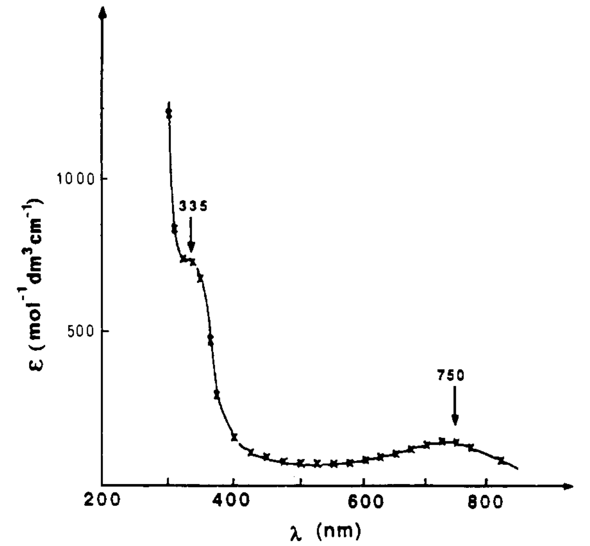

Figure 3. Electronic absorption spectrum of $[VCl_3(4\text{-pic})_3]_2O_2$ in CH_3CN and CH_2Cl_2 solutions.

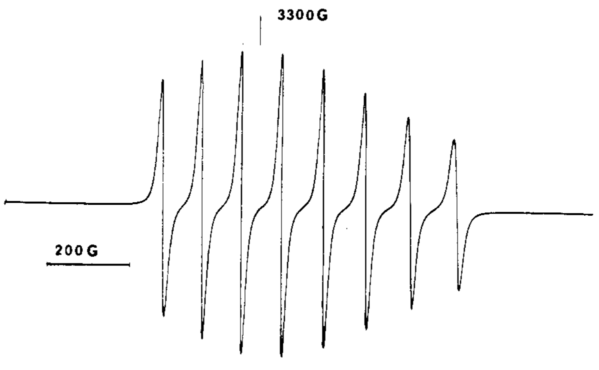

Figure 4. EPR spectrum of $VOCl_2(4\text{-pic})_2$ in acetonitrile at room temperature.

without any oxygen liberation (no reducing species is produced in pulse-radiolyzed pure CH_2Cl_2, the $CH_2Cl_2^{\bullet-}$ radical anion being quickly transformed into Cl^- and $CH_2Cl^\bullet$).

We showed that the vanadium(III) complex $VCl_3(4\text{-pic})_3$ is able to coordinate molecular oxygen according to a dimeric superoxo mode and ascertained our hypothesis by radiolysis experiments. This radiolysis technique therefore appears to be suitable for determining the structures of oxygen-carrying compounds and even giving an insight into their mechanism.

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Registry No. $VCl_3(4\text{-pic})_3$, 107333-90-4; $[VCl_3(4\text{-pic})_3]_2O_2$, 111005-83-5; O_2, 7782-44-7; CH_3CN, 75-05-8; CH_2Cl_2, 75-09-2; $VOCl_2(4\text{-pic})_3$, 52593-61-0.

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Aerobic Oxidation of Cyclohexene with a Phosphine-Ruthenium(II)-Aquo Catalyst

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The activation of molecular oxygen by transition-metal complexes, with a focus on organic substrate oxidation, is a topic of much current research.[1-16] In particular, the reductive activation of dioxygen is characteristic of the widely occurring hemoprotein cytochrome P-450,[17-20] where the catalytic organic substrate oxidation cycle of cytochrome P-450 has been suggested to include a high-valent iron-oxo intermediate as the active oxidant. In this regard, many transition-metal complexes have been studied as organic substrate oxidizers, including cobalt,[21-23] copper,[24] chromium,[25-29] iron,[30-35] manganese,[36-42] and ruthenium[43-46] complexes.

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Table I. Products of Cyclohexene Oxidation after 24 h: Product Distribution of Catalytic Aerobic Oxidation versus the Product Distribution from a Stoichiometric Oxidant

	equiv[a] of oxidized products		
reactant	2-cyclo-hexen-1-one	2-cyclo-hexen-1-ol	cyclo-hexene oxide
$[(bpy)_2(PPh_3)Ru^{II}(OH_2)]^{2+}$ [b]	27.4 (16)[f]	13.7 (8)	1.70 (1)
$[(bpy)_2(PPh_3)Ru^{II}(OH_2)]^{2+}$ [c]	11.0 (14)	7.50 (9)	0.80 (1)
$[(bpy)_2(PPh_3)Ru^{II}Cl]^{+}$ [d]	0	0	0
$[(bpy)_2(PPh_3)Ru^{IV}{=}O]^{2+}$ [e]	0.64 (16)	0.32 (8)	0.04 (1)

[a] The equiv of products = mol of products/mol of ruthenium complex. [b] Catalytic reaction was run in dry *o*-dichlorobenzene under 1 atm of $O_2(g)$. [c] Catalytic reaction was run in dry methylene chloride under 1 atm of $O_2(g)$. [d] Reaction was run in dry *o*-dichlorobenzene under 1 atm of $O_2(g)$, under the same conditions as the active catalyst. [e] Stoichiometric reaction was run in dry *o*-dichlorobenzene in an inert-atmosphere glovebox. [f] Values in parentheses indicate the relative product distributions. Note that the product distributions for the catalytic activation of dioxygen utilizing the phosphine–ruthenium(II)–aquo complex and the stoichiometric oxidation utilizing the analogous phosphine–ruthenium(IV)–oxo complex are identical in *o*-dichlorobenzene.

Recently, we reported the isolation of stable, ruthenium(IV)–oxo complexes that utilize a tertiary phosphine ligand in a position cis to the oxo ligand.[46] These complexes are active stoichiometric oxidants, oxidizing a variety of substrates, including alcohols, olefins, aldehydes, phosphines, sulfides, and sulfoxides.[47] In addition, the coordinated phosphine ligand has affected both the rate of oxidation of certain substrates based on the hydrophobic nature of the substrate[48] and the solubility of the complex, where the phosphine–ruthenium(IV)–oxo complexes are soluble in nonpolar, noncoordinating solvents such as methylene chloride and *o*-dichlorobenzene. We now wish to report that these phosphine–ruthenium(IV)–oxo complexes, as well as the analogous phosphine–ruthenium(II)–aquo complexes, catalyze the aerobic oxidation of cyclohexene. Furthermore, the activation of molecular oxygen occurs at room pressure and temperature, without the need of a coreductant, and the active oxidant in the catalytic cycle appears to be the phosphine–ruthenium(IV)–oxo species.

Experimental Section

Materials. *o*-Dichlorobenzene was obtained from Aldrich Chemical Co. and purified by vacuum distillation, and methylene chloride (GCMS grade) was obtained from Fischer Scientific Co. and was used without further purification. Both solvents were dried immediately prior to their use by passing them down a column of activated alumina. Cyclohexene was purchased from Aldrich and was purified by vacuum distillation immediately prior to its use. The complexes $[(bpy)_2(PPh_3)Ru^{II}Cl](ClO_4)$,[46] $[(bpy)_2(PPh_3)Ru^{II}(OH_2)](ClO_4)_2$,[46] $[(bpy)_2(PPh_3)Ru^{IV}O](ClO_4)_2$,[46] and $[(trpy)(bpy)Ru^{II}(OH_2)](ClO_4)_2$[49] were synthesized by following the published procedures. The cyclic voltammetry and UV/vis spectroscopic measurements were consistent with the published properties for these complexes. The complex $[(trpy)(biq)Ru^{II}(OH_2)](ClO_4)_2$ was synthesized by a modification of a published procedure.[49] The complex $[(bpy)_2(PPh_3)Ru^{II}(acetone)](ClO_4)_2$ was synthesized by dissolving $[(bpy)_2(PPh_3)Ru^{II}(OH_2)](ClO_4)_2$ in acetone (distilled from potassium permanganate) in an inert-atmosphere glovebox. After the solution was stirred for 12 h, the phosphine–ruthenium(II)–acetone complex was precipitated from solution with pentane and dried in vacuo. The infrared spectroscopic and electrochemical properties of the complex were consistent with the coordination of an acetone ligand.

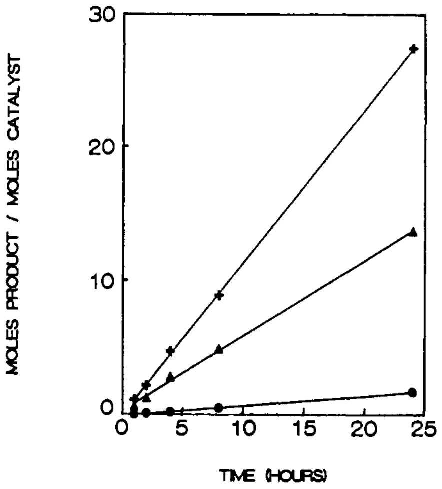

Figure 1. Aerobic oxidation of cyclohexene catalyzed by $[(bpy)_2(PPh_3)Ru^{II}(OH_2)]^{2+}$ in dry *o*-dichlorobenzene under 1 atm of $O_2(g)$ at 25 °C. (+) 2-cyclohexen-1-one; (▲) 2-cyclohexen-1-ol; (●) cyclohexene oxide.

Procedures and Instrumentation. In a typical experiment, 1.5 mmol of cyclohexene was combined with 0.005 mmol of $[(bpy)_2(PPh_3)Ru^{II}(OH_2)](ClO_4)_2$ in 2.5 mL of dry solvent, and the solution was stirred in the absence of light for 1, 2, 4, 8, or 24 h. At the end of the reaction, an equal volume of pentane was added to the reaction mixture, precipitating the catalyst. The metal product was separated from the organic solution and analyzed by cyclic voltammetry utilizing an IBM EC/225 voltammetric analyzer. The organic solution was injected into a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector, and toluene was added (after removal of the catalyst) as an internal standard. Product distributions were checked with a Hewlett-Packard 5890 gas chromatograph with a mass spectrometry detector. Kinetic measurements for the reaction of $[(bpy)_2(PPh_3)Ru^{IV}(O)](ClO_4)_2$ with cyclohexene in *o*-dichlorobenzene were conducted spectrophotometrically with a Beckman DU 2400 instrument. Oxygen pressure reactions were conducted with a Parr high-pressure apparatus.

Results and Discussion

General Observations. Results for the oxidation of cyclohexene are given in Table I. The reaction of 0.015 mmol of $[(bpy)_2(PPh_3)Ru^{II}(OH_2)](ClO_4)_2$, complex **1**, with $O_2(g)$ and cyclohexene (1.5 mmol) in methylene chloride (2.5 ml) yields 0.16 mmol of 2-cyclohexen-1-one, 0.11 mmol of 2-cyclohexen-1-ol, and 0.01 mmol of cyclohexene oxide after 24 h. The rate of product formation for the reaction mixture after 2 h in methylene chloride begins to decline due to formation of the catalytically inactive complex $[(bpy)_2(PPh_3)Ru^{II}Cl]^+$, complex **2**, in solution. The formation of complex **2** was determined electrochemically, and the cyclic voltammograms of the catalyst following workup of the reaction show only **1** and **2** in amounts proportional to the loss in activity of the catalytic system. For example, after 24 h, the ruthenium mixture consisted of 65% chloro species and 35% aquo species, and the corresponding activity of the catalyst was only

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35% of the original activity.[50] Complex **2** is formed from the decomposition of methylene chloride, in which free hydrogen chloride is formed. *o*-Dichlorobenzene does not decompose under the conditions of cyclohexene oxidation, and thus the oxidation of cyclohexene in *o*-dichlorobenzene leaves the catalyst quantitatively unchanged. The product distribution from the oxidation of cyclohexene (1.5 mmol) in *o*-dichlorobenzene (2.5 mL), catalyzed by complex **1** (0.005 mmol), under 1 atm of dioxygen is plotted in Figure 1. The rate of product formation over a 24-h period is constant, with the initial catalyst **1** being isolated quantitatively intact at the end of the reaction. The formation of 2-cyclohexen-1-one occurs at the rate of 0.006 mmol/h along with 0.003 mmol of 2-cyclohexen-1-ol and trace amounts of cyclohexene oxide. This rate of product formation corresponds to a turnover number of 70 for 24 h of catalysis, where the 4-electron oxidation of cyclohexene to 2-cyclohexen-1-one is considered to require the reaction of 2 equiv of the active form of the catalyst to produce this product. Notably, with modification of the concentrations of catalyst and substrate, much higher turnover numbers can be achieved for this system. For example, by combining 0.001 mmol of catalyst with 5.6 mmol of cyclohexene in 2.5 mL of *o*-dichlorobenzene under 1 atm of oxygen yielded a turnover number of 1560 for 24 h.

In the absence of oxygen, the reaction of **1** with cyclohexene in dry methylene chloride or *o*-dichlorobenzene fails to produce any oxidized products, indicating that dioxygen is necessary for the catalytic oxidation of cyclohexene. While phosphine–ruthenium(II)–aquo complexes function as catalysts in the aerobic oxidation of cyclohexene, not all ruthenium(II) complexes proved to be active catalysts. Complex **2**, the chloro-substituted analogue of complex **1**, does not catalyze the aerobic oxidation of cyclohexene. Also, when sterically small ligands were used exclusively in the ruthenium coordination sphere, such as with $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}(OH_2)}](\mathrm{ClO_4})_2$ (where trpy = 2,2′,2″-terpyridine), no catalytic activity was observed. However, when the sterically hindered ligand biq (where biq = 2,2′-biquinoline) was used in place of bpy in the complex $[(\mathrm{trpy})(\mathrm{biq})\mathrm{Ru^{II}(OH_2)}](\mathrm{ClO_4})_2$, catalytic activity was observed. In addition, water is not a necessary ligand for catalysis to occur, for $[(\mathrm{bpy})_2(\mathrm{PPh_3})\mathrm{Ru^{II}}(\mathrm{acetone})](\mathrm{ClO_4})_2$, the acetone-substituted analogue of complex **1**, is an effective catalyst in the oxidation of cyclohexene and produces turnover numbers and product distributions similar to those for the the catalytic oxidation of cyclohexene by complex **1**. These observations suggest that an open coordination site is necessary on the ruthenium(II) center for oxygen activation to occur in these complexes. This open coordination site can be generated dissociatively by using sterically large ligands, such as tertiary phosphines or 2,2′-biquinoline, in conjunction with a weak ligand such as water or acetone.

Kinetic Studies. Cyclohexene oxidations were conducted by varying the amount of catalyst while holding the concentration of cyclohexene constant, and also by varying the amount of cyclohexene with a fixed amount of catalyst. The rate of product formation was found to have a linear dependence on both catalyst and cyclohexene concentration. The dependence of the reaction rate on oxygen pressure was also studied, and the rate of product formation was independent of oxygen pressure over the range 1–30 atm. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from the linear plot of ln (k/T) versus $1/T$ for the catalytic oxidation of cyclohexene in *o*-dichlorobenzene solution were calculated to be 9.1 ± 1.3 kcal/mol and −38.5 ± 4.1 eu, respectively. Notably, the activation parameters calculated for the stoichiometric oxidation of cyclohexene in ortho-dichlorobenzene using the reagent $[(\mathrm{bpy})_2(\mathrm{PPh_3})\mathrm{Ru^{IV}O}](\mathrm{ClO_4})_2$ were 8.0 ± 2.8 kcal/mol and −34.6 ± 9.8 eu for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. These observations are consistent with the proposal of the phosphine–ruthenium(IV)–oxo species as the active oxidizing agent in the aerobic catalytic oxidation of cyclohexene.

Mechanistic Studies. In order to investigate the possibility that a free-radical mechanism was occurring in these oxidations, reactions were conducted in the presence of free-radical traps, such as *m*-dinitrobenzene or butylated hydroxytoluene. The ruthenium catalyst was found not to be functioning as a radical initiator in the autoxidation of cyclohexene, because the product distributions and the turnover numbers for the oxidation of cyclohexene remained identical in the presence and absence of *m*-dinitrobenzene[51] and BHT[8a] (butylated hydroxytoluene) radical scavengers. In order to determine if perchlorate activation was occurring in these systems, the tetrafluoroborate and hexafluorophosphate salts of **1** were also synthesized. Both of these complexes proved to catalyze cyclohexene oxidations where the product distributions were the same as those obtained with the perchlorate salt of complex **1**. Thus, perchlorate activation is not responsible for substrate oxidation. Manometric measurements of the uptake of oxygen in this catalytic oxidation showed that, for every 1 mol of oxygen consumed, 2 mol of oxidized olefin (or water) was produced. The production of 2-cyclohexen-1-one in the catalytic oxidation of cyclohexene was accompanied by the formation of an equal amount of water as a byproduct in this 4-electron oxidation.

On the basis of the above observations, a catalytic cycle can be proposed, where **1**, in a noncoordinating solvent, yields a five-coordinate complex with a free coordination site upon the loss of a water ligand. Two five-coordinate phosphine–ruthenium(II) complexes would then combine with a molecule of dioxygen to form a dinuclear, O_2-bridged intermediate, reminiscent of iron(II) porphyrin chemistry.[52] Homolytic cleavage of the O–O bond would then yield two phosphine–ruthenium(IV)–oxo molecules, the proposed active oxidizing intermediate in the substrate oxidation process. In the oxidation of olefins we have observed a phosphine–ruthenium(II)-oxidized substrate intermediate, with the oxidized organic substrate being coordinated to the ruthenium(II) complex.[47] Finally, the phosphine–ruthenium(II)-oxidized substrate complex could then dissociate the oxidized product, regenerating the five-coordinate complex, which would continue in the catalytic cycle.

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(50) The percentage of complex in solution was determined from the cyclic voltammogram of the mixture in CH_2Cl_2 with 0.1 M tetrabutylammonium tetrafluoroborate electrolyte present. The ratio of peak currents were taken as proportional to the ratio of concentrations of the two analytes by following the Randles–Sevcik equation for stationary electrode voltammetry. See: Kissinger, P. T.; Heineman, W. R. *Laboratory Techniques in Electroanalytical Chemistry*; Marcel Dekker: New York, 1984.

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