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# Specific Oxidation of $[Rh(CO)_2Cl]_2$ by $O_2$ via the Coordination of in Situ Generated HOOH. Implications for the Rh(III)/Cu(II)-Catalyzed $O_2$ Oxidation of 1-Alkenes to 2-Ketones

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**Abstract**: The oxidation of 1-hexene to 2-hexanone catalyzed by Rh(III)/Cu(II) mixtures is investigated. In order to study the reactions that rhodium undergoes to form an active catalyst, $[Rh(CO)_2Cl]_2$ (A) is used as a catalyst precursor. A number of results are obtained that indicate that this species must be converted to a rhodium(III) complex before catalysis occurs. With A as a catalyst precursor in the absence of Cu(II), long induction periods are observed for catalytic oxidations. Rhodium(I) is oxidized to rhodium(III) chloride during the induction period. Furthermore, at higher chloride/rhodium ratios (up to a 10:1 mole ratio), greater initial rates and catalyst stabilities are found. These observations are used as partial justification for characterizing rhodium(III) as an active catalyst in the oxidation of 1-hexene to 2-hexanone. The oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) chloride is investigated in detail. An unusual mechanism for this reaction is proposed. Hydrogen peroxide, produced in situ from the reduction of $O_2$ by alcohol solvent, oxidizes $[Rh(CO)_2Cl]_2$. An intermediate hydroperoxide complex is formed in the course of the oxidation to rhodium(III) which contains a coordinated carbonyl ligand [Rh(CO)(OOH)(?)] (B). This intermediate is studied in dilute solution and is found to decompose immediately when attempts are made to isolate it. Very few stable hydroperoxide and alkylperoxide complexes of the platinum metals have been reported; some are capable of oxidizing terminal olefins to 2-ketones. In contrast, the oxidation of $[Rh(C_8H_{14})_2Cl]_2$ to rhodium(III) chloride under identical conditions is much faster and proceeds by a mechanism avoiding detectable quantities of this hydroperoxo intermediate, while $[Rh(P(tolyl)_3)(CO)Cl]_2$ is not oxidized even after 48 h. The oxidation of A to B occurs only in solvents capable of reducing $O_2$.

## Introduction

Over the past several years a number of rhodium catalyzed oxidations of hydrocarbons by dioxygen have been reported which appear to involve neither free radical autoxidation processes nor simple Wacker chemistry.[1] Included in this class of non-free radical oxidations is the Rh(III)/Cu(II)-cocatalyzed oxidation of terminal olefins to 2-ketones with ≥98% specificity[1a] (reaction 1). Mimoun and co-workers[1a,b] proposed a reaction mechanism

$$2CH_2{=}CHR + O_2 \rightarrow 2CH_3C(O)R \tag{1}$$

for this system involving coordination of both $O_2$ and olefin to a rhodium(I) catalyst, a rearrangement to a peroxymetallocycle, and conversion to a rhodium(III) oxo complex and 1 equiv of ketone. The rhodium(I) catalyst is reformed by converting a second alkene to ketone, using the oxo complex in a Wacker type process. Within the class of non-free radical oxidations, this Rh(III)/Cu(II) catalyst system is unique for a number of reasons. The utilization of both atoms of molecular oxygen to form the desired oxidation products (ketone in this case) is most noteworthy. Other features include the dependence of the reaction on ethanol or isopropyl alcohol as solvents (apparently for their reduction properties), the need for 3 equiv of chloride ion and an equivalent of Cu(II) for maximum activity, and the observation that $RhCl_3{\cdot}3H_2O$ as the precursor produces a catalyst of greater activity than does a rhodium(I) complex. The Rh(III)/Cu(II)-catalyzed olefin oxidation system is also much more efficient, specific, and stable than previously reported non-free radical systems.

Mimoun proposed that the catalyst in the Rh(III)/Cu(II) oxidation system is a rhodium(I) complex produced from the ethanol reduction of $RhCl_3$ and Cu(II) in the initiation step shown in eq 2. The following observations led to this proposal: (1) active

$$\begin{aligned} RhCl_3 + 2CH_2{=}CHR + Cu(ClO_4)_2 + 1.5CH_3CH_2OH \rightarrow \\ [Rh(CH_2{=}CHR)_2]ClO_4 + CuCl_{(s)} + HClO_4 + 2HCl + \\ 1.5CH_3CHO \end{aligned} \tag{2}$$

catalysts are formed by using $[Rh(C_8H_{14})_2Cl]_2$ in the presence of 2 equiv of HCl instead of $RhCl_3{\cdot}3H_2O$, (2) an amount of acetaldehyde roughly equal to the moles of catalyst used is produced from ethanol oxidation at the beginning of the catalytic reaction, and (3) 85% of the Cu(II) precipitates as CuCl at the beginning of the 1-hexene oxidation. It is proposed that this reduced rhodium(I) complex coordinates dioxygen to initiate the reaction in eq 1.

We used[2] the suggestion that the active catalyst was a rhodium(I) complex to prepare a silica gel–organosulfide-supported rhodium(I) carbonyl complex, $[SG]{-}SRh(CO)_2S_n'$ ($S' \equiv$ solvent). It was found[2] that this heterogenized complex produces an active and surprisingly stable catalyst for the oxidation of 1-hexene to 2-hexanone. During the course of our investigation of reaction 1 using $[SG]{-}SRh(CO)_2S_n'$ as the catalyst, we also studied the analogous homogeneous catalytic oxidation using $[Rh(CO)_2Cl]_2$ as the precursor and made a number of observations which cannot be accommodated by the proposed initiation step (eq 2). In the first part of this article, we discuss these experiments and propose a new characterization of the active catalyst as a rhodium(III) chloride complex. This proposal is consistent with both the earlier[1a] and presently reported results.

Our determination that the rhodium species that initiates oxidation of 1-hexene by $O_2$ is a rhodium(III) chloride complex includes an investigation of the oxidation of the rhodium(I) precursor $[Rh(CO)_2Cl]_2$ by $O_2$ to a rhodium(III) chloride, both in the presence and absence of 1-hexene. The formation of the active catalyst for 1-hexene oxidation correlates with the oxidation of Rh(I) to Rh(III). This oxidation of $[Rh(CO)_2Cl]_2$ exhibits interesting characteristics, and a thorough study of the reaction of $O_2$ with $[Rh(CO)_2Cl]_2$ to form $RhCl_3$ in the absence of 1-hexene revealed an unusual mechanism. The second part of this article presents the results of this study, which indicate the oxidation of $[Rh(CO)_2Cl]_2$ occurs via the coordination of HOOH, produced in situ from the ethanol reduction of $O_2$.

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[†] University of Florida.

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(1) (a) Mimoun, H.; Machirant, M. M. P.; de Roch, I. S. *J. Am. Chem. Soc.* **1978**, *100*, 5437. (b) Mimoun, H.; Igersheim, F. *Nouv. J. Chem.* **1980**, *4*, 161. (c) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, *883*. (d) Farrar, J.; Holland, D.; Milner, D. J. *Ibid.* **1975**, *815*. (e) Farrar, J.; Holland, D.; Milner, D. J. *Ibid.* **1975**, 2440.

(2) Nyberg, E. D.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 4966.

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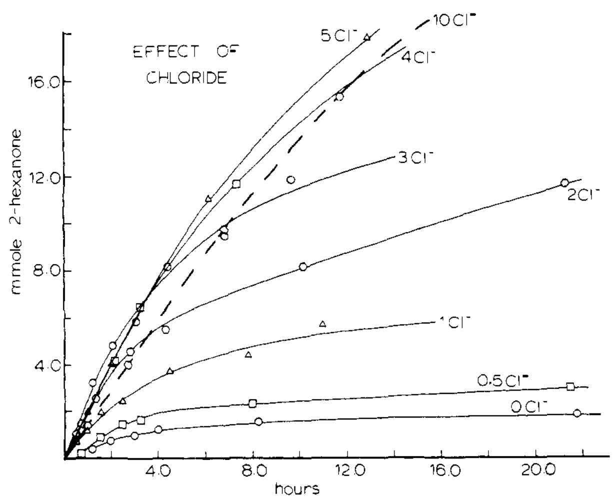

**Figure 1.** Reactions were run with 1.21 mM $[Rh(CO)_2S'_n]BF_4$, 1.21 mM $Cu(NO_3)_2{\cdot}2.5H_2O$, 2.43 mM $H_2SO_4$, 9.31 mM 2-heptanone (as internal standard), and 61 mL of 3/1 (v/v) ethanol/1-hexene solvent/substrate. The amounts of chloride used (as NaCl) are shown in the figure as equivalents relative to rhodium. Reactions were carried out at 70 °C, 3.7 atm of $O_2$.

## Results and Discussion

**Characterization of the Catalyst as a Rhodium(III) Chloride Complex.** The rhodium carbonyl dimer (A) was selected as the catalyst precursor due to the facile loss of the CO ligands in the presence of $O_2$, the presumed need for a rhodium(I) catalyst to coordinate $O_2$ and olefin, and the usefulness of the CO ligands for infrared analyses. Employing A as a homogeneous catalyst for reaction 1 at various chloride concentrations and in the presence of Cu(II) at 70 °C, the data in Figure 1 was obtained. Note that the maximum initial 1-hexene oxidation rate (indicated by the amount of 2-hexanone produced) is achieved using a chloride/rhodium mole ratio of 3:1, as was originally reported for this system at 40 °C.[1a] However, increasing the chloride/rhodium ratio to 5:1 at 70 °C causes a considerable increase in catalyst stability with little change in the initial rates, in contrast to the result obtained at 40 °C, where a large drop in activity was found for the 5:1 ratio. (For example, after 20 h at 70 °C with a 3:1 Cl/Rh mole ratio, the catalytic activity is only 7.5% of the initial value, while after the same time period with a 5:1 Cl/Rh ratio the activity is 34% the initial rate.) Increasing the chloride/rhodium ratio to 10 causes an even further increase in catalyst stability at 70 °C (the activity after 20 h is 51% of the initial rate). A similar beneficial effect of increasing the Cl:Rh ratio to 5:1 was observed in analogous experiments with Cu(II) absent. This suggests that a specific interaction of chloride with rhodium and not copper leads to catalyst improvement. Furthermore, the marked dependences of both initial rate and catalyst stability on such large chloride concentrations suggest a rhodium(III)–chloride interaction. These results, along with others to be presented, indicate that a rhodium(III) chloride complex is the catalyst or the immediate precursor.

Further evidence of the rhodium(III) nature of the species that initiates catalysis was obtained from a study of the oxidation of 1-hexene at 70 °C using $[Rh(CO)_2Cl]_2$, $H_2SO_4$, and NaCl at various pressures of dioxygen in the complete absence of Cu(II). As is evident in Figure 2, the oxidation of 1-hexene to 2-hexanone is efficiently catalyzed at 70 °C in the absence of Cu(II). In contrast, copper(II) is needed[1a] for facile reaction at 40 °C. Most significantly an induction period of 1–4 h always precedes the formation of 2-hexanone in the rhodium-only system. The length of the induction period depends to the first order on the dioxygen pressure and is accompanied by a change of solution color from light yellow (characteristic of A) to bright orange [typical of rhodium(III) chloride complexes[3]]. The use of $RhCl_3{\cdot}3H_2O$ rather than A, or the addition of as little as 0.1 equiv of Cu(II), results in the elimination of this induction period. These observations are consistent with an oxidation of A by dioxygen over the course of the induction period forming a rhodium(III) chloride complex which is either the active catalyst or an immediate precursor.

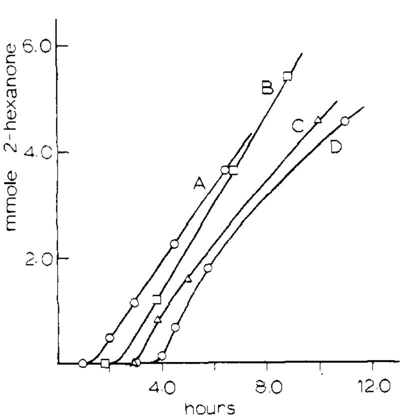

**Figure 2.** Reaction conditions are the same as those employed for Figure 1, using a 5:1 Cl/Rh mole ratio in the absence of Cu(II). The $O_2$ pressures are for A, 3.7 atm; B, 1.9 atm; C, 1.4 atm; and D, 1.0 atm.

A more direct determination of the character of the active rhodium catalyst was obtained from the reaction of $[Rh(CO)_2Cl]_2$, dioxygen, and HCl in ethanol solvent at 40 °C, and in the absence of 1-hexene. After 12 h a bright orange complex (C), isolated as $RhCl_3(H_2O)_2{\cdot}CH_3CH_2OH$, was obtained from reaction 3. The

$$[Rh(CO)_2Cl]_2 + 4HCl + 2O_2 + 4CH_3CH_2OH \rightarrow RhCl_3(H_2O)_2{\cdot}CH_3CH_2OH + 2CH_3CHO + 4CO \quad (3)$$

rhodium product was characterized by elemental analysis, molecular weight determination, and its infrared and visible spectra.[4] The stoichiometry for reaction 3 was verified in both A and HCl, but this was not possible for $O_2$, $CH_3CH_2OH$, and $CH_3CHO$ due to the catalysis of reaction 4 by C (vide infra). The addition of

$$2CH_3CHROH + O_2 \rightarrow 2CH_3CRO + 2H_2O \quad (4)$$
$$R \equiv CH_3 \text{ or } H$$

an equivalent of Cu(II) or the use of $[Rh(C_8H_{14})_2Cl]_2$ as the rhodium(I) precursor considerably speeds up reaction 3 (vide infra) but does not affect its outcome. Compound C catalyzes the oxidation of 1-hexene to 2-hexaone as efficiently as $RhCl_3{\cdot}3H_2O$ and without the occurrence of the induction period observed when using A as the catalyst precursor under identical conditions (see Figure 2). The observed solution color changes and other results described above, indicate that under reaction conditions for the catalytic oxidation of 1-hexene (reaction 1), the rhodium(III) complex (C) is produced from the oxidation of the rhodium(I) complex (A). An explanation for the role of copper(II) and a more detailed study of reaction 3 will be discussed in the second part of this article.

To rule out the possibility that $RhCl_3{\cdot}3H_2O$ (or C) may be subsequently reducd to a rhodium(I) complex by alcohol solvent to initiate catalysis (as proposed by Mimoum in reaction 2), we investigated the initiation step using $RhCl_3{\cdot}3H_2O$ and $Cu(NO_3)_2{\cdot}2.5H_2O$ as precursors. For our study we chose isopropyl alcohol as solvent since upon oxidation this alcohol forms acetone which is much easier to quantitatively measure than the more volatile acetaldehyde (produced from ethanol). Using GLC, we found that in the presence of 1 equiv of Cu(II) only 0.5 equiv of acetone is produced immediately on mixing all reagents necessary for the catalytic oxidation of 1-hexene and that its concentration remains constant for at least 0.5 h. From this result we can rule out the simultaneous reduction of Rh(III) and Cu(II) proposed

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(3) Wolsey, W. C.; Reynolds, C. A.; Kleinberg, J. *Inorg. Chem.* **1963**, *2*, 463.

(4) When the mixture was in ethanol for 96 h the electronic absorption band for $RhCl_3{\cdot}3H_2O$ at 510 nm shifts to 483 nm which is very similar to that found for C (at 480 nm). This posssibly may be due to a substitution of one $H_2O$ in $RhCl_3{\cdot}3H_2O$ by an ethanol molecule.

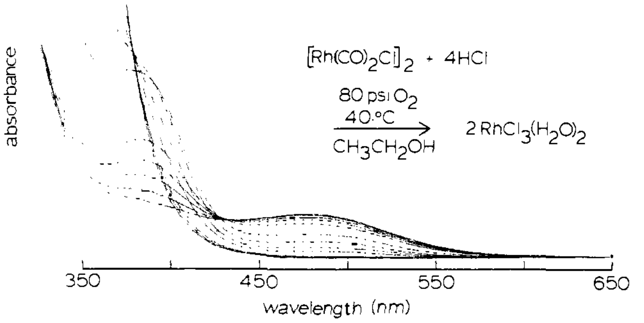

**Figure 3.** $[Rh(CO)_2Cl]_2$ concentration is $0.98 \times 10^{-3}$ M. Spectra were recorded over a 12-h period.

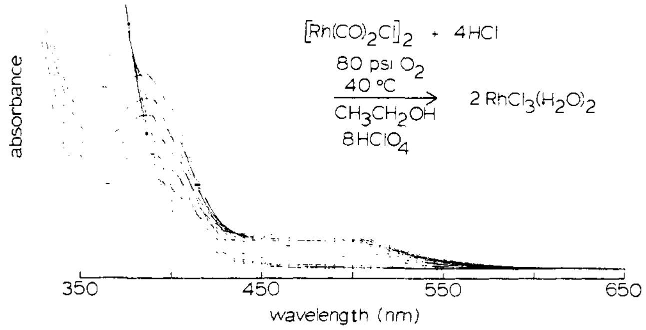

**Figure 4.** Same conditions as in Figure 3 but with added $HClO_4$ to $7.84 \times 10^{-3}$ M.

in reaction 2 because this would require the oxidation of 1.5 equiv of isopropyl alcohol. We propose that reaction 5 initiates the

$$Cl^- + Cu^{2+} + 0.5(CH_3)_2CHOH \xrightarrow[\text{isopropyl alcohol, 1-hexene}]{\text{1 atm } O_2 \text{ at 40 °C}} CuCl_{(s)} + 0.5(CH_3)_2CO + H^+ \quad (5)$$

catalytic cycle for this system when $RhCl_3 \cdot 3H_2O$ is used as the catalyst precursor. Our proposal requires that only enough reducing equivalents are provided by isopropyl alcohol for the reduction of $Cu^{2+}$ to form CuCl. Copper(I) chloride may be isolated from the reaction mixture in 85% yield without affecting the catalytic oxidation.[1a]

**Mechanism of the $O_2$ Oxidation of $[Rh(CO)_2Cl]_2$ to Rhodium(III) Chloride.** The oxidation of $[Rh(CO)_2Cl]_2$ (A) to rhodium(III) trichloride (C) by $O_2$ was originally studied because of our interest in characterizing the active catalyst for the Rh/Cu-cocatalyzed 1-hexene oxidation (reaction 1). Copper(II) was excluded in these initial investigations to facilitate the interpretation of the electronic absorption spectra, elemental analysis, and molecular weight data. The substrate 1-hexene was excluded from these solutions to avoid its catalytic oxidation to 2-hexanone after the formation of the rhodium(III) chloride product. As described in the previous section, the exclusion of Cu(II) and 1-hexene during these studies proved to be quite useful for characterizing the rhodium catalyst. The oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) chloride was generally monitored by electronic absorption spectroscopy in order to determine the reaction's end point. In the course of these studies it was found that at elevated $O_2$ pressures (3–5 atm) an unusual intermediate exhibiting a visible absorption band at 385 nm could be detected. This observation led to a detailed investigation of the mechanism of the $O_2$ oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) chloride in reaction 3, and the results are presented below.

The electronic spectral changes accompanying the oxidation of the $[Rh(CO)_2Cl]_2$ (A) to rhodium(III) chloride (C) in the absence of both Cu(II) and 1-hexene is shown in Figure 3 as a series of spectra recorded over the course of the reaction. The growth and decay of an intermediate (B) with an absorbance at 385 nm is noted. The charge-transfer band beginning at the shortest wavelength is a result of A, while the band at 480 nm is produced by C. As shown in Figure 4, intermediate B is more stable in the presence of excess Brønsted acid ($8HClO_4$/A). The presence of two isosbestic points (at 377 and 435 nm) in both Figures 3 and 4 suggests the formation and subsequent reactivity of only one intermediate. The isosbestic point at 377 nm is a result of the reaction of A to form B at the beginning of reaction 3 (before much final product C has been formed). Early in the reaction the decomposition of B to C becomes quite pronounced, and this point disappears. The second isosbestic point emerges at 435 nm when all A has been consumed and results from the exclusive reaction of B to form C.

The initial rate of formation of B was found by visible spectroscopy to follow the rate expression shown in eq 6, which is

$$\frac{-d[A]}{dt} \text{ or } \frac{-d[B]}{dt} = k[H^+][O_2] \quad (6)$$

independent of the concentration of A. The zero-order dependence on [A] rules out a mechanism involving initially the formation of a rhodium hydride followed by the insertion of dioxygen to form a rhodium hydroperoxide intermediate, which occurs with $K_2[RhH(CN)_4(H_2O)]$,[5e] and is proposed in two other studies.[6] The rate law in eq 6 is surprising because it indicates that the initial step or steps in reaction 3 (those including and preceding the rate-determining step) involve a reaction between $H^+$, $O_2$, and possibly $CH_3CH_2OH$, forming an intermediate oxidant which subsequently reacts with $[Rh(CO)_2Cl]_2$.

We investigated the possibility that peroxide could play the role of direct oxidant in reaction 3. This was confirmed by experiments involving the titration of A with HOOH to form C in the absence of dioxygen, monitored by visible spectroscopy (reaction 7, in which

$$[Rh(CO)_2Cl]_2 + 4HCl + 2HOOH + S' \rightarrow 2RhCl_3(H_2O)_2 \cdot S' + 4CO \quad (7)$$

S′ is solvent). Because HOOH slowly disproportionates or is reduced in ethanol, as well as being consumed in a competing side reaction (vide infra), the oxidation of A to C in this solvent goes to only 70% completion. Very significantly the oxidation of A by HOOH proceeds with the formation of the same intermediate [B] as produced with $O_2$ as oxidant, indicating that reaction 7 and reaction 3 occur through similar mechanisms. The kinetic rate law for reaction 7 was determined by using Fourier transform infrared spectroscopy (FT IR) to monitor the consumption of A, and is shown in eq 8. Several reports describe the reaction between

$$-d[A]/dt = k([Rh(CO)_2Cl]_2)[HOOH] \quad (8)$$

a metal complex and peroxide to form a coordination compound.[5a–d] The reaction in eq 7 proceeding as described above would exhibit the rate law shown in eq 8. On the basis of these arguments and those that follow, we propose that intermediate B results from the coordination of HOOH to $[Rh(CO)_2Cl]_2$. A proton NMR analysis at −70 °C showed no evidence for B possessing a hydride ligand. Any hydride species generated from the oxidative addition of HOOH to A apparently are acidic, and fast exchange of all protons with the alcohol solvent is very likely occurring.

The characterization of B was assisted by an FT IR spectroscopic study of reaction 7. Immediately on adding HOOH to a solution of A and HCl in ethanol, the formation of a complex exhibiting a CO stretching band at 2102 $cm^{-1}$ is observed, and this band increases in intensity at the expense of the bands due to A (at 1995 and 2069 $cm^{-1}$; Figure 5). The growth and subsequent decay of the CO band at 2102 $cm^{-1}$ was found to correlate directly with the band due to B at 385 nm observed in the elec-

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(5) (a) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495. (b) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (c) Michelin, R. A. *Inorg. Chim. Acta* **1979**, *37*, L491. (d) Booth, B. L.; Haszeldine, R. N.; Neuss, G. R. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1074. (e) Roberts, H. L.; Symes, W. R. *J. Chem. Soc. A* **1968**, 1450. (f) Tatsumo, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832.

(6) (a) Johnston, L. E.; Page, J. A. *Can. J. Chem.* **1969**, *47*, 4241. (b) Grundy, K. R.; Laing, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1500.

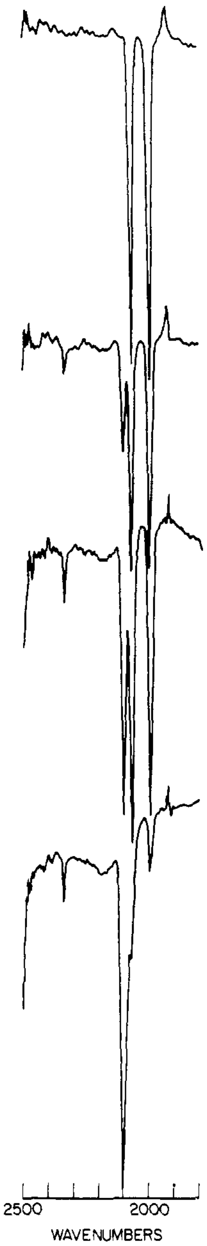


**Figure 5.** Spectra were recorded over a period of 1.83 h. Top spectrum is that for $[Rh(CO)_2Cl]_2$. Reaction was run with $0.84 \times 10^{-3}$ M $[Rh(CO)_2Cl]_2$, $3.34 \times 10^{-3}$ M HCl, 25 mL of ethanol, 1 atm of $O_2$, 40 °C, and initiated by the addition of HOOH to $1.67 \times 10^{-3}$ M. From top to bottom, spectra were recorded at 0, 0.25, 0.55, and 1.83 h.

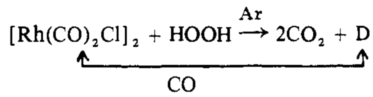
tronic absorption spectra. Therefore, intermediate B retains one CO ligand. The assignment of the band at 2102 $cm^{-1}$ to coordinated CO was confirmed by use of $^{13}CO$ in the experiment.

That B is a hydroperoxo rather than a $\mu$-peroxo complex is evidenced by our ability to substitute *tert*-butyl hydroperoxide (*t*-BuOOH) for HOOH in reaction 7 to obtain a much slower reaction and the formation of an intermediate analogous to B with an electronic absorption band at about 385 nm[7] and an infrared CO stretch at 2099 $cm^{-1}$, 3 $cm^{-1}$ lower than that found for B with HOOH. Since *t*-BuOOH is not known to bridge two rhodium species in the $\mu$-peroxo configuration, we suggest that B is not a $\mu$-peroxo complex. Only a limited number of stable hydroperoxide and alkyl peroxide complexes of the platinum metals have been reported[5] (not including those with Schiff base or bio-type ligands), and some of these are capable of oxidizing terminal olefins to 2-ketones.[5a,b] Intermediate B is only formed in the presence of HCl and is not formed on substituting either $HClO_4$ or $N(C_2H_5)_4Cl\cdot H_2O$ for HCl. Thus, both a proton and an additional chloride are required in the formation of the intermediate. We propose that intermediate B is $H_2[Rh(CO)Cl_2(OOH)]$, produced as shown in eq 9. Use of the oxidation state formalism

$$[Rh(CO)_2Cl]_2 + 2HOOH + 2HCl \rightarrow 2H_2[Rh(CO)Cl_2(OOH)] + 2CO \quad (9)$$

to describe these species is potentially misleading. An oxidative addition of HOOH to a Rh(I) complex produces $HRh^{III}OOH$. Deprotonation generates $Rh^{I}OOH^-$. In this formalism, we propose that $H_2[Rh(CO)Cl_2(OOH)]$ is a rhodium(I) complex. After a number of attempts we have not been able to observe the O–O stretch between 800 and 900 $cm^{-1}$ expected for a coordinated peroxo group in the infrared spectrum. This is due to the low concentrations we must employ to stabilize this intermediate, the poor window in this region of the infrared spectrum for ethanol solvent, and the hydrogen bonding in this system which would broaden this band. When the intermediate is generated with $O_2$ and excess $O_2$ is removed, it spontaneously decomposes to rhodium(III) chloride over several hours. This is consistent with the formulation of this intermediate as $H_2[Rh(CO)Cl_2(OOH)]$, for this species possesses two oxidizing equivalents in the peroxo (or hydroperoxo) ligand.

Intermediate B is not formed in the absence of HCl in reaction 7, but the reaction in eq 10 occurs under argon, producing free



$$[Rh(CO)_2Cl]_2 + HOOH \xrightarrow{Ar} 2CO_2 + D \quad (10)$$
$$D \xrightarrow{CO} [Rh(CO)_2Cl]_2$$

$CO_2$ from the oxidation of a CO ligand, and a very deep brown rhodium(I) complex (D) exhibiting a broad CO stretching band at 2048 $cm^{-1}$. $[Rh(CO)_2Cl]_2$ could be reformed from D by exposure to a CO atmosphere, and thus the production of $CO_2$ from the CO oxidation by HOOH is catalytic in A in a CO atmosphere. This reaction has been previously reported in benzene,[8] where D precipitates. It is reported[8] that redissolving this solid in ethanol and exposing it to CO leads to the formation of a rhodium(I) carbonyl complex with a spectrum *similar* to A. Reforming $[Rh(CO)_2Cl]_2$ from D under CO is significant because it indicates that D is a rhodium(I) complex and that the irreversible oxidation of rhodium(I) to rhodium(III) by HOOH in ethanol is slow relative to the oxidation of the CO ligands to $CO_2$ (which takes several hours). These results further suggest that in the presence of HCl the reaction between A and HOOH produces the relatively stable rhodium(I) hydroperoxo coordination complex B as an intermediate. In the presence of HCl reaction 7 is faster than reaction 10, and the majority of HOOH is consumed to form B rather than $CO_2$ and D. That reaction 10 does occur to a small extent in the presence of HCl can be seen in Figure 5, in which the band at 2337 $cm^{-1}$ due to $CO_2$ is evident. This competing reaction accounts, at least in part, for the incompleteness noted for the titration of A with HOOH in reaction 7.

The stabilization of B by excess Brønsted acid, evidenced by a comparison of the electronic absorption spectra in Figures 3 and 4, can be explained by considering the deprotonation of the RhOOH group as the initiation step for the reaction of B to form C. A further investigation of the decomposition characteristics of B also proved to be useful. Upon isolation of a mixture of B and C by quick evaporation of a dilute solution to dryness under vacuum, B decomposes within a minute to a wet solid. An infrared spectrum of this product revealed a large concentration of water in addition to a high-energy CO stretching band at 2132 $cm^{-1}$ (shifted from 2102 $cm^{-1}$ for B). These are the results expected from the fast, autocatalytic decomposition of a hydroperoxo complex. The reduction of the hydroperoxo ligand by Rh(I) will produce $H_2O$ and a rhodium (III) carbonyl. This oxidized metal

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[7] This reaction is so slow with *t*-BuOOH that only a low concentration of analogous intermediate builds up, and the electronic absorption band due to it is only poorly resolved. Therefore, we have not obtained an accurate measure of its energy.

[8] Harvie, I. J.; McQuillan, F. J. *J. Chem. Soc., Chem. Commun.* **1976**, 369.

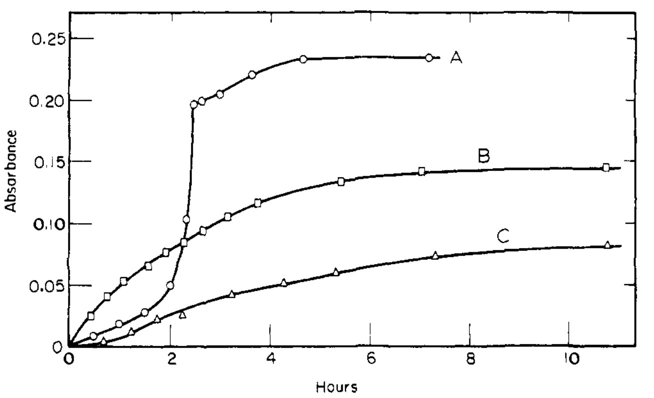

**Figure 6.** Absorbance was monitored for C at 480 nm. Reaction conditions are the same as those in Figure 3. The concentrations in $[Rh(CO)_2Cl]_2$ are for A, 1.47 M; B, 0.98 M; and C, 0.68 M.

complex will be much poorer at $\pi$ back-bonding into the CO than was the rhodium(I) in B, and therefore its stretching frequency would be shifted nearer to that for free CO (at 2143 $cm^{-1}$). Finally, in Figure 6 are presented data which illustrate the effect of increasing the rhodium concentration on the rate of decomposition of the intermediate. This rate was measured by monitoring the electronic absorbance for C at 480 nm. It is evident that at a threshold concentration in A between $0.98 \times 10^{-3}$ M and $1.47 \times 10^{-3}$ M, the reaction of B to form C becomes autocatalytic in character. At $0.98 \times 10^{-3}$ and $0.68 \times 10^{-3}$ M this reaction follows a much more regular course. These results indicate that a free radical decomposition of intermediate B is a sustained process only above the threshold rhodium concentration. Indeed, the electronic absorption spectra indicate that at much higher concentrations, reaction 3 is less specific to the exclusive formation of C. In this case the band at 480 nm for C is present only as a plateau due to the absorbance of a secondary rhodium(III) product which absorbs at lower wavelengths.

The characterization of intermediate B and the rate law in eq 6 have an importance not yet discussed. They indicate that in reaction 3, hydroperoxide is initially formed from the Brønsted acid catalyzed reduction of dioxygen by ethanol or isopropyl alcohol solvents (eq 11). The oxidation of primary and secondary

$$CH_3CHROH + O_2 \rightarrow CH_3CRO + HOOH \qquad (11)$$
$$R \equiv CH_3 \text{ or } H$$

alcohols to aldehydes and ketones using dioxygen has been known for some time.[9,10] These oxidations may be divided into two categories: (1) free radical initiated reactions, using asoisobutyronitrile (AIBN) for example, and (2) metal-catalyzed oxidations. The principal difference is that oxidations of the first type may produce HOOH stoichiometrically[9] (eq 11) as long as precautions are taken to stabilize hydrogen peroxide while oxidations of the second type produce water[10] (eq 4), because the metals which catalyze HOOH formation also catalyze decomposition of hydroperoxides to $H_2O$ and $O_2$ very efficiently. Thus, there is literature precedence supporting our proposal that HOOH is produced (albeit inefficiently) with a Brønsted acid as a catalyst.[11]

Under our reaction conditions the HOOH concentration reaches a very low steady-state value, accounting for the slow initial rate of oxidation of A (eq 3) and our inability to detect HOOH by iodometric techniques in acidic ethanol solutions under $O_2$. However, we have obtained indirect evidence of HOOH production in two series of experiments in which $H^+$, Cu(II) and Rh(III) were checked for their ability to (1) speed up the oxidation of A (eq 3) by producing HOOH catalytically from the alcohol reduction of $O_2$ and (2) catalyze the oxidation of isopropyl alcohol (eq 4) as measured by acetone production. For the investigation of the effect of these three reagents on the rate of oxidation of A (eq 3), we worked at 1 atm rather than at 80 psi of $O_2$ (5.4 atm) because the reaction is much slower at this reduced pressure. As shown in experiment D in Table I, no final product is observed at 480 nm in the electronic absorption spectra in the absence of $HClO_4$, Cu(II) or Rh(III) after 1 h, and the reaction takes 36 h to come to completion. In contrast, the addition of 0.1 equiv of Cu(II) or Rh(III) at the beginning of the oxidation of A (eq 3) results in a much faster reaction, with Cu(II) being most efficient (experiments A and B). Doubling the acid concentration also speeds up the reaction but to a much lesser extent (experiment C). From this data it appears Cu(II) and Rh(III), and to a much lesser extent $H^+$, catalyze the production of HOOH from ethanol reduction of $O_2$, and this causes the increased rates observed for the oxidation of A (eq 3) in their presence.

Table I

| experiment | catalyst[a] | relative absorbance for II at 480 nm at 1.0 h | time for completion of reaction 3 |
|---|---|---|---|
| A | 0.15 mM Cu(II) | 14 | 4 |
| B | 0.17 mM Rh(III) | 3 | 10 |
| C | 4.2 mM $HClO_4$ | 0[b] | 14 |
| D | none | 0 | 36 |
| E | "incubation"[c] | 1 | 7 |

[a] These reactions were run at 40 °C and 1 atm of $O_2$, using $0.80 \times 10^{-3}$ M $[Rh(CO)_2Cl]_2$, $3.2 \times 10^{-3}$ M HCl, and 22.5 *m*L of ethanol as solvent, in addition to the catalyst listed. [b] No final product II could be detected after 1.0 h. [c] This run involved stirring $3.2 \times 10^{-3}$ M HCl and $3.2 \times 10^{-3}$ M $HClO_4$ in ethanol at 40 °C and 1 atm of $O_2$ for 48 h, followed by the addition of $[Rh(CO)_2Cl]_2$ to a $0.90 \times 10^{-3}$ M concentration.

Substantiation of this was found from our investigation of the effectiveness of Cu(II), Rh(III), and $H^+$ in catalyzing the oxidation of isopropyl alcohol (eq 4). Their effectiveness at the beginning of this reaction follows the order Cu(II) $\sim$ Rh(III) $\gg$ $H^+$, with rhodium resulting in 19 turnovers (acetone/rhodium) in 25 h and $H^+$ producing only a trace amount of acetone.[12] The consumption of dioxygen when Rh(III) was used for reaction 4 was also followed on a gas burette for several hours and is linear over that time, indicating this catalyst is not slowly rendered inactive. It is reasonable to suggest that HOOH, or peroxo metal complexes, are formed as intermediates in reaction 4 and that the efficient catalysis of this oxidation is evidence of the ability of a reagent to catalyze the production of peroxide from the alcohol reduction of $O_2$. Because both Cu(II) and Rh(III) are efficient hydroperoxide decomposition catalysts, the HOOH is produced at a very low steady-state concentration and may in fact never leave the coordination sphere of the catalysts.

Experiment E in Table I demonstrates unequivocably that an intermediate oxidant (HOOH) is formed in the presence of only HCl, $HClO_4$, ethanol, and $O_2$. This has been labeled an "incubation" experiment because it involved stirring $3.2 \times 10^{-3}$ M each of HCl and $HClO_4$ in ethanol under 1 atm of $O_2$ at 40 °C for 48 h, followed by the addition of the $[Rh(CO)_2Cl]_2$ to initiate reaction 3. In this case upon adding A no induction period was observed and the reaction was complete in only 7 h compared to the 36 h necessary when mixing all reagents from the start. In agreement with the rate law in eq 6, this further indicates that the first step or steps in the oxidation of A involve the production of HOOH from $H^+$, $O_2$, and $CH_3CH_2OH$ and that hydroperoxide is the reagent directly responsible for the oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) chloride in ethanol via a hydroperoxorhodium complex intermediate. Our proposed mechanism for this

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[9] Kunugi, T.; Matsuura, T.; Oguni, S. *Hydrocarbon Process* **1965**, *44*, 116.

[10] Simington, R. M.; Adkins, H. *J. Am. Chem. Soc.* **1928**, *50*, 1449.

[11] It is possible that trace amounts of metals which may be present in the absolute ethanol or ispropyl alcohol solvents are also catalyzing HOOH production. However, Brønsted acid undoubtedly plays a role due to the dependence on $[H^+]$ found in eq 5.

[12] The measurement of small amounts of acetone production by GLC was not extremely accurate due to the presence of some acetone in our isopropyl alcohol solvent. Cu(II) was only active over the first 30 min due to its reaction with the acetone produced.

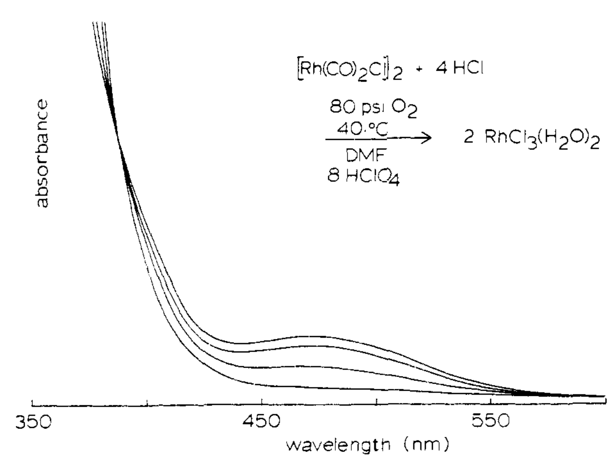

**Figure 7.** Same conditions as in Figure 4 but with dimethylformamide (DMF) rather than ethanol as solvent.

oxidation is shown in Scheme I and is substantiated by all of the preceding evidence and arguments.

**Scheme I**

$$CH_3CHROH + O_2 \rightleftharpoons CH_3CRO + HOOH \quad (a)$$

$$[Rh(CO)_2Cl]_2 + 2HCl + 2HOOH \rightleftharpoons 2[Rh(CO)Cl_2(OOH)]^{2-} + 4H^+ + 2CO \quad (b)$$

$$[Rh(CO)Cl_2(OOH)]^{2-} + 2H^+ \rightleftharpoons [Rh(CO)Cl_2(OO)]^{3-} + 3H^+ \quad (c)$$

$$[Rh(CO)Cl_2(OO)]^{3-} + 4H^+ + Cl^- + CH_3CHROH \rightarrow RhCl_3(H_2O)_2{\cdot}CH_3CHROH + CO \quad (d)$$

An intermediate analogous to B is not produced when $[Rh(C_8H_{14})_2Cl]_2$ is used instead of $[Rh(CO)_2Cl]_2$ as the rhodium(I) starting material in a reaction similar to that in eq 3. In this case the reaction to form rhodium(III) chloride is complete in only 40 min (compared to 12 h under identical conditions with A), and no evidence of stable intermediates is found in the electronic absorption spectra. In contrast, $[Rh(P(tolyl)_3)(CO)Cl]_2$ is not oxidized to rhodium(III) chloride even after 48 h.

Since Scheme I requires solvent reducing equivalents to produce HOOH and subsequently $[Rh(CO)Cl_2(OOH)]$ from $O_2$, any solvent capable of this $O_2$ reduction could lead to the oxidation of A by this mechanism. Indeed, we have found that methanol, ethanol, isopropyl alcohol, and to a lesser extent tetrahydrofuran (THF), all produce B as an intermediate in the oxidation of A by $O_2$. In THF this could appear through the intermediacy of THF hydroperoxide, produced from the abstraction of an $\alpha$-hydrogen atom by $O_2$ and a subsequent radical coupling reaction. THF–hydroperoxide may react with $[Rh(CO)_2Cl]_2$ as do both HOOH and *t*-BuOOH. In contrast, use of the typically nonreducing solvents *tert*-butyl alcohol, acetone,[13] and *N*,*N*-dimethylformamide (DMF) does result in oxidation of $[Rh(CO)_2Cl]_2$ without forming B as a stable intermediate. In *tert*-butyl alcohol and acetone the reaction is very fast, finishing in 40 min under conditions for which it takes 10 h for completion in ethanol. In DMF the reaction is much slower (also taking 10 h) and was monitored by electronic absorption spectroscopy. In this solvent only one isosbestic point is observed (at 390 nm) due to the production of rhodium(III) trichloride from the oxidation of $[Rh(CO)_2Cl]_2$ without the formation of any stable intermediates (Figure 7).

It is interesting that the oxidation of A (eq 3) proceeds through the coordination of HOOH to $[Rh(CO)_2Cl]_2$ in primary and secondary alcohol solvents rather than proceeding by the alternative mechanism that seems to occur in *tert*-butyl alcohol, acetone, and DMF. When THF is used as solvent the reaction is much faster and only poor resolution of the electronic absorption band due to B is observed. This is due to a lower concentration of B relative to that found in the alcohols, and possibly a lower energy absorption band.[14] In THF it may be that both mechanisms are functioning, which would explain the low concentration of B observed. It is important to note that we cannot rule out the alternate mechanism occurring in methanol, ethanol, and isopropyl alcohol solvents to a small degree. However, it is clear from the magnitude of the bands due to B in the electronic absorption and infrared spectra, as well as data from the kinetic rate law in eq 6, that Scheme I involving the coordination of HOOH to $[Rh(CO)_2Cl]_2$ is dominant in primary and secondary alcohols.

## Conclusion

The characterization of B as $H_2[Rh(CO)Cl_2(OOH)]$ is interesting because it serves as a rare example of a hydroperoxo complex which exists in the absence of bio-type or Schiff-base ligands. Because of its considerable stability, which seems to be at least partially dependent on the presence of the CO ligand, we do not suggest this is an intermediate in the catalytic oxidations of 1-hexene to 2-hexanone. Workup to this point concerning the oxidation of 1-hexene by B is inconclusive and indicates $H_2[Rh(CO)Cl_2(OOH)]$ is at best only slightly reactive for the production of 2-hexanone. This is not surprising in light of the fact that B is a rhodium(I) hydroperoxo complex, and the catalyst for the oxidation of 1-hexene appears to be a rhodium(III) complex. Our demonstration of the ability of primary and secondary alcohols to form low concentrations of HOOH from the reduction of dioxygen may also be significant. The results showing that $H^+$, Cu(II), and Rh(III) are all capable of catalyzing the alcohol reduction of $O_2$ to HOOH may extend to a number of other metal complexes. They also suggest that substrate oxidations by $O_2$ via HOOH formation may be more prevalent than is currently realized. Due to the low concentrations of HOOH produced, this reaction is particularly noteworthy for systems in which extended exposure of reagents to the alcohol and $O_2$ is necessary.

We are presently investigating the ability of HOOH and *tert*-butyl hydroperoxide (*t*-BuOOH) to oxidize 1-hexene. This study has conclusively shown that in the absence of $O_2$ and in both ethanol and *tert*-butyl alcohol solvents (the latter lacking reducing equivalents), both HOOH and *t*-BuOOH are very effective reagents for the $RhCl_3{\cdot}3H_2O$ catalyzed production of specifically 2-hexanone from the oxidation of 1-hexene. This provides still further substantiation for concluding that the catalyst for reaction 1 is a rhodium(III) chloride complex, and these results will be reported in a manuscript currently in preparation.

## Experimental Section

All solvents and reagents were of reagent grade and used without further purification. $[Rh(CO)_2Cl]_2$ was prepared as reported in the literature.[15] Hydrogen peroxide and *tert*-butyl peroxide were used as 30% and 70% aqueous solutions, respectively, and were standardized iodometrically. HCl, $H_2SO_4$, and $HClO_4$ were used as their concentrated aqueous solutions.

Infrared spectra were recorded on a Nicolet 7000 Series Fourier transform infrared spectrometer. GLC spectra were obtained with a Varian Model 940 FID instrument using a 3-m, $^1/_{16}$ in. i.d. copper column packed with Chromasorb P supported diethylene glycol adipate. For the detection of acetone a column temperature of 60 °C was employed, and for measurement of 2-hexanone a temperature of 93 °C was used. The production of 2-hexanone was quantitated by using 2-heptanone as an internal standard. The electronic absorption spectra were recorded on a Cary 14, and all samples were run in air at ambient temperatures and pressures. Care was taken to verify that the intermediates monitored by this technique were stable over the course of the measurements. The molecular weight of C was determined in methanol by vapor pressure osmometry.

**Catalytic Oxidations of 1-Hexene.** All catalytic 1-hexene oxidations were run in 250-mL Parr pressure bottles equipped with brass Swagelok

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(13) The band in the electronic absorption spectra due to the rhodium(III) trichloride prepared in acetone was poorly resolved due to the concurrent acid-catalyzed aldol condensation of acetone under these conditions. This latter reaction produced a band of its own in the electronic spectra which overlapped that for the rhodium(III) trichloride.

(14) This latter explanation is somewhat speculative due to the poor resolution, as was the case for the *t*-BuOOH adduct (see ref 7).

(15) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

pressure heads. These were constructed to allow purging with $O_2$, as well as sampling of the solution under reaction conditions during the course of the reactions. 2-Hexanone production was measured by GLC.

A typical catalytic reaction was run as follows: to a 250-mL Parr bottle were added 0.074 mmol of $[Rh(CO)_2S'_n]BF_4$ (prepared as earlier reported[2] and used immediately), 0.0171 g of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.074 mmol), 0.0219 g of NaCl (0.375 mmol—for the case in which a 5:1 mole ratio chloride/rhodium was desired), 0.41 mL of 0.36 M $H_2SO_4$ (0.148 mmol; as an ethanol solution prepared from aqueous concentrated $H_2SO_4$), 0.568 mmol of 2-heptanone, 45 mL of absolute ethanol, and 15 mL of 1-hexene (purged through alumina to remove peroxides). This mixture was purged 5 times with 60 psi of $O_2$, set to 40 psi of $O_2$, and the reaction initiated by placing in a 70 °C oil bath.

**Preparation of $RhCl_3(H_2O)_2 \cdot CH_3CH_2OH$ (II).** Compound C was prepared for characterization studies most easily under 40 psi of $O_2$ at 70 °C by mixing 0.0514 g of $[Rh(CO)_2Cl]_2$ (0.132 mmol), 1.10 mL of 0.48 M HCl (in ethanol, 0.528 mmol), and 15 mL of ethanol. This produced a bright orange solution after a reaction overnight, from which C was isolated by rotovaping to dryness and drying in vacuo. $M_r$ for $H_4O_2Cl_3Rh$ calcd, 245; found, 226. Anal. Calcd for $C_2H_{10}O_3Cl_3Rh$: C, 8.24; H, 3.46; Cl, 36.50. Found: C, 8.41; H, 2.69; Cl, 37.17.

**Determination of Acetone Production. (A) In Presence of 1-Hexene.** The measurement of acetone produced in the initial stage of the Rh/Cu-catalyzed oxidation of 1-hexene with isopropyl alcohol as solvent was made by GLC as follows: To a 50-mL round-bottom flask were added to 0.159 g of $RhCl_3 \cdot 3H_2O$ (0.604 mmol), 0.137 g of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.589 mmol), and a stir bar. This was purged 20 min with $O_2$ at 40 °C and 30 mL of an $O_2$-purged, 9/1 (v/v) solution of isopropyl alcohol/1-hexene added to initiate the reaction. GLC's were recorded after 4, 8, 17, 25, and 40 min. The amount of acetone produced was determined by comparison of peak heights with standards at the same time under identical conditions. When this 1:1 Cu/Rh ratio was used, 0.5 mol of acetone was formed per mole or rhodium in the first 4–8 min. No further production was observed. When a 2:1 Cu/Rh mole ratio was used, continuous, catalytic production of acetone was observed.

**(B) In Absence of 1-Hexene.** The catlaytic production of acetone from the $O_2$ oxidation of isopropyl alcohol was observed when 1-hexene was excluded from the solutions. $RhCl_3 \cdot 3H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, and $HClO_4$ were all used as catalysts for this reaction. In a typical run, 0.0369 g of $RhCl_3 \cdot 3H_2O$ (0.140 mmol) and a stir bar were placed in a 15-mL round-bottom flask and purged 20 min with $O_2$ at 40 °C. Into this was syringed 7 mL of isopropyl alcohol, purged itself with $O_2$ at 40 °C, to initiate the reaction. Acetone production was measured as described above.

**Titration of $[Rh(CO)_2Cl]_2$ with HOOH.** Because the reaction of HOOH with $[Rh(CO)_2Cl]_2$ (A) is quite slow in ethanol, it was run at 40 °C. The visible spectrum of the intermediate, $H_2[Rh(CO)Cl_2(OOH)]$ (B), is most clearly observed by first adding 1.0 equiv of HOOH, followed an hour later by 0.5 equiv. The first addition causes the reaction of much of the starting material A (which overlaps the band at 385 nm), so that after the second addition the band due to C at 385 nm is easily observable in the electronic absorption spectrum. Intermediate B is easily detected in the oxidation of A by HOOH by using FT IR. Since there is no overlap of the carbonyl bands of A and B, the intermediate is detected in the first addition of HOOH. HOOH was diluted in ethanol immediately before use. Aqueous dilution causes the addition of too much $H_2O$, which retards the reaction considerably.

**Acknowledgment.** We gratefully acknowledge the generous support of this research by the National Science Foundation and the Office of Naval Research.

**Registry No.** $O_2$, 7782-44-7; $Cu(NO_3)_2$, 3251-23-8; NaCl, 7647-14-5; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[RhCl_3(H_2O)_2 \cdot CH_3CH_2OH]$, 85236-98-2; HOOH, 7722-84-1; 1-hexene, 592-41-6; 2-hexanone, 591-78-6; chloride, 16887-00-6.

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# Activation of Methane with Metal Atoms at 10 K without Photolysis

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**Abstract:** Codeposition of methane with metal atoms at 10 K leads to reaction with Al atoms but not with Mg, Ca, Ti, Cr, Fe, Co, Ni, Pd, Cu, Ag, Au, Ga, In, or Sn. The unusual reactivity of Al is ascribed to its $^2P$ radical character, coupled with comparatively high Al–H and Al–C bond strengths.

Activation of alkanes by small "naked" nickel clusters has been accomplished as low as −130 °C.[1] Clean metal surfaces of other group 8 metals have shown similar high reactivities at relatively low temperatures.[2] Also, it has been reported that Zr atoms react with alkanes as low as −196 °C.[3]

Under matrix isolation conditions of 10–50 K (−263 to −223 °C) no evidence of reaction of bare metal atoms or clusters with alkanes has been found, although many attempts have been made. Ozin and co-workers have studied V atoms in a variety of alkane media in the 10–50 K range.[4] Likewise, we have carried out similar studies with Ni atoms and other metals.

Photolytic activation of alkanes using metal atoms is quite different, however. Gas-phase M*–alkane reactions have been known for many years.[5] And recently this approach has been extended to matrix-isolated metal atoms in frozen methane and ethane.[6,7] Billups and co-workers[6] reported photolytic activity of Mn, Fe, Co, Cu, Zn, Ag, and Au atoms with $CH_4$. Ozin and co-workers[7] reported activity for Cu atoms with both $CH_4$ and $C_2H_6$ (C–H cleavage only).[7]

We have recently reported unusually high activities of certain metal atoms with $CH_3Br$ at 10 K, especially Al and Ga, and attributed this to the low ionization potentials of these atoms coupled with their high M–Br bond strengths.[8] Note that no photolytic activation was necessary. Likewise, Hauge, Kauffman, and Margrave have elucidated the spontaneous reaction of Al and Ga atoms with $H_2O$.[9]

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