminal olefins to methyl ketones by O<sub>2</sub> under very mild conditions of temperature and oxygen pressure. The reactivity of olefins decreased somewhat when the molecular weight increased

from 1-pentene to 1-dodecene, but the selectivity of the reaction remained high even for terminal olefins of high molecular weight. Isomerization of the double bond of the olefin occurred only to a small extent, and the amount of internal olefins found at the end of the reaction was less than ca. 10% of the non-consumed terminal olefin. Oxidation of 1,7-octadiene occurred at a high rate and gave mainly 1-octen-7-one with some isomerization to internal linear diolefin (expt 15). It is remarkable that, with these rhodium catalysts, neither terminal aldehydes nor internal ketones have been observed as by-products. This sharply contrasts with the behavior of the corresponding palladium system. In this latter case, terminal aldehydes result from the anti-Markovnikov addition of the hydroxide ion to the olefin coordinated to palladium, whereas internal ketones arise from the oxidation of internal olefins formed by the isomerization of terminal olefins.<sup>12,23</sup> This does not seem to occur in the case of rhodium.

Terminal olefins substituted at the second carbon atom, e.g., 2-ethyl-1-hexene, were unreactive (expt 16). The catalyst did not oxidize isobutene. Small amounts of ethyl *tert*-butyl ether were formed however, resulting from the addition of ethanol to isobutene. Also, precipitation of rhodium occurred in the form of a yellow insoluble polymeric complex, which analyzed as RhCl<sub>2</sub>C<sub>4</sub>H<sub>7</sub> and which probably has the structure of a polymeric chloro π allylic complex of rhodium(III).





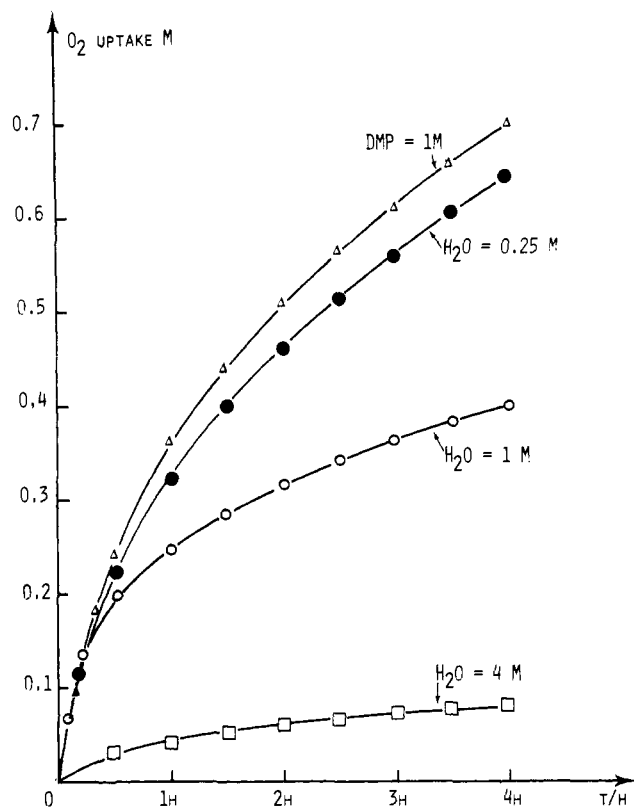
**Figure 1.** Rh-Cu catalyzed oxidation of 1-octene: (O),  $O_2 \times 2$  uptake; ( $\Delta$ ) 1-octene consumption, ( $\square$ ) 2-octanone formation. Reaction conditions:  $RhCl_3 \cdot 3H_2O$ , 0.02 M;  $Cu(ClO_4)_2(HMPA)_4$ , 0.04 M;  $PO_2$ , 860 mmHg; 1-octene, 3.18 M;  $H_2O$  (coming from reactants), 0.25 M; solvent, absolute ethanol; temp, 40 °C.

Butadiene was also very slowly oxidized but polymerized to very pure crystalline *trans*-1,4-polybutadiene which precipitated from the reaction medium.<sup>24</sup>

**(c) Oxidation of 1-Octene by  $O_2$  Catalyzed by  $RhCl_3-Cu(ClO_4)_2(HMPA)_4$ . Some Kinetic Studies.** Figure 1 shows a typical plot of oxygen uptake, 1-octene consumption and 2-octanone formation vs. time when 1-octene is oxidized by  $O_2$  in the presence of catalytic amounts of  $RhCl_3 + 2Cu(ClO_4)_2(HMPA)_4$ .

A close correspondence between the three curves was observed, illustrating the very high selectivity of the reaction. No induction period was observed, but a white precipitate of copper(I) chloride appeared during the initial stage of the reaction. Since catalyst activity decayed gradually with time, only initial kinetic rates were determined. These were measured from oxygen-uptake data. Initial rates were proportional to the concentration of copper(II) perchlorate when copper to rhodium ratios are below 1:1. Increasing the copper concentration at  $Cu/Rh \geq 1$  did not affect the rate of the reaction. Using a  $Cu/Rh$  ratio equal to 1, the removal of copper(I) chloride which precipitated at the initial stage of the reaction had no effect on the rate of the reaction. Analysis of the remaining copper in the solution showed that about 85% of the copper had been eliminated from the reaction mixture as  $CuCl$ .

When the ratio copper/rhodium = 2:1, linear dependence of initial rates on the concentration of rhodium trichloride and 1-octene, respectively, was observed by plots of initial rate vs. concentration of catalyst and olefin. These plots passed through the origin, and a value of  $k_2 = 5.5 \cdot 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$  was obtained for the second-order kinetic constant at 40 °C. Initial rates were unaffected by changing the partial pressure of  $O_2$  from 400 to 1200 mmHg. However, under low partial pressure of oxygen, the activity of the catalyst decayed much more slowly than with higher partial pressures of oxygen. The initial rate of 2-octanone formation agrees with the following kinetic expression:



**Figure 2.** Dependence of addition of water or DMP on the Rh-Cu catalyzed oxidation of 1-octene by  $O_2$ . Experimental conditions are the same as in Figure 1.

$$\text{initial rate} = k_2[\text{rhodium}][\text{olefin}][O_2]^\circ$$

From the Arrhenius plots of  $\log k_2$  vs.  $1/T$  K at 30, 40, 50, 60 °C, the activation energy  $E_a \sim 10.5 \text{ kcal mol}^{-1}$  was obtained.

Experiments were carried out in an attempt to explain the decay of activity of the catalyst. Addition of 2-octanone at the beginning of the reaction (0.1 and 0.7 M, respectively) showed no inhibitory effect. Likewise, addition of aldehydes like octanal and acetaldehyde had no effect. Isomerization of 1-octene to internal octenes which are much less easily oxidized in presence of the catalyst (vide infra) can be eliminated as a cause, since isomerization occurs to such a low extent, i.e., 0.2% at 40 °C, 1% at 50 °C, and 3% at 60 °C.




**(d) Influence of Water and 2,2-Dimethoxypropane (DMP).** The previous experiments were carried out with a water content in the medium of ca. 0.5% weight (0.25 M) coming from hydrated rhodium salt and solvent impurities (GLC determination on Porapak Q column). Figure 2 shows that addition of water, even in small quantities, at the initial stage of the oxidation of 1-octene by  $O_2$ , catalyzed by  $RhCl_3-2Cu(ClO_4)_2(HMPA)_4$ , results in a dramatic decrease in the activity of the catalyst. In the same way, addition of excess DMP to remove the small quantities of free water present in the reaction mixtures caused an enhancement of the catalytic activity. Infrared determination of the water content in the medium can be carried out by measuring the carbonyl-stretching vibration of acetone resulting from the hydration of DMP.<sup>25</sup> The value of the water content obtained by this method closely corresponded to the parallel GLC determination. This shows that the presence of excess DMP captures most of the free water present in the medium. In contrast, Figure 3 shows that addition of small amounts of water considerably enhances the activity of the  $PdCl_2-CuCl_2$  system for the oxidation of 1-octene under the same conditions, and addition of excess DMP causes a deactivation of the catalyst. In the presence of 1 M

**Table III.** Oxidation of Internal Olefins Catalyzed by  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} - \text{Cu}(\text{ClO}_4)_2(\text{HMPA})_4$ 

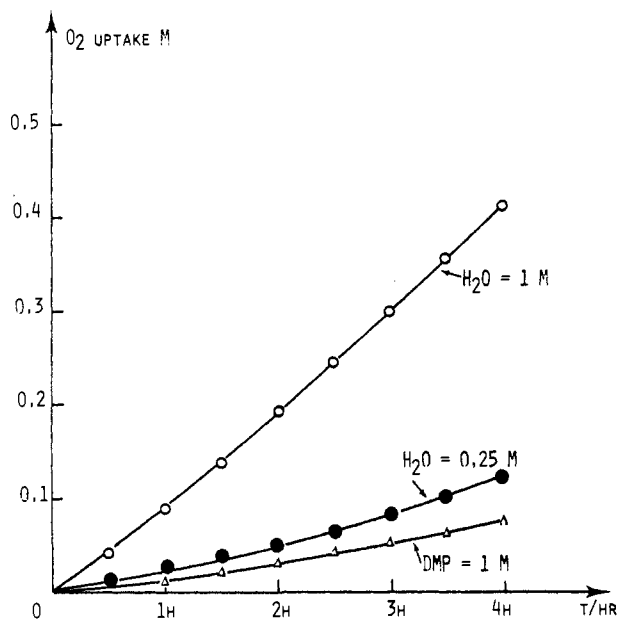
expt	conditions <sup>a</sup>	olefin	O <sub>2</sub> uptake, M	products, mol L <sup>-1</sup>	select.	turn. no.
17	I	<i>cis</i> -2-butene	1.2	2-butanone, 0.5	45	
18	II	cyclopentene	0.32	3-ethoxy-1-butene, 0.59	55	109
19	II	cyclohexene	0.08	(see Table IV)		30
20	II	cycloheptene	0.16	cycloheptanone, 0.3	92	15

<sup>a</sup> Reaction conditions. I: temp, 80 °C; olefin, 5.8 M; solvent, ethanol; pressure, 9 atm; O<sub>2</sub> pressure, 2 atm;  $\text{RhCl}_3$ , 0.01 M;  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 0.02 M;  $\text{H}_2\text{O}$ , ~0.5 M; reaction time, 4 h. II: temp, 40 °C; olefin, 2.5 M; solvent, isopropyl alcohol; O<sub>2</sub> pressure, 860 mmHg;  $\text{RhCl}_3$ , 0.02 M;  $\text{Cu}(\text{ClO}_4)_2(\text{HMPA})_4$ , 0.04 M;  $\text{H}_2\text{O}$ , 0.25 M; reaction time, 4 h.

**Table IV.** Oxidation of Cyclopentene<sup>a</sup>—Influence of Water and DMP

expt	H <sub>2</sub> O or DMP concn	Selectivity, <sup>b</sup> %			O <sub>2</sub> uptake, M	turn. no.
						
21	H <sub>2</sub> O, 1.5 M	11	72.3	16.6	0.42	40
22	H <sub>2</sub> O, 0.25 M	7.4	75.3	17.2	0.32	30
23	DMP, 1 M	3.2	76.8	19.9	0.16	15

<sup>a</sup> Reaction conditions were the same as condition II in Table III. <sup>b</sup> Based on consumed cyclopentene.



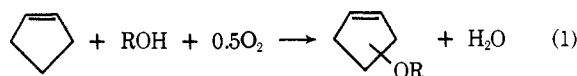
**Figure 3.** Dependence of addition of water and DMP on the Pd-Cu catalyzed oxidation of 1-octene by O<sub>2</sub>. Reaction conditions:  $\text{PdCl}_2$ , 0.02 M;  $\text{CuCl}_2$ , 0.04 M; 1-octene, 3.18 M;  $\text{PO}_2$ , 860 mmHg; solvent, absolute ethanol; temp, 40 °C.

water (2%) and under the conditions given in Figure 3, 16% 4-octanone, 28% 3-octanone, and 56% 2-octanone, respectively, were obtained from the oxidation of 1-octene. This contrasts with the 98% selectivity in 2-octanone observed with the corresponding rhodium catalyst.

Hence, water appears to be *necessary* for catalytic activity in the *palladium* (Wacker-type) catalyst but is an *inhibitor* in the *rhodium* systems described here. Clearly, despite the apparent superficial similarity between the Pd(II)-Cu(II) and Rh(III)-Cu(II) oxidation catalysts, there are *profound mechanistic differences*.

**Part 2. Oxidation of Internal Olefins to Ketones and Allylic Ethers.** Table III lists some representative results obtained when internal olefins are oxidized by O<sub>2</sub> in alcoholic  $\text{RhCl}_3 - \text{Cu}(\text{ClO}_4)_2(\text{HMPA})_4$  solutions. Generally, internal

olefins were oxidized much more slowly than terminal ones. For example, the reactivity of 2-hexene was approximately 15 times lower than that of 1-hexene. However, both the reactivity and the nature of the products depend considerably on the olefin. This is best illustrated by first considering the behavior of cyclic monoolefins. In isopropyl alcohol, cyclopentene was oxidized at a high rate (corresponding roughly to the reactivity of 1-dodecene) to mainly 3- and 4-isopropoxycyclopentene with only small amounts of cyclopentanone (Table IV). This oxidative substitution of alcohols on cyclopentene can be represented by the following eq 1.



In contrast, cycloheptene was oxidized to cycloheptanone with high selectivity (expt 20). Cyclohexene was rather unreactive and showed intermediate behavior.

The behavior of these rhodium catalysts is quite different from that of palladium, since the latter gives mainly saturated cyclic ketones from the oxidation of cyclic monoolefins.

The source of the strikingly different behavior observed during the oxidation of the various cyclic olefins using rhodium may be traced to the nature of the olefinic complexes formed by the reaction of the olefins with rhodium trichloride. Reaction of cycloheptene with rhodium trichloride in alcoholic solvent gave the well-known olefinic binuclear  $\pi$  complex of rhodium(I)  $[\text{Rh}(\text{C}_7\text{H}_{12})_2\text{Cl}]_2$ .<sup>26</sup> No reaction was found with cyclohexene, but an insoluble polymeric complex was obtained from the reaction with cyclopentene.<sup>26</sup> Elemental analysis of this insoluble material gave the formula  $\text{RhCl}_2\text{C}_3\text{H}_7$  corresponding to a polymeric  $\pi$  allylic complex of rhodium(III) analogous to that obtained previously with isobutene and to the described polymeric  $\pi$  allylic complex obtained with *t*-1, *t*-5, *t*-9-cyclododecatriene.<sup>27</sup>

Addition of water or excess DMP to the rhodium-copper catalyzed oxidation of cyclopentene in isopropyl alcohol resulted in a completely *opposite* effect to that found for terminal olefins. Table IV shows that addition of excess DMP causes a decrease in the oxidation rate with a decrease in the formation of cyclopentanone. Further, addition of water increases the rate of oxidation and the amount of cyclopentanone formed.

**Table V.** Oxidation of 1-Octene and Styrene Catalyzed by Rhodium Complexes without Addition of Copper<sup>a</sup>

expt	olefin, 2.5 M	rhodium, 0.02 M	O <sub>2</sub> uptake, M	products, M	turn. no.
24	1-octene	[RhCl(C <sub>8</sub> H <sub>14</sub> ) <sub>2</sub> ] <sub>2</sub>	0.02	2-octanone, 0.018; heptanal, 0.004	1
25 <sup>b</sup>	1-octene	[RhCl(C <sub>8</sub> H <sub>14</sub> ) <sub>2</sub> ] <sub>2</sub>	0.08	2-octanone, 0.12; heptanal, ~0	6
26	1-octene	Rh(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.23	2-octanone, 0.34; heptanal, 0.016	17
27	styrene <sup>c</sup>	Rh(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.16	PhCOCH <sub>3</sub> , 0.17; PhCHO, 0.02	8
28	styrene	[RhCl(C <sub>8</sub> H <sub>14</sub> ) <sub>2</sub> ] <sub>2</sub> + 2NH <sub>4</sub> PF <sub>6</sub>	0.12	PhCOCH <sub>3</sub> , 0.01; PhCHO, 0.11	12

<sup>a</sup> Reaction conditions: temp, 60 °C; reaction time, 4 h; olefin, 2.5 M; solvent, ethanol; rhodium, 0.02 M; DMP, 2 M; O<sub>2</sub> pressure, 860 mm Hg. <sup>b</sup> HClO<sub>4</sub>, 0.06 M. <sup>c</sup> Styrene contains 0.001% 4-*tert*-butylpyrocatechol to prevent radical chain oxidation.

On the contrary, cycloheptene showed a *similar* behavior toward addition of water in comparison with terminal olefins. A twofold decrease in the formation of cycloheptanone was observed when small amounts of water (2%) were added to the reaction medium. Oxidation of *cis*-2-butene (expt 17) gave approximately equal amounts of 2-butanone and 3-ethoxy-1-butene. Double-bond migration to the adjacent position must have occurred for the formation of the allylic ether. However, it must be noted that no isomerization of *cis*-2-butene to *trans*-2-butene was observed during the reaction.

Oxidation of *trans*-2-butene also gave equivalent quantities of 2-butanone and 3-ethoxy-1-butene but occurred at a rate three times lower.

**Part 3. Rhodium-Catalyzed Oxidation of 1-Octene and Styrene by O<sub>2</sub> without Addition of Copper Salts.** Table V lists some representative oxidations of 1-octene and styrene catalyzed by [RhCl(cyclooctene)<sub>2</sub>]<sub>2</sub> and Rh(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O at 60 °C in ethanolic solvents.

[RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub> promotes the stoichiometric oxidation of 1-octene to a mixture of 82% 2-octanone and 18% heptanal (expt 24). Addition of anhydrous perchloric acid<sup>29</sup> (HClO<sub>4</sub>/Rh, 3:1) raised the turnover number to 6, producing only 2-octanone (expt 25). The same effect was observed with addition of the same amounts of hydrochloric acid.

Rhodium(III) perchlorate alone, used in the presence of excess DMP, was a good catalyst (17 mol of ketone was produced per mol of rhodium) for the oxidation of 1-octene (expt 26) and styrene (expt 27). Slight amounts of heptanal (4%) and benzaldehyde (10%), respectively, were also produced. The absence of DMP and the presence of small quantities of water caused a fourfold decrease in the rate of oxidation of 1-octene with the formation of only 2-octanone. Thus, the presence of copper as well as of chloride ion and water is not necessary for catalytic activity. However, the activity of Rh(ClO<sub>4</sub>)<sub>3</sub> was about five times less than the activity of the RhCl<sub>3</sub>·3H<sub>2</sub>O-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub> couple under the same conditions. A rhodium complex resulting from addition of ammonium hexafluorophosphate to [RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub> (probably cationic) showed a different distribution of acetophenone and benzal-

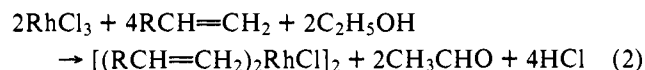
dehyde produced by oxidation of styrene (expt 28). More benzaldehyde [PhCHO/Rh, 6:1] than acetophenone [PhCOCH<sub>3</sub>/Rh, 1:1] was obtained.

## Discussion and Mechanisms

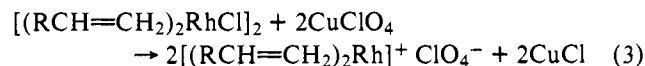
The following observations must be explained in any mechanism proposed for oxidation catalyzed by rhodium. (1) In contrast to the corresponding palladium system, water is not involved in the oxidation of terminal olefins to methyl ketones using rhodium. In fact, it is an inhibitor. Hence, molecular oxygen is the source of the oxygen atom found in the ketone, and a classical Wacker-type mechanism cannot be involved. (2) Rhodium species without cocatalysts can catalyze the oxidation of terminal olefins. Furthermore, since the products of this oxidation are identical to those found when copper(II) is also added, it seems probable that copper does not play a direct role in the oxidative process. (3) The products formed by oxidation of internal olefins seem to be traceable to the nature of the rhodium-olefin interaction. For olefins which form the dimeric bridged  $\pi$  complexes of rhodium(I) [(olefin)<sub>2</sub>RhCl]<sub>2</sub> (e.g., cycloheptene), ketones are the predominant products. However where a  $\pi$  allylic complex of rhodium(III) (e.g., [Rh( $\pi$  allyl)Cl]<sub>2</sub>)<sub>n</sub> is produced, allylic ether results (e.g., for cyclopentene).

Owing to the complexity of the reaction medium and the difficulty of isolating any active intermediate from the catalytic solutions, it seems rather hazardous to make an accurate assessment about the nature of the active species involved in this reaction. However, we can make several proposals which seem to agree with the experimental data.

In the case of the oxidation of terminal olefins and cycloheptene to ketones, the occurrence of olefinic  $\pi$  complexes of rhodium(I) seems highly probable. These can be obtained from the reaction of rhodium trichloride with the olefin in alcoholic solvent, according to eq 2.<sup>30</sup>

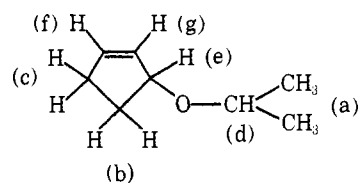


This would explain the stoichiometric formation of acetaldehyde from ethanol, the inhibition by chloride ion which would prevent olefin complexation on Rh(I), and the observed acid character of the reaction medium. The formation of copper(I) chloride during the RhCl<sub>3</sub>-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub> catalyzed oxidation indicates that anion exchange between rhodium trichloride and cupric perchlorate must have occurred, together with a reduction of copper(II) to copper(I). Hence, a reoxidation of the rhodium(I) complex produced according to eq 2 by copper(II) perchlorate may give rise to copper(I) perchlorate and a rhodium(III) chloro perchlorate species. The reaction of copper(I) perchlorate with the rhodium(I)-olefinic complex formed by eq 2 could produce an olefinic  $\pi$  complex of rhodium(I), probably cationic, and copper(I) chloride, according to eq 3.<sup>31</sup>



Such a cationic olefinic-rhodium(I) perchlorate complex may also be involved when rhodium(III) perchlorate is used without cocatalyst (expt 26).

We therefore tentatively suggest that the mechanism of the oxidation of terminal olefins to methyl ketones arises from an





when the rhodium(III) oxo intermediate [D] cannot undergo a return to the reduced rhodium(I) species [A] (Scheme I). We might then tentatively attribute to [D] the ability to oxidize olefins to aldehydes, involving a [2 + 2] interaction between the olefin and the metal-oxo group, via a four-centered intermediate. This would break down into the carbonyl compound and a rhodium-carbene complex.<sup>41-43</sup> Reaction of dioxygen with the latter compound would regenerate the rhodium oxo species and the other half-oxidized olefin.<sup>44,45</sup>

We are now trying to obtain more evidence about this latter possibility, which would be of considerable interest for the realization of mild four-electron oxidation by dioxygen without need for the "unavoidable" coreducing agents.

## Experimental Section

**Materials.** Olefins were passed through a column containing active alumina to remove peroxidic impurities, distilled over sodium before use, and stored under argon. Alcoholic solvents were distilled over CaCO<sub>3</sub>, and stored over 4-Å molecular sieves. Rhodium trichloride containing 3.2 mol of water (determined by thermogravimetric method) per mol of rhodium was purchased from Comptoir Lyon Allemand. Copper(II) perchlorate and nitrate were commercial samples (Koch Light).

**Preparation of the Complexes.** Cu(NO<sub>3</sub>)<sub>2</sub>(HMPA)<sub>4</sub> and Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub> were synthesized according to the procedure of Donoghue and Drago<sup>18</sup> and stored in a desiccator over P<sub>2</sub>O<sub>5</sub>. [RhCl(cyclooctene)<sub>2</sub>]<sub>2</sub> was prepared according to the method given by Van der Ent and Onderdelinden.<sup>46</sup> Rh(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O was obtained from the reaction of a 60% solution of perchloric acid on rhodium trichloride, according to Ayres and Forrester.<sup>28</sup>

**Dichloro- $\pi$ -2-methylallylrhodium(III).** This polymeric complex was precipitated during the oxidation of isobutene in ethanol catalyzed by RhCl<sub>3</sub>-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub> at 80 °C and 9 atm pressure. It was removed from the reaction mixture by filtration, washed repeatedly with ethyl alcohol and diethyl ether, and dried in vacuo: IR (thin film, KBr plate) 1425 (m), 1380 (s), 1350 (w), 1320 (m), 1140 (w), 1110 (w), 1080 (w), 1030 (m), 1015 (m) ( $\pi$  allyl vibrations), 830 (s), 620 (w), 560 (2) ( $\pi$  allyl), 330, 250 (m) (Rh-Cl stretching vibrations). Anal. Calcd for C<sub>4</sub>H<sub>7</sub>Cl<sub>2</sub>Rh: C, 20.96; H, 3.05; Cl, 31.0; Rh, 44.9. Found: C, 20.88; H, 3.09; Cl, 31.15; Rh, 44.7.

**Dichloro- $\pi$ -cyclopentenyrrhodium(III)** This  $\pi$  allylic polymeric complex of Rh(III) with cyclopentene was prepared by pouring 6 mL of cyclopentene (65 mmol) into a solution of 2 g of RhCl<sub>3</sub>·3H<sub>2</sub>O (7.4 mmol) in 20 mL of absolute ethanol. The brick-red complex precipitates after 2 days reaction at room temperature. This complex is insoluble in alcohols, methylene chloride, and most organic solvents, except basic solvents (e.g., DMF) or amines (e.g., pyridine, aniline), with which adducts such as C<sub>5</sub>H<sub>7</sub>RhCl<sub>2</sub>L<sub>2</sub> are presumably formed<sup>27</sup> (L = amine): IR (Nujol Mulls) 3070 (w), 1410 (s), 1000 (m) ( $\pi$  allyl vibration), 850 (s), 815 (m), 560 (w) ( $\pi$  allyl), 400 (w), 280 (m) (Rh-Cl vibration). Anal. Calcd for C<sub>5</sub>H<sub>7</sub>Cl<sub>2</sub>Rh: C, 24.89; H, 2.90; Cl, 29.46; Rh, 42.73. Found: C, 23.3; H, 2.8; Cl, 31.2; Rh, 44.2.

**Procedure and Method.** Higher olefins were oxidized in a flat-bottomed double-jacketed glass flask connected to a sensitive gas-burette system and to a vacuum-argon line. In a typical procedure, the components of the catalyst were dissolved in the alcoholic solvent containing an internal standard (*m*-xylene), and the solution was equilibrated for 15 min before the reaction was started. The olefin was introduced at the initial stage of the reaction, and the evolution of the reaction was followed by oxygen uptake measurements and GLC analysis of aliquot samples. The oxidation of gaseous lower olefins such as butene were conducted in a stainless-steel autoclave maintained at constant pressure and connected to an oxygen line. Analytical gas-liquid partition chromatography (GLC) was performed on a Girdel flame-ionization model gas chromatograph, using different columns depending on the requested analyses: a 3-m-long column of ODPN 30% on chromosorb was used to separate the different olefin isomers. For the identification of oxygenated products, we use either a 3-m-long column of dinonylphthalate 30% on firebrick (acid washed) for the low boiling-point products or a 3-m-long column of diethylene glycol succinate 20% on chromosorb for the higher boiling-point oxygenated products. Water determination: the water content of solutions was measured on an Intersmat IGC 12 M gas chromatograph fitted with a katharometer detector and using a 2-m-long column of Porapak Q.

**Identification of Products.** The oxygenated products were isolated from the reaction mixture using gas-liquid chromatography on a preparative scale, Thomson THN 101.

**Apparatus.** The products were identified by comparison of the IR and NMR spectra with authentic samples; the infrared spectrum was recorded on a Perkin-Elmer Model 457, and the NMR spectrum of protons on a Varian 60 Mc. The <sup>13</sup>C NMR spectrum was recorded on a Varian CFT 20, solvent CDCl<sub>3</sub>, pulse width 10 Hz, pulse delay 5 s. Mass spectra were obtained on a mass spectrometer AEI Model MS 12.

**1-Octen-7-one.** This product was obtained from the oxidation of 1,7-octadiene by oxygen in ethanolic solvent catalyzed by RhCl<sub>3</sub>·3H<sub>2</sub>O-Cu(ClO<sub>4</sub>)<sub>2</sub>(HMPA)<sub>4</sub>: NMR (CCl<sub>4</sub>):  $\delta$  1.5 (m, 4), 2 (s, 3), 1.8-2.1 (m, 2), 2.3 (t, 2), 4.7-8 (m, 2), 5.2-6 (m, 2); MS *m/e* 43 (100), 68 (70), 58 (30), 41 (26), 55 (25), 67 (22), 29 (22), 39 (18), 28 (17), 71 (13), 126 (MW 7). Anal. Calcd for C<sub>8</sub>H<sub>14</sub>O: C, 76.19; H, 11.1; Found: C, 75.9; H, 11.4.

NMR (CCl<sub>4</sub>)  $\delta$  a 1.05 (d), b 1.5-2 (m), c 2.2 (m), d 3.5 (m), e 4.4 (m), f, g (m); NMR (CFT <sup>13</sup>CDCl<sub>3</sub> solvent) a 22.5, b 31, c 40, d 70, e 82.5, f 132, g 134; MS *m/e* 84 (100), 77 (90), 83 (80), 45 (56), 43 (55), 55 (52), 41 (55), 76 (37), 39 (35), 56 (30), 126 (MW 8).

**Note Added in Proof.** Since this manuscript has been submitted, a further support for the occurrence of the oxygen activation *path A* (Scheme I) has been afforded by the selective obtention of methyl ketones from the reaction of terminal olefins with rhodium dioxygen complexes such as [Rh(AsPh<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> under anhydrous conditions. A peroxometalocyclic intermediate such as [C] has been isolated using tetracyanoethylene as an olefin.<sup>47</sup>

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