Acknowledgment. Thanks are due to Prof. Dr. K. Vrieze for his interest in this work, to Dr. D. M. Grove for helpful discussions and critical reading of the manuscript, and to Dr. A. J. M. Duisenberg for collecting the X-ray data.

Registry No. 3, 83311-98-2; **4a**, 82112-96-7; **4b**, 67507-09-9; **4c**, 82112-97-8; **5a**, 95532-50-6; **5b**, 95532-53-9; **5c**, 95532-51-7; **5d**, 95532-54-0; **5e**, 95552-59-3; **6a**, 95532-56-2; **6b**, 95532-58-4; **6c**, 95532-59-5; **6d**, 95532-61-9; **7**, 95532-52-8; *o,o'*-$(Me_2NCH_2)_2C_6H_3Me$, 95532-49-3; MeI, 74-88-4; CD_3I, 865-50-9; MeBr, 74-83-9; MeOTf, 333-27-7; *o*-tolylithium, 6699-93-0; *p*-tolylithium, 2417-95-0.

Supplementary Material Available: Observed and calculated structure factors for **5b**, Tables I–IV and VI for positional and thermal parameters, bond distances, bond angles, and torsion angles for **5b**, and Figure 7, an ORTEP drawing giving a view of **5b** (27 pages). Ordering information is given on any current masthead page.

Investigations of the Mechanism of the Rh/Cu- and Rh-Catalyzed Oxidation of Terminal Olefins with O_2

Russell S. Drago,* Anne Zuzich, and Eric D. Nyberg

Contribution from the Chemistry Department, University of Florida, Gainesville, Florida 32611.
Received February 23, 1984

Abstract: The mechanism of the Rh(III)-catalyzed oxidation of 1-hexene to 2-hexanone, both with and without a Cu(II) co-catalyst, is investigated. In the absence of Cu(II), only one oxygen atom of dioxygen is found to be incorporated into ketone product. This contrasts with the previously reported observation that in the presence of the Cu(II) co-catalyst both oxygen atoms of O_2 are incorporated into product. Similarly, the Rh(III) catalyst without Cu(II) isomerizes 1-hexene to a large extent, in contrast to the previously reported Rh/Cu catalyst system. Both acetone and water are found to be produced continuously when isopropyl alcohol is the solvent in the absence of Cu(II), while neither are formed continuously when Cu(II) is present. Furthermore, it is shown that H_2O_2 and *t*-BuOOH may be used as the 1-hexene oxidant under anaerobic conditions in the presence or absence of Cu(II), producing 2-ketone. These observations are incorporated into tentative mechanisms which specify key roles for copper that lead to differences in reactivity.

Transition-metal-catalyzed oxidations of hydrocarbons generally exhibit poor product specificity due to free radical mechanisms predominating in these reactions. Very often the only role of the metal complex is to initiate free radical autoxidation by decomposing trace quantities of peroxides.[1] Improved product specificity may be obtained when free radical processes are avoided, as evidenced by the groups 5 and 6 metal-catalyzed olefin epoxidation reactions[2] (using peroxides) and the Pd/Cu-cocatalyzed Wacker process.[3] These latter reactions are more specific because the principle bond-breaking and -reforming steps occur at the metal catalyst center. A relatively new class of transition-metal-catalyzed olefin oxidations with O_2 have been reported which also appear to involve the metal-centered reaction between oxidant and olefin,[4,5] while avoiding the Wacker-type hydroxometalation process. The mechanism suggested for these oxidations involves the consecutive coordination of olefin and O_2 to a rhodium(I) catalyst, a rearrangement to a peroxymetallocycle, and a decomposition to primarily 2-ketone. Most noteworthy among these is the homogeneous oxidation studied by Mimoun and co-workers,[5] which utilizes 98% of the oxygen atoms in dioxygen for 2-ketone production. This system is unique for its extraordinary selectivity as well as its activity, stability, and dependence on alcohol solvents. Another feature of the Rh(III)/Cu(II) systems is the zero-order dependence of its rate law on P_{O_2}.

We have recently reported a new characterization of the rhodium catalyst for this Rh/Cu olefin oxidation at 40 °C and implicated the rhodium(III) chloride complex produced in eq 1.[6]

$$RhCl_3 + Cu^{2+} + {}^1/_2(CH_3)_2CHOH \rightarrow RhCl_2^+ + CuCl(s) + {}^1/_2(CH_3)_2CO + H^+ \quad (1)$$

This is evidenced by the stoichiometry of eq 1 in acetone, the observation of an induction period in the 1-hexene oxidation when employing $[Rh(CO)_2Cl]_2$ as the catalyst precursor, and the need for 3 or more equivalents of chloride in the initial mixtures for maximum activity (at both 40 °C[5] and 70 °C[6]). Equation 1 is not meant to suggest the only role for Cu(II) in this system is the precipitation of chloride. In fact, the familar redox chemistry of copper ion requires consideration of its role in any oxidation occurring in its presence.

We have studied the $RhCl_3 \cdot 3H_2O$-catalyzed olefin oxidation in the presence and absence of Cu(II) in an attempt to more completely elucidate the roles of this co-ion in the more complex Rh(III)/Cu(II) system. This reaction without Cu(II) was reported to proceed at vastly reduced rates, with only a few turnovers and with only 6% selectivity.[5] Our characterization of the $RhCl_3$-catalyzed reaction includes an examination of peroxides as olefin oxidants. The results are incorporated in specific proposals for the mechanisms of the $RhCl_3$- and Rh(III)/Cu(II)-catalyzed oxidations of olefins by O_2.

(1) Sheldon, R. A.;Kochi, J. K. "Metal Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; Chapters 3 and 9 and references therein.

(2) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63 and references therein.

(3) (a) Smidt, J. *Angew. Chem.* **1959**, *71*, 176. (b) Smidt, J.; Hapner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sable, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 80.

(4) (a) Dudley, C. W.; Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1974**, 1926. (b) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883. (c) Farrar, J.; Holland, D.; Milner, D. J. *J. Chem. Soc., Dalton Trans.* **1975**, 815. (d) Holland, D.; Milner, D. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2440.

(5) (a) Mimoun, H.; Machirant, M. M. P.; Seree de Roch, I. *J. Am. Chem. Soc.* **1978**, *100* 5437. (b) Ingersheim, I.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161.

(6) Nyberg, E. D.; Pribich, D. C.; Drago, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 3538.

0002-7863/85/1507-2898$01.50/0 © 1985 American Chemical Society

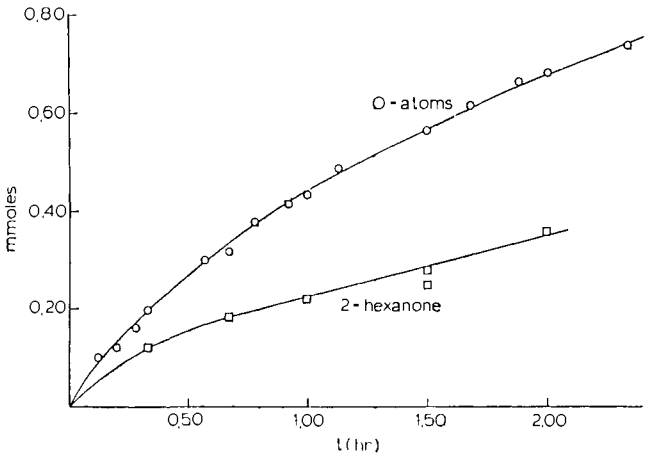

Figure 1. Rhodium-catalyzed oxidation of 1-hexene. The reaction was monitored on a gas buret. The catalyst solution was prepared by mixing 0.111 mmol of rhodium(III) trichloride (produced in situ from $[Rh(CO)_2Cl]_2$ oxidation[6]), 0.71 mmol of 2-heptanone (as internal standard), and 22.5 mL of ethanol. The reaction was carried out under 1 atm of O_2 at 40 °C and was initiated by the addition of 7.5 mL of 1-hexene.

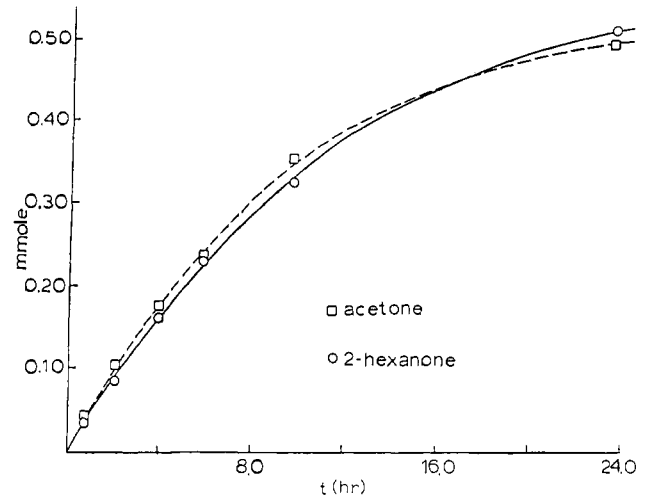

Figure 2. Rhodium-catalyzed reaction of 1-hexene with O_2 in 2-propanol solvent under 40 psig of O_2 at 40 °C. The catalyst solution was prepared by mixing 0.111 mmol of rhodium(III) trichloride trihydrate, 0.61 mmol 2-octanone (as internal standard), 22.5 mL of 2-propanol, and 7.5 mL of 1-hexene.

Results and Discussion

(A) The $RhCl_3$-Catalyzed Oxidation of 1-Hexene by O_2. The two most striking differences between the $RhCl_3$- and Rh(III)/Cu(II)-catalyzed oxidations of 1-hexene are the utilization of only one (or less) oxygen atom of O_2 for 2-ketone production and the decreased rates observed in the absence of Cu(II). In Figure 1 is presented a comparison of oxygen atoms consumed with 2-hexanone produced with 3.7×10^{-3} M $RhCl_3$ (produced in situ via oxidation of $[Rh(CO)_2Cl]_2$[6]) as the catalyst. This rhodium concentration is only 19% that employed by Mimoun and co-workers.[5] The observation that only 50% of the O atoms are incorporated in 2-hexanone contrasts with the >98% utilization found in the presence of Cu(II).[5] When $RhCl_3 \cdot 3H_2O$ is used, only 3.3 turnovers (2-hexanone/Rh) are observed in 2.0 h, although the catalyst is still quite active at this point. In contrast, the Rh(III)/Cu(II) cocatalyst produces 22.5 turnovers after 2.0 h under identical conditions.

The 50% selectivity of oxygen atoms for 2-hexanone production found with 3.7×10^{-3} M $RhCl_3$ in the absence of Cu(II) suggests the concomitant consumption of oxygen to form H_2O. Since the complete reduction of O_2 requires four electrons, and 1-hexene is providing only two, alcohol solvent must supply the remainder. This was demonstrated by employing 2-propanol as solvent, which produces acetone upon oxidation. The 1/1 acetone/ketone product profile in Figure 2 establishes the stoichiometry for the $RhCl_3$-catalyzed olefin oxidation shown in eq 2. The continuous formation of water during reaction 2 was detected by GLC, but it could not be quantitated.

Table I. Acetone and 2-Hexanone Production for the $RhCl_3$-Catalyzed Oxidation of 1-Hexene by O_2 in 2-Propanol Solvent

expts[a]	$[RhCl_3]$, M	mmol of Acetone	mmol of 2-hexanone	acetone/ 2-hexanone mol ratio
1	0.0019	0.51	0.41	1.2
2	0.0037	0.78	0.77	1.0
3	0.0066	3.6	1.9	1.9
4	0.018	5.8	1.6	3.6
5	0.037	8.4	1.9	4.4

[a] These reactions were carried out at 40 psi and 40 °C, with the appropriate amount of $RhCl_3 \cdot 3H_2O$, 4.84 mmol of 2-octanone (GLC internal standard), 45 mL of 2-propanol, and 15 mL of 1-hexene. Reaction time was 24 h.

$$CH_2{=}CHR + O_2 + CH_3CHR'OH \xrightarrow{RhCl_3} CH_3CRO + CH_3CR'O + H_2O \quad (2)$$

The rate law for reaction 2 was also determined, measured by initial rates of 2-hexanone formation, and is given in eq 3. Most

$$\text{rate} = d[RC(=O)CH_3]/dt = k[RhCl_3][1\text{-hexene}] \quad (3)$$

notably, the rate law is independent of P_{O_2}, a feature shared with the Rh(III)/Cu(II)-cocatalyst system. Initial rates were unaffected by changing the initial oxygen pressure from 0 to 80 psig. Plots of log [initial rate] vs. log [concentration] for $RhCl_3$ and 1-hexene give reaction orders of 0.97 and 1.0, respectively.[7] The addition of a 77-fold excess of the free radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol or *N*-phenyl-1-naphthylamine did not affect the initial rates of the 1-hexene oxidation, further indicating that it is not a free radical oxidation.

At higher concentrations of $RhCl_3$, acetone production increases relative to that of 2-hexanone as illustrated in Table I. This results from the $RhCl_3$-catalyzed alcohol reduction of O_2 directly to H_2O (eq 4), as reported previously.[6] Reaction 4 probably occurs via

$$2CH_3CHR'OH + O_2 \rightarrow 2CH_3CR'O + 2H_2O \quad (4)$$

a metal-catalyzed decomposition of peroxide which becomes more important at higher rhodium concentrations (vide infra). Increasing $[RhCl_3]$ results in a decrease in reaction selectivity, which explains the poor selectivity (6%) with respect to oxygen consumption observed by Mimoun and co-workers with 0.02 M $RhCl_3$ as the catalyst.[5] Water has a deleterious effect on the $RhCl_3$-catalyzed oxidation of olefins,[5] and its continuous formation in both reactions 2 and 4 may be a factor in the catalyst deactivation. The rhodium/copper catalyst may have a longer lifetime because water is not formed in this reaction.

One further observation concerning this reaction is worthy of note for it has mechanistic implications. When $RhCl_3$ alone is employed as the catalyst, extensive isomerization of 1-hexene is observed by GLC. This constrasts the Rh/Cu system, for which it was reported[5] that at the end of the reaction, the amount of internal olefins was less than 10% of the unreacted terminal olefin. The fact that much of the terminal olefin is isomerized in the $RhCl_3$-catalyzed reaction may also partially account for the decreased activity compared to the Rh/Cu system. Linear internal olefins are oxidized much more slowly by both $RhCl_3$ and Rh/Cu[5] catalysts than are terminal olefins.

(B) The Rh(III)- and Rh(III)/Cu(II)-Catalyzed Oxidations of 1-Hexene by H_2O_2 and *t*-BuOOH. The selectivities of both the $RhCl_3$- and Rh(III)/Cu(II)-catalyzed 1-hexene oxidations strongly suggest metal-centered reactions are occurring. Since water has been ruled out as the oxidant in this system,[5] and the oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) in ethanol was shown to proceed via the in situ generation of HOOH,[6] we investigated the usefulness

(7) Zuzich, Anne Ph.D. Thesis, University of Florida, 1985.

Table II.

expt[a]	solvent	cocatalyst	mol of oxidant/mol of RH	turnovers[b] (h)			
1	EtOH	none	O_2 (40 psi)	0.37 (0.05)	1.2 (0.2)	1.8 (0.4)	
2	EtOH	none	3.1 HOOH	0.49 (0.05)	0.83 (0.2)	1.34 (0.4)	2.6 (2.2)
3	EtOH	none	6.0 HOOH	0.38 (0.05)	1.0 (0.2)	1.6 (0.4)	3.4 (2.2)
4	EtOH	none	12.0 HOOH	0.75 (0.05)	2.7 (0.4)	4.6 2 (2.1)	
5	*t*-BuOH	none	1.8 HOOH	0.66 (0.08)	1.1 (0.8)	1.2 (1.8)	
6	*t*-BuOH	none	3.1 HOOH	0.11 (0.05)	0.35 (0.2)	0.61 (0.4)	2.0 (3.4)
7	*t*-BuOH	none	12.0 HOOH	0.12 (0.08)	0.30 (0.4)	4.3 (4.8)	
8	*t*-BuOH	none	.70 BuOOH	0.040 (0.07)			
9	*t*-BuOH	none	2.9 BuOOH	1.0 (0.08)	1.0 (0.2)	1.3 (1.3)	
10	*t*-BuOH	none	5.8 BuOOH	0.24 (0.04)	0.52 (0.2)	0.62 (0.4)	4.8 (6.5)
11	EtOH	1.0 Cu	6.2 HOOH	5.7 (0.1)	6.4 (0.3)	6.7 (0.4)	6.7 (2.8)
12	EtOH	2.0 Cu	6.2 HOOH	2.4 (0.04)	4.1 (0.2)	4.4 (0.4)	4.8 (2.7)
13	EtOH	0.5 Cu	6.3 HOOH	2.4 (0.05)	3.1 (0.2)	3.3 (0.4)	4.1 (2.6)
14	*t*-BuOH	1.0 Cu	5.9 (BuOH)	0.24 (0.05)	0.38 (0.2)	0.62 (0.4)	2.0 (6.9)

[a] These reactions were carried out at 40 °C under argon, using 0.128 mmol of $RhCl_3 \cdot 3H_2O$, 0.14 mmol of 2-heptanone or 0.24 mmol of 2-octanone (GLC internal standards), 1.30 mL of 1-hexene substrate, and 4.00 mL of solvent listed. [b] Turnovers = total mol of 2-hexanone produced per mol of $RhCl_3 \cdot 3H_2O$ at the time indicated. The reactions were not carried to completion but arbitrarily stopped when comparative data were obtained.

of peroxides as oxidants for the 1-hexene oxidation. Under conditions identical with those used for the study of reaction 2 except for the exclusion of O_2, $RhCl_3 \cdot 3H_2O$ was found to oxidize 1-hexene to 2-hexanone with either HOOH or *t*-BuOOH as oxidant (Table II).

These inert atmosphere olefin oxidations occurred in both the presence and absence of Cu(II) and have the stoichiometry shown in eq 5 (written for HOOH). Table II contains the results of a number of oxidations with O_2, HOOH, and *t*-BuOOH in ethanol and *tert*-butyl alcohol under a variety of conditions.

$$CH_2{=}CHR + HOOH \rightarrow CH_3CRO + H_2O \qquad (5)$$

Several conclusions may be drawn from these data. The peroxide oxidations of 1-hexene catalyzed by both $RhCl_3 \cdot 3H_2O$ and the Rh(III)/Cu(II) are catalytic (turnovers > 1). This was observed for both HOOH and *t*-BuOOH, in ethanol and *tert*-butyl alcohol solvents. The use of greater initial quantities of peroxide causes an increase in total turnovers (see experiments 2–4), but the percent HOOH utilized for 2-hexanone formation decreases in this series. The utility of *tert*-butyl alcohol as solvent for this reaction (experiments 5–10 and 14) demonstrates that an initial solvent reduction of $RhCl_3$ to Rh(I) is not occurring in this system, in agreement with the conclusion drawn for the analogous O_2 oxidation.

An important role for Cu(II) is indicated by the enhanced initial rates of peroxide oxidation of olefin observed in experiments 11–13, compared to experiment 3 without Cu(II). Significantly, this initial rate enhancement is not observed in *tert*-butyl alcohol solvent (experiment 14). Since the precipitation of CuCl is observed at the end of the experiment in these ethanol oxidations, it is concluded that reaction 1 is the initiation step in the Rh(III)/Cu(II)-cocatalyzed HOOH olefin oxidations, as it is for the O_2 oxidations. Experiment 11 is particularly noteworthy in that all the initially added HOOH is quickly consumed to form 2-hexanone via eq 5 (in less than 20 min). The use of an excess of Cu(II) (2 equiv) results in a decrease in product selectivity (only 75% HOOH is consumed to form 2-hexanone), although selectivity in this case is still greater than that in the absence of Cu(II). This suggests Cu(II) may decompose HOOH before the $RhCl_2^+$ catalyst may utilize it for olefin oxidation (a conclusion also drawn for O_2 oxidations employing excess Cu(II), vide infra).

The similarity in the characteristics of the $RhCl_3$ and Rh(III)/Cu(II) olefin oxidations with O_2 and HOOH is remarkable. The primary olefin oxidation product is 2-hexanone (~5% 2-hexanol is also observed), and the O_2 and HOOH reaction rates are comparable. The inclusion of Cu(II) in reducing solvents results in the unsaturation of $RhCl_3$ in both systems, forming $RhCl_2^+$ and CuCl, and causes a significant increase in initial rates and product selectivities (using 1 equiv of Cu(II)). The observations with O_2 and HOOH as oxidants suggest related mechanisms are operating for both the $RhCl_3$ and Rh(III)/Cu(II) catalytic systems.

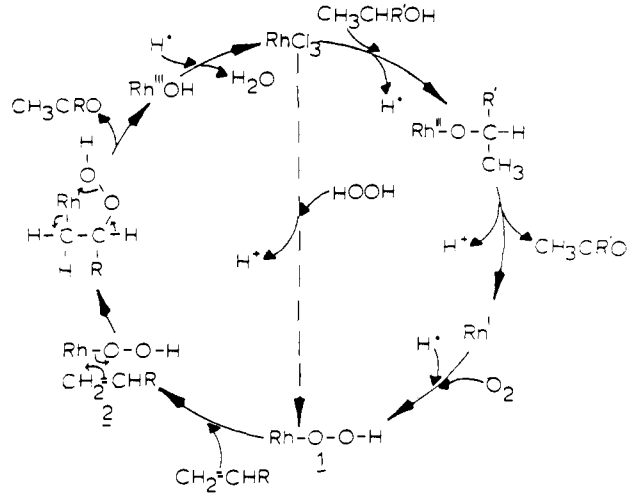

Figure 3. Proposed mechanism for the $RhCl_3$-catalyzed oxidation of terminal olefins (without Cu(II)).

(C) Mechanism of the $RhCl_3$-Catalyzed Oxidation. The catalytic cycle proposed for the $RhCl_3$-catalyzed terminal olefin oxidation by O_2 is shown in Figure 3. This mechanism incorporates all the reported features of this reaction. Alcohol reduction of dioxygen to a rhodium-coordinated hydroperoxo complex is proposed in the first half of the cycle. This probably proceeds via a two-step process involving the two-electron alcohol reduction of $RhCl_3$ and the fast reaction of the resulting rhodium(I) or rhodium hydrido complex with O_2 to form RhOOH. Rhodium trihalide complexes have been shown to be capable of oxidizing primary alcohols to aldehydes and secondary alcohols to ketones,[8a] with the subsequent formation of rhodium hydrides. Rhodium hydroperoxidic species are known to result from the insertion of O_2 into a Rh–H bond.[8b,c] Alternatively, intermediate **1** may result from protonation of a rhodium peroxo complex. This hydroperoxo complex may also be formed via the direct reaction of rhodium(III) with HOOH, as indicated by the dashed line in the cycle of Figure 3. The reaction with HOOH circumvents that part of the cycle in which solvent oxidation and reaction with O_2 generate RhOOH.

The coordination of the peroxy group to a rhodium(III) (or other high-valent group 8 metal) rather than a Mo(VI) epoxidation catalyst[9] results in two distinguishing properties. First, the oxygen of the peroxide is more weakly bound to the rhodium(III) complex, so it maintains more nucleophilic character. Second, the group

(8) (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231 and references therein. (b) Roberts, H. L.; Symes, W. R. *J. Chem. Soc. A* **1968**, 1450. (c) Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1976**, 369.

(9) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. A. Chem. Soc.* **1972**, *94*, 295.

8 metal complexes may coordinate alkenes, bringing them into the proximity of the peroxy group. As a result, the intermediate $RhCH_2CHROOH$ is produced. A rotamer of this compound is configurationally set to transfer a hydroxide ion to rhodium(III) and decompose to ketone by proton transfer to the terminal carbon atom. If either the formation or decomposition of the intermediate formed in this step is considered rate limiting, a steady-state treatment of this mechanism predicts a first-order dependence of the rate law on $[RhCl_3]$ and [1-hexene] and a zero-order dependence on $[O_2]$.

The mechanism proposed in Figure 3 is similar to those suggested for the $[CF_3CO_2Pd(t\text{-BuOOH})]_4$-catalyzed *t*-BuOOH oxidation of olefin to 2-ketone in 98% yield[10a] and the $Pd(OAc)_2$-catalyzed HOOH oxidation of olefin to the same product.[10b] In the former system it was found that the carboxylate bridging ligand, RCO_2^-, has a strong influence on the catalytic activity of the palladium tetramer, with the more electron withdrawing carboxylate ligands creating more active catalysts. For example, $CF_3CO_2^-$ produces a catalyst 130 times more active than does $CH_3CO_2^-$. Thus increasing the Lewis acidity of the Pd(II) cluster considerably enhances its effectiveness for the catalytic oxidation of 1-hexene to 2-hexanone. The similarity between the product specificities found for the terminal olefin oxidations catalyzed by $[CF_3CO_2Pd(t\text{-BuOO})]_4$ with *t*-BuOOH, and for the Rh(III)/Cu(II) system with O_2 as oxidant, was explicitly mentioned in the report on the palladium tetramer catalyst. Both of these reactions produce ≥98% 2-ketone from the available oxidizing equivalents (two for BuOOH, four for O_2).

The isomerization of 1-hexene observed in this system is expected in the context of our proposed mechanism. In ethanol solvent, $RhCl_3$ is well known as an olefin isomerization catalyst.[11a] The mechanism of this reaction has been studied extensively[11a,b] and involves a rhodium(III) hydrido olefin complex. Isomerization proceeds by an addition, elimination mechanism. The fact that 1-hexene isomerization occurs in the $RhCl_3$-catalyzed oxidation implies the presence of hydrido rhodium(III) complexes. The observation that isomerization occurs to a lesser extent in the Rh/Cu system suggests that if rhodium(III) hydrides are formed, they undergo rapid redox reactions with Cu(II). The increased acetone production relative to 2-hexanone (eq 4) at high $[RhCl_3]$ described earlier may be explained in the context of the proposed mechanism. As $[RhCl_3]$ increases, the peroxide concentration in solution increases as well. A metal-catalyzed decomposition of peroxide results in the formation of H_2O. This increasing peroxide decomposition at higher concentrations of rhodium catalyst accounts for the inefficient utilization of O_2 in the rhodium-catalyzed reaction reported by Mimoun and co-workers.[5]

(D) Mechanism of the Rh(III)/Cu(II)-Catalyzed Oxidation of 1-Hexene by O_2. A mechanism proposed for this system must account for the pronounced increase in rate and the incorporation of both O atoms of O_2 into the ketone product that result by adding copper(II) to the rhodium(III) catalyst. In the Rh/Cu system, copper(II) may play several roles.

We have proposed that one important role of Cu(II) is the stoichiometric unsaturation of $RhCl_3$ in the initiation step shown in eq 1, forming the rhodium(III) dichloride catalyst. This may be a several step process involving the alcohol reduction of $RhCl_3$ to a rhodium(I) complex, followed by reaction with two Cu(II) ions to form $RhCl_2^+$, CuCl, and Cu(I) as shown in eq 1. This chloride labilization process was suggested earlier.[5]

A second role for copper ion concerns its involvement in the reduction of O_2 to H_2O_2. We reported earlier that ethanol reacts slowly with O_2 to form aldehyde and H_2O_2.[6] Both Copper(II) and rhodium(III) catalyze this reaction, presumably via the intermediacy of Cu(I) or Rh(I) species, but copper is more effective.[6] Thus, we propose that the Cu(I)/Cu(II) couple plays a key role

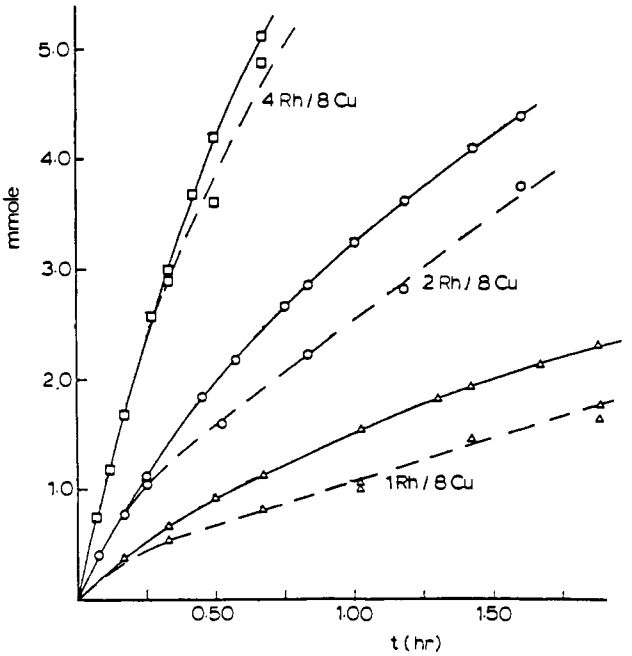

Figure 4. Effect of increasing the Rh(III)/Cu(II) ratio on the 1-hexene oxidations. The solid line represents millimoles of O_2 consumed and the dashed line millimoles of 2-hexanone formed. A 9.4 mM $Cu(NO_3)_2 \cdot 2.5H_2O$ solution was used in all experiments, and the rhodium concentration was increased from 1.2 mM $RhCl_3 \cdot 3H_2O$, to 2.4 mM, to 4.7 mM—labeled as 1Rh/8Cu, 2Rh/8Cu, and 4Rh/8Cu, respectively.

in the 1-hexene oxidation by reducing O_2 to peroxide. This may occur via the one-electron reduction to superoxide, which is then converted to H_2O_2.[12] The H_2O_2 is quickly captured by the rhodium(III) catalyst, forming RhOOH. This in effect corresponds to a copper-catalyzed path for forming the same RhOOH species involved in the $RhCl_3$-catalyzed reaction. Further substantiation for HOOH intermediacy in the O_2 oxidation is provided by the high selectivities and reaction rates reported in Table II for the Rh(III)/Cu(II)-catalyzed HOOH oxidations of 1-hexene in ethanol. This proposal differs substantially from the original suggestion that the catalytic cycle begins with the formation of a coordination complex between rhodium(I) and O_2.

Consistent with the above proposal is our observation that the specificity of these 1-hexene oxidations decreases as the Cu/Rh ratio is increased from 2:1 to 4:1 and 8:1 (Figure 4). At higher copper concentrations, the decomposition of HOOH to H_2O and O_2 becomes more favorable, as was noted for the direct HOOH olefin oxidations. Therefore, the decreased specificity of the Rh(III)/Cu(II) catalyst at high Cu/Rh ratios is a result of the increasing importance of the overall four-electron reduction of O_2 to H_2O in copper-catalyzed reaction 4 relative to the olefin oxidation by intermediacy of HOOH in reaction 5.

We offer two specific proposals to account for the Rh(III)/Cu(II) results (Figure 5, A and B). Both incorporate the earlier discussed initiation and Cu(I)/Cu(II) O_2 reduction steps, forming RhOOH. These suggested mechanisms also accommodate the reported reaction kinetics for the Rh(III)/Cu(II) O_2 oxidations, which are zero order in $[O_2]$. The next two steps in the catalytic cycle in Figure 5A involve the reaction of RhOOH with alkene as discussed previously for the rhodium only case. A similar (unprotonated) five-membered metallocycle intermediate has been proposed by Mimoun, and as suggested[5] copper could play a role similar to that involved in Wacker chemistry to allow reaction of $Rh^{III}OH$ with alkene to form ketone and rhodium(I). The subsequent fast oxidation of rhodium(I) to the Rh(III) catalyst by two copper(II) ions in the final step reforms CuCl, completing the cycle. The mechanism whereby copper facilitates oxygen atom transfer from $Rh^{III}OH$ to olefin is not well understood, just as

(10) (a) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fisher, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (b) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387.

(11) (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapters 2 and 3 and references therein. (b) Cramer, R. *J. Am. Chem. Soc.* **1966**, *88*, 2272.

(12) Gray, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 56.

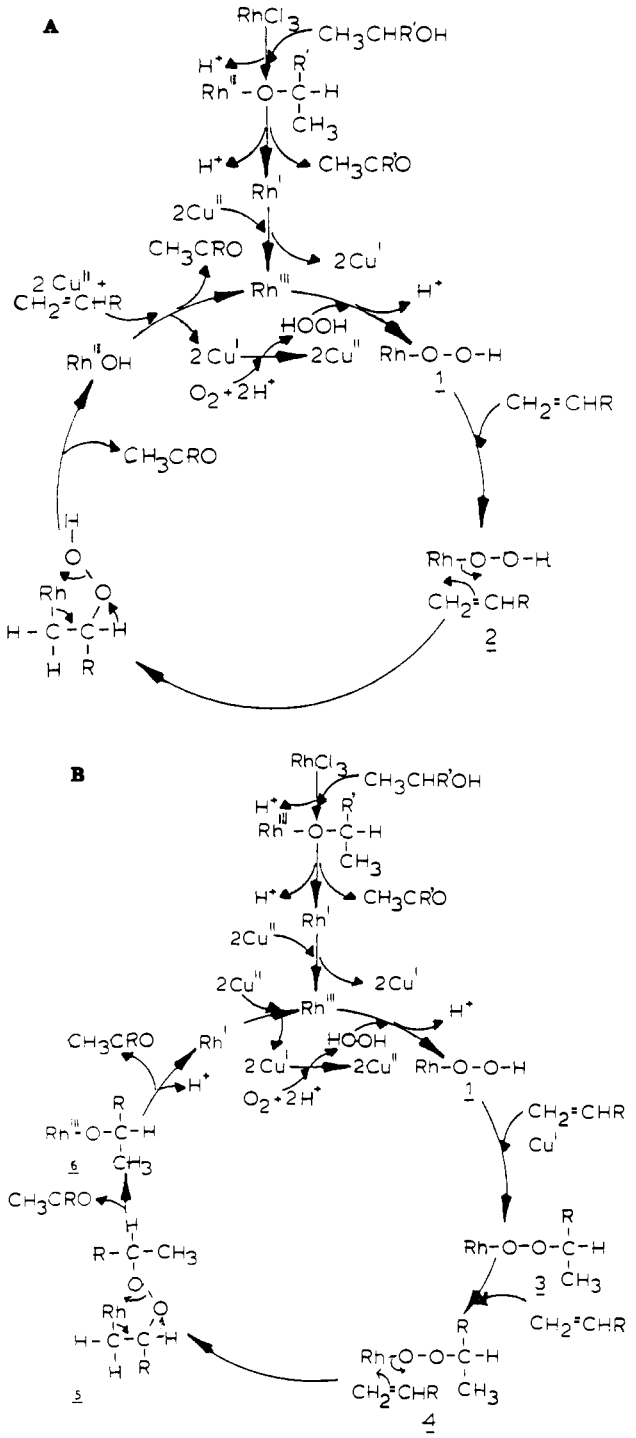

Figure 5. Two suggested mechanisms for the Rh(III)/Cu(II)-co-catalyzed O_2 oxidation of terminal olefins.

we do not understand these details in Wacker chemistry.

In the second proposal (Figure 5B) copper(I) catalyzes the addition of RhOOH to the olefinic double bond of an alkene, producing a rhodium alkylperoxidic species, **3**. Cu(I) is well known to bind olefins,[13] including 1-hexene,[14] making them more electrophilic. An excess of olefin may stabilize these adducts.[13,14] MOOR species similar to **3** have been characterized for M = Ir,[15] Co,[16,17] Pd,[10,18,19] and Pt.[18,20] Some are capable of oxidizing terminal olefins to methyl ketones.[18,19-22] Intermediate **3** may attack a second mole of alkene to form the four-center-type of intermediate **4**. In this case, the product is ketone and a Rh(III) alkoxy species **6** which decomposes as in the catalyst formation step to form Rh(I) and ketone. Electron transfer from Rh(I) to copper(II) completes the cycle, reforming $RhCl_2^+$ and Cu(I).

Conclusion

A detailed study of the rhodium-catalyzed oxidation of 1-hexene to 2-hexanone indicates that solvent reduction of O_2 to H_2O_2 is a key feature of this process of dioxygen activation. The effectiveness of H_2O_2 to effect both the rhodium- and rhodium/copper-catalyzed reactions supports the intermediacy of coordinated peroxo complexes in the reactions. These studies demonstrate that the rhodium system utilizes only one of the oxygen atoms of O_2 to form ketone in contrast to the rhodium/copper system which uses both. Some key roles that copper plays to account for this difference and the enhanced rates of the rhodium/copper system are proposed. These involve a role in generating the Cl_2Rh^{III} catalyst, in catalyzing the reduction of O_2 to peroxide, and in effecting oxidation by the second oxygen atom of O_2 either by facilitating a Wacker-type of process or catalyzing double-bond addition.

Experimental Section

All solvents and reagents were of reagent grade and were used without further purification. Olefins were passed through a column containing active alumina to remove peroxidic impurities before use. $RhCl_3 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were purchased from Alfa. $[Rh(CO)_2Cl]_2$ was prepared as reported in the literature.[23] Hydrogen peroxide and *tert*-butyl hydroperoxide were used as 30% and 70% aqueous solutions, respectively, and were standardized iodometrically.

GLC Spectra were obtained with a Varian Model 3700 instrument fitted with a flame ionization detector with a 3-m, $^1/_8$ in. o.d. stainless steel column prepacked with Chromasorb P supported diethylene glycol adipate. For the detection of acetone a column temperature of 70 °C was employed, and for measurement of 2-hexanone a temperature of 100 °C was used. The production of 2-hexanone was quantitated by using 2-heptanone or 2-octanone as an internal standard.

Catalytic Oxidations of 1-Hexene. (A) Ambient O_2 Pressure Experiments. The oxidations of 1-hexene at ambient pressures of O_2 were monitored on the O_2-uptake apparatus previously described.[24] The manometer was filled with the solvent employed for the catalytic oxidation (ethanol or 2-propanol). The reaction was run in a three-necked round-bottomed flask to allow sampling through a septum. Aliquots were examined for oxidation products with GLC, with 2-heptanone or 2-octanone as internal standards.

A typical reaction was run as follows: To a 50-mL three-necked round-bottomed flask were added 0.111 mmol of rhodium(III) trichloride (as $RhCl_3 \cdot 3H_2O$ or $RhCl_3 \cdot 2H_2O \cdot CH_3CH_2OH$[6]), 0.71 mmol of 2-heptanone (as internal standard), and 22.5 mL of ethanol. Solutions were purged for 30 min with bubbling O_2, and reactions were initiated by the addition of 7.5 mL of 1-hexene substrate.

(B) O_2 Experiments at 40 psi. Catalytic oxidations at 40 psi of O_2 were carried out with 250-mL Parr pressure bottles equipped with brass Swagelok pressure heads as previously described.[6] This allows periodic sampling of reaction solution for examination by GLC.

Reaction solutions were prepared as described above for 1-atm experiments, except oxidations were initiated by submerging in a 40 °C oil bath rather than by adding 1-hexene to preheated solutions.

Determination of Acetone Production. The measurement of acetone produced in the Rh- and Rh/Cu-catalyzed oxidations of 1-hexene with 2-propanol solvent was made by GLC as described above. Water determination was made with a Varian Model 3700 gas chromatograph fitted with a thermal conductivity detector with a 2-m stainless-steel column prepacked with Porapak Q.

(13) (a) Herberhold, M. "Metal π Complexes"; Elsevier: New York, 1974; Vol. II, Part 1, pp 227-232. (b) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522 and references therein.
(14) Pasquoli, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *Inorg. Chem.* **1979**, *18*, 3535.
(15) Booth, B. L.; Hazeldine, R. N.; Meuss, G. R. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1074.
(16) Nishinaga, A.; Nishizawa, K.; Tomita, H.; Matsurra, T. *J. Am. Chem. Soc.* **1977**, *99*, 1287.
(17) Giannotti, C.; Fontaire, C.; Chiapori, A.; Riche, C. *J. Organomet. Chem.* **1976**, *113*, 57.
(18) Strukul, G.; Renzo, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495.
(19) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387.
(20) Bregeault, J. M.; Mimoun, H. *Nouv. J. Chim.* **1981**, *5*, 287.
(21) Sheldon, R.; Van Doorn, J. A. *J. Catal.* **1973**, *31*, 427.
(22) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; 935.
(23) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.
(24) Drago, R. S.; Gaul, J.; Zombeck, A.; Straub, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 1033.

Determination of 1-Hexene Isomerization. 1-Hexene and *cis*- and *trans*-2-hexene were identified by GLC with a 3-m, $^1/_8$ in. o.d. stainless-steel column prepacked with 0.2% Carbowax on carbopack. A column temperature of 130 °C was used.

Catalytic Oxidations with H_2O_2. The experimental procedure used for these oxidations was as follows, using experiment 3 as a specific example: a solution of 0.0336 g of $RhCl_3 \cdot 3H_2O$ (0.128 mmol), 4.00 mL of ethanol, and 0.14 mmol of 2-heptanone or 2-octanone (GLC internal standard) was purged for 60 min with argon and heated to 40 °C for 7 min, and 0.63 mL of 0.63 M H_2O_2 (diluted in ethanol from aqueous 5 M H_2O_2) (0.398 mmol of H_2O_2) was added. This was immediately followed by the addition of 1.30 mL of alumina purged 1-hexene to initiate reaction.

Acknowledgment. The authors acknowledge the support of this research by the National Science Foundation through Grant 84-08149.

Registry No. $RhCl_3$, 10049-07-7; Cu, 15158-11-9; 1-hexene, 592-41-6.

Steric and Electronic Effects of Ligand Variation on Cobalt Dioxygen Catalysts

Barry B. Corden,[†] Russell S. Drago,*[‡] and Richard P. Perito[†]

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611, and the Department of Chemistry, Fred Stark Pearson Laboratory, Tufts University, Medford, Massachusetts 02155. *Received March 5, 1984*

Abstract: We report herein the observation that electronic and steric factors of cobalt dioxygen complexes with systematically derivatized pentadentate Schiff-base ligands affect their ability to catalyze the oxidation of substituted phenols and alter the rate of catalyst decomposition. The electronic and steric factors can be separated sufficiently to indicate that the activity of the cobalt dioxygen catalyst roughly parallels the trends in basicity of the bound O_2 suggested by EPR cobalt hyperfine coupling constants of the adducts and predicted from the electronic effects of substituents.

In recent work from this laboratory[1,2] a spin-pairing (radical coupling) model has been proposed to account for the binding of O_2 to transition-metal complexes. One of the unique aspects of this model is the relationship of the negative charge on the bound O_2 (expressed as electron transfer) to the ligand field strength of the groups coordinated to cobalt(II). Interpretation of the EPR spectra of various Co–O_2 adducts indicates[1] a very substantial variation in the extent of electron transfer leading to semiquantitative estimates of 0.1 to 0.8 fractional negative charge on the bound O_2. These differences should lead to variations in the basicity,[3] nucleophilicity, and radical reactivity of the coordinated O_2. Such variations should have significant implications for understanding the catalysis of certain biological[4a–d] and industrial oxidations.[4e–g]

The design of a system to probe variation in the reactivity of a bound O_2 is complicated. The metal-bound O_2 must be implicated in the reaction mechanism, and variation in its electronic properties must influence the rate or product distribution. One candidate for study involves the fairly well understood[5–7] catalytic oxidation of 2,6-disubstituted phenols to the corresponding quinones by cobalt(II) Schiff base complexes. A recent study[7] of the kinetics and mechanism of the oxidation of 2,6-dimethylphenol (DMP) by CoSMDPT (Figure 1) in the presence of molecular oxygen indicates that the active catalyst plays a role in two different steps in the reaction: first in initiating the reaction through hydrogen atom abstraction to form the phenoxy radical and then in the rate-determining step where the phenoxy radical combines with the cobalt-dioxygen complex which decomposes quickly to the quinone. This scheme is summarized in Figure 1.

The kinetic rate law determined for the oxidation of DMP by CoSMDPT in toluene at 25 °C with this mechanism is consistent and is given in eq 1. The value of k_T is 2.1×10^{-3} $(M^2\ s)^{-1}$ if

$$d[BQ]/dt = k_T[Co][O_2][DMP] \quad (1)$$

it is assumed that the catalyst is completely oxygenated, and no catalyst is decomposed during the period of initial rate data accumulation. Materials such as 2,2,2-trifluoroethanol that are more effective at hydrogen bonding to the bound O_2 than DMP inhibit the reaction. The phenoxy radicals couple to produce diphenoquinone via step e when step d is slowed, for example, by decreasing the cobalt–O_2 concentration.

In addition to reactivity trends, the influence of ligand variation on catalyst stability may provide insight into the nature of its decomposition. The CoSMDPT oxidation of DMP undergoes about 70 turnovers and slowly dies thereafter. Addition of a base (Na_2CO_3) slows the catalyst decomposition by about fourfold. The oxygen content of the spent catalyst is elevated to a 6:1 O/Co ratio compared to the 2:1 ratio present in the original catalyst, CoSMDPT.[7] It is proposed that hydrogen peroxide formed from decomposition of HO_2 in step d oxidizes and cleaves the ligand leading to carboxylic acids.

According to the proposed mechanism,[7] the metal complex plays two important roles in the catalysis of the oxidation: (1) coordination activates the O_2 molecule and enhances its basicity and

[†] Tufts University.
[‡] University of Florida.

(1) Tovrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144.
(2) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353 and references therein.
(3) Drago, R. S.; Cannady, J. P.; Leslie, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 6014.
(4) (a) Eichhorn, G. L., Ed. "Inorganic Biochemistry"; Elsevier Scientific: New York, NY, 1973. (b) Ochiai, E. "Bioinorganic Chemistry"; Allyn and Bacon: Boston, MA 1977. (c) Spiro, T. G., Ed. "Metal Ion Activation of Dioxygen"; Wiley: New York, NY 1980. (d) Musso, H. "Oxidative Coupling of Phenols"; Taylor, W. I., Pattersby, A. R., Eds.; Marcel Dekker: New York, NY 1967. (e) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272. (f) Benson, D. "Mechanisms of Oxidations by Metal Ions"; Elsevier Scientific: New York, NY 1976. (g) Nishinaga, A. "Fundamental Research in Homogeneous Catalysis"; Ishi, Y., Tsutsui, M., Eds.; Plenum Press: New York, NY, 1978.
(5) (a) Nishinaga, A.; Tomia, H. *J. Mol. Catal.* **1980**, *7*, 179. (b) Hay, A. S. *J. Polym. Sci.* **1962**, *58*, 581.
(6) VanDort, H. M.; Guerson, H. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 529.
(7) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580 and references therein.

0002-7863/85/1507-2903$01.50/0 © 1985 American Chemical Society