J. Am. Chem. Soc. **1998,** *120,* 11969−11976

Molecular Oxygen Activation by a Ruthenium-Substituted “Sandwich” Type Polyoxometalate

Ronny Neumann* and Mazal Dahan

Contribution from the Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University of Jerusalem, Jerusalem, Israel 91904

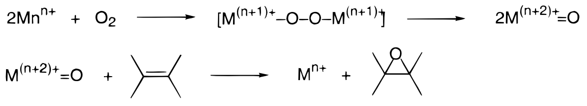
Received December 15, 1997

Abstract: The ruthenium-substituted “sandwich” type polyoxometalate $[WZnRu^{III}_2(XW_9O_{34})_2]^{11-}$ where X = Zn^{II} or Co^{II} has been shown to be unique in its ability to catalyze the selective hydroxylation of adamantane at the tertiary carbon position with molecular oxygen as the oxygen donor. The hydroxylation features an adamantane:dioxygen stoichiometry of 2:1. Kinetic studies of the reaction show that the reaction is second order in the ruthenium-substituted polyoxometalate and zero order in adamantane. The reaction rate dependence on molecular oxygen is complicated. Highest reaction rates were observed at approximately 1 atm of dioxygen, but the rates decreased at lower (0.2 atm) and higher (3 atm) dioxygen pressures. Kinetic analysis as a function of temperature showed a low entropy of activation, indicating a highly ordered transition state. The reaction commenced only after an induction period related to formation of the “active” species from the precursor polyoxometalate. Alternatively, the induction period could be eliminated by adding a reducing agent. The induction period was found to be a function of both the reaction temperature and oxidation pressure. Coordination studies carried out via UV−vis and IR spectroscopy indicate the formation of a ruthenium(IV) oxo or μ-peroxo ruthenium(III) dimeric species as the active oxygenation species. This formulation is supported by the ESR spectra observed upon addition of spin traps such as 2-methyl-2-nitrosopropane or 5,5-dimethyl-1-pyrroline *N*-oxide to the reaction mixtures. In the oxidation of alkenes, catalytic and highly selective epoxidation may be observed. Especially informative was the catalytic epoxidation of *trans*-cyclooctene, which yielded a *trans*:*cis*-cyclooctene oxide ratio of 20:1, providing strong evidence of a nonradical oxidation pathway. On the basis of the reaction stoichiometry, spectroscopic evidence, reaction probes, and kinetic studies, a mechanism is proposed calling for a dioxygenase type activation of molecular oxygen via complexation to a ruthenium(II) species followed by formation of a ruthenium(IV) oxo species via a ruthenium(III) μ-peroxo intermediate.

Introduction

The use of molecular oxygen for oxidation of organic substrates is carried out principally in four ways. Ground state triplet oxygen can be activated, usually photochemically, to singlet oxygen which is highly reactive toward organic substrates.[1] Second, organic free radicals, formed by hydrogen abstraction from a hydrocarbon react with molecular oxygen by a chain reaction termed autoxidation to form alkyl hydroperoxides which can be decomposed separately or in situ to other oxygenated products.[2] Additionally, organic substrates can be oxygenated or dehydrogenated by transition metal catalysts to form a product and a reduced catalyst. The reduced catalyst can be reoxidized (recycled) by molecular oxygen. These types of reaction are typified by Mars−van Krevelen[3] and Wacker[4] type mechanisms. Finally, transition metals may bind molecular oxygen to form a complex involving metal to oxygen charge transfer.[5] The peroxo or oxo complex ultimately formed is often active in selective oxidation reactions. Activation in this manner is often observed in living systems catalyzed by oxygenase enzymes. Common monooxygenases such as the heme type cytochrome P-450 and the non-heme methane monooxygenase operate in the presence of an electron and proton donor to insert one oxygen atom of molecular oxygen into the organic substrate while the other oxygen is reduced to water.[6] The rarer dioxygenases, on the other hand, catalyze insertion of both oxygen atoms into two substrate molecules without requiring a sacrificial reducing agent.

The challenge of developing a practical dioxygenase catalyst is demanding because, in general, oxidation reactions in the presence of a transition metal based compound and absence of a reducing agent will proceed by a metal-catalyzed autoxidation reaction. A primary motivation for development of such dioxygenase catalysts is therefore the possibility of achieving epoxidation of alkenes by an addition reaction, eq 1, rather than a primarily allylic substitution reaction observed for the free



(1)

---

[1] Wasserman, H. H.; Murray, R. W. *Singlet Oxygen*; Academic Press: New York, 1969.

[2] Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.

[3] Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980.

[4] Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, The Netherlands, 1980.

[5] Simandi, L. I. *Catalytic Activation of Dioxygen by Metal Complexes*; Kluwer: Dordrecht, The Netherlands, 1992.

[6] (a) Ortiz de Montellano, P. *Cytochrome P-450*; Plenum Press: New York, 1986. (b) Fieg, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759. (c) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504.

10.1021/ja974243b CCC: $15.00

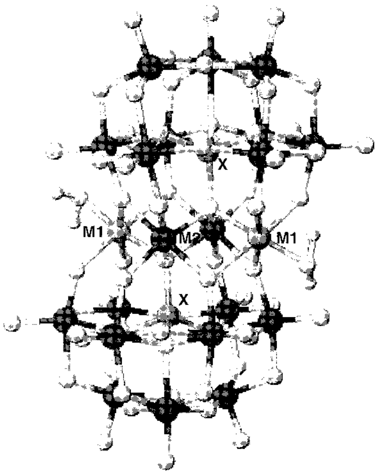
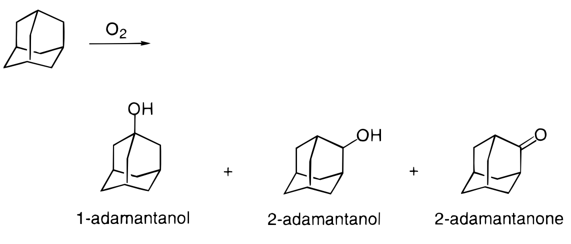


Figure 1. Structure of the "sandwich" type transition metal substituted polyoxometalate.

radical mechanism. Although a vast number of model and biomimetic systems for monooxygenase type reactions have evolved over the last 20 years, progress toward dioxygenase models and synthetic catalysts has been comparatively very meager. Most notable has been the use of sterically hindered ruthenium porphyrins for alkene epoxidation with molecular oxygen.[7] Unfortunately, the relatively limited thermal stability of the porphyrin nucleus under oxidative conditions has prevented commercialization of a porphyrin-based process. Recently, we communicated the use of a ruthenium-substituted polyoxometalate, $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ (Figure 1, where M1 = Ru^{III}, M2 = Zn, and X = Zn), an inorganic catalyst that is much more stable to oxidative decomposition, as a compound effective for the dioxygenase type activation of molecular oxygen.[8] In this article, we present our complete results on the activation of molecular oxygen by $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ using kinetic studies, spectroscopic measurements, and probe molecules. The investigation leads to the formulation of a nonradical dioxygenase type mechanism.

Results and Discussion

Hydroxylation of Adamantane. The hydroxylation of adamantane with molecular oxygen,[9] eq 2, was used in the evaluation of the catalytic behavior of the transition metal substituted "sandwich" type polyoxometalates of the type shown in Figure 1. From the results presented in Table 1, one may observe that the presence of ruthenium or to a significantly lesser degree palladium in the M1 position was imperative for selective catalytic formation of 1-adamantanol. The selectivity remained unchanged for long reaction periods and for more than 500 turnovers. This observed selectivity was very different from the product distribution when adamantane was autoxidized in the presence of transition metal compounds such as cobalt acetate or with transition metal substituted Keggin type polyoxometalates. Other transition metal substituted analogues where M2 and X = Zn and M1 = Co^{II}, Rh^{III}, Mn^{II}, Ni^{II}, Cu^{II}, Pt^{II}, or Zn^{II} showed no oxidation products whereas for M2 and X = Zn and M1 = Fe^{III} a typical autoxidation profile was observed. Interestingly, for M1 = Ru^{III}, when the zinc atom at the M2 position was replaced with Co^{II} or Ru^{III} all catalytic activity was lost. On the other hand, when the heteroatom X was changed to Co^{II} but the M2 position remained Zn^{II}, catalytic activity was retained. Thus, the presence of zinc(II), a nonoxidizable atom at the M2 position, appears crucial for catalytic activity whereas the presence of a redox metal at this position was detrimental to catalytic activity. On the other hand, the redox properties of the heteroatom that is X = Zn^{II} versus Co^{II} had little effect.



(2)

After the observation of the initial catalytic reaction with $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$, **1**, as most active catalyst, further research was carried out using this polyoxometalate exclusively. Addition of 0.25 mmol of free radical reaction inhibitors, including *tert*-butylcatechol, BTH, and BHA, under the reaction conditions described in Table 1 showed no significant decline in the conversion of adamantane to 1-adamantanol. This was initial evidence for a non free radical reaction. Further evidence already reported[8,9] which tended to discount an autoxidation mechanism included the following: (a) there was no oxidation of alkylaromatics such as cumene under reaction conditions even though such compounds are more susceptible to autoxidation compared to adamantane, (b) for the oxidation of adamantane-*1,3*-d_2 a kinetic isotope effect (KIE) of 5.7 ± 0.2 was observed compared to a KIE of ~2 for autoxidation, and (c) the use of $^{18}O_2$ in place of $^{16}O_2$ showed no formation of $H_2{}^{18}O$ expected for both autoxidation and monooxygenase type mechanisms.

In an additional new experiment, we monitored the oxygen consumption concurrently with the adamantane conversion by attaching a manometer to the reaction vial to measure the decrease in oxygen pressure. Thus, for reactions in a 5 mL reaction vial containing 0.25 mmol of adamantane and 0.25 μmol of $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ in 0.5 mL of 1,2-dichloroethane under 1 atm of O_2 carried out at 80 °C for 2 days, an average for three runs of 1.05 ± 10% equiv of molecular oxygen was consumed/2 equiv of adamantane that underwent hydroxylation. This evidence definitely supports a dioxygenase type mechanism, eq 1, and is incompatible with both monooxygenase and autoxidation mechanisms.

The reaction profiles, Figure 2, showed that the reaction was initiated only after a significant induction period, although the induction period could be eliminated by addition of a reducing agent such as zinc metal with reactions proceeding at postinduction rates.[8] The induction period was inversely proportional to the reaction temperature (15, 11, 10, 8, and 4 h for 70, 75, 80, 85, and 90 °C, respectively). Once the reactions were initiated, they were zero order in adamantane. The observed zero-order rate constants computed from the slopes of the reaction profile in the postinduction time period yielded $\Delta H^{\ddagger}_{25}$ = 7.22 kcal/mol and $\Delta S^{\ddagger}_{25}$ = −54.9 cal/(mol K) according to the Eyring equation. The low entropy of activation observed is indicative of a highly ordered transition state in the rate-determining step.

---

[7] (a) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. (b) Groves, J. T.; Ahn, K. H. *Inorg. Chem.* **1987**, *26*, 3831. (c) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137. (d) Marchin, J.-C.; Ramasseul, R. *J. Chem. Soc., Chem. Commun.* **1988**, 298.

[8] Neumann, R.; Dahan, M. *Nature* **1997**, *388*, 353.

[9] (a) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1587. (b) Neumann, R.; Khenkin, A. M. *Inorg. Chem.* **1995**, *34*, 5753.

Table 1. Adamantane Oxidation with Molecular Oxygen Catalyzed by $[W(M2)(M1)_2(XW_9O_{34})_2]^{q-}$ "Sandwich" Type Polyoxometalates[a]

polyoxometalate	product yields, mol % 1-adamantanol	2-adamantanol	2-adamantanone
X, M2 = Zn^{II}; M1 = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Rh^{III}, Pt^{II}			
X, M2 = Zn; M1 = Fe^{III}	5.3	1.6	1.0
X, M2 = Zn^{II}; M1 = Ru^{III}	12.3 (56.8)[a]		
X, M2 = Zn^{II}; M1 = Pd^{II}	1.9		
X = Zn^{II}; M1, M2 = Ru^{III}			
X = Zn^{II}; M1 = Co^{II}; M2 = Ru^{III}			
X = Co^{II}; M1 = Zn^{II}; M2 = Ru^{III}	11.7		

[a] Reaction conditions: 0.25 mmol of adamantane, 0.25 μmol of polyoxometalate, $[W(M2)(M1)_2(XW_9O_{34})_2]^{q-}$ as its trioctylmethylammonium salt, 0.5 mL of 1,2-dichloroethane, 1 atm of oxygen (~10 mL in a closed reactor), 80 °C, 24 h. [b] After 72 h.

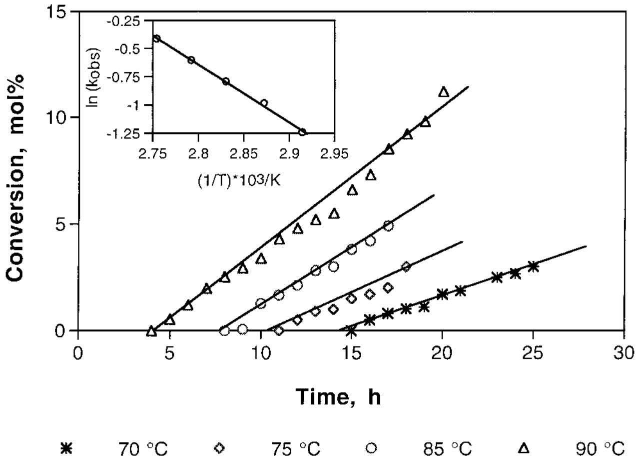


Figure 2. Reaction profiles of adamantane oxidation at different temperatures. Reaction conditions: 2.5 mmol of adamantane, 2.5 μmol of polyoxometalate, $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ as its trioctylmethylammonium salt, 5 mL of 1,2-dichloroethane, 1 atm of oxygen (~25 mL in a closed reactor). The reaction was also carried out 80 °C (not shown for clarity), and the results (insert) were used for the Eyring plot ($r^2 = 0.96$). Measurements taken every hour showing no reaction during the induction period (prior to reaction initiation) are not shown for clarity.

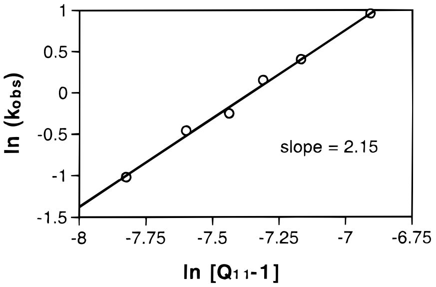


Figure 3. Logarithmic plot of the observed zero-order rate constant as a function of catalyst concentration. Reaction conditions: 2.5 mmol of adamantane, 2.0−5.0 μmol of polyoxometalate, $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ as its trioctylmethylammonium salt, 5 mL of 1,2-dichloroethane, 1 atm of oxygen (~25 mL in a closed reactor). Observed zero rate constants were computed from initial reaction rates as determined by adamantane to 1-adamantanol oxidation.

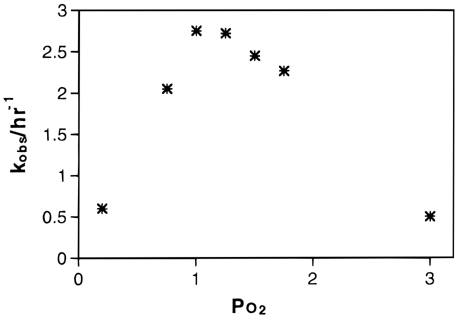


Figure 4. Zero-order rate constants as a function of the molecular oxygen pressure. Reaction conditions: 2.5 mmol of adamantane, 2.5 μmol of polyoxometalate, $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ as its trioctylmethylammonium salt, 5 mL of 1,2-dichloroethane, 0.2−3 atm of oxygen (~25 mL in a closed reactor). Observed zero rate constants were computed from initial reaction rates as determined by adamantane to 1-adamantanol oxidation.

Further kinetic studies involved the determination of the reaction order in catalyst and molecular oxygen. A logarithmic plot of the zero-order observed rate constants taken from initial rates of adamantane conversion (postinduction) versus total catalyst concentration yields the order of the reaction as the slope, eq 3. In Figure 3 is presented the plot for the order in

$$dP/dt = k_{obs}[\text{adamantane}]^a[O_2]^b[Ru_T]^c$$

$$\ln k_{obs} = a \ln [\text{adamantane}] + b \ln [O_2] + c \ln [Ru_T] \quad (3)$$

$$\text{since } a = 0 \text{ and for initial rates } b \cong 0, \quad \ln k_{obs} = c \ln [Ru_T]$$

catalyst concentration over a range of 0.2−0.08 mol % polyoxometalate. The calculated order was 2.15 ($r^2 = 0.98$). The induction period was ~10 h at all polyoxometalate concentrations. The finding from the kinetic studies showing that the rate of hydroxylation reaction is a function to the second order of the polyoxometalate concentration is unusual. This coupled with the low entropy of activation shows that a polyoxometalate transformation is involved in the rate-determining step which has a highly ordered transition state. The observed rate dependence on the polyoxometalate is much different from what one would expect for a metal-catalyzed autoxidation type reaction.

A similar set of reactions involving 2.5 mmol of adamantane, 2.5 μmol of polyoxometalate, $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$, as its trioctylmethylammonium salt, 5.0 mL of 1,2-dichloroethane, and an oxygen pressure ranging from 0.2 to 3 atm showed that the reaction rate had a complicated dependence on the molecular oxygen pressure, Figure 4. Maximum reaction rates, again expressed as zero-order rate constants under initial rate conditions, were observed at 1−1.5 atm of molecular oxygen. At lower and higher pressures, reaction rates decreased significantly. Further analysis of this last result is instructive by assuming the solubility of oxygen in the reaction solvent, 1,2-dichloroethane, to be 0.23 mL (STP) of O_2/mL of solvent (similar to that of $CHCl_3$ and CCl_4).[10] This translates into ~50 μmol of O_2 in 5 mL of solvent at 1 atm (maximum rate) containing 2.5 μmol of polyoxometalate (5.0 μmol of Ru). Thus, under these conditions of maximum rate, dioxygen is an approximately 20-fold excess relative to the polyoxometalate

---

[10] Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1963; Vol. 1, Part 1, p 575.

in the solution and this excess is retained throughout the reaction as dioxygen is in approximately constant excess in the gas phase above the solution (pressure decreases only 2−5%). It is crucially important to note that oxygen is, however, in limited concentration relative to adamantane. When the reaction is carried out at lower oxygen pressures such as $P_{O_2} = 0.2$ atm ($P_t = 1$ atm), oxygen is no longer in significant excess in the solution versus the catalyst, and thus becoming a limiting reagent, and the rate is significantly lower (by a factor of ∼5).[11] These kinetic results indicate that a reaction between the polyoxometalate and dioxygen is involved in the rate-determining step. This is further supported by the fact that at elevated molecular oxygen pressures, e.g. $P_{O_2} = 3$ atm, the reaction is inhibited due to saturation oxygen binding of the ruthenium centers (see mechanistic discussion below for more detail). It may be also noted that although the reaction had a complicated dependence on molecular oxygen, the source of oxygen in the 1-adamantanol product was dioxygen. Thus, hydroxylation of adamantane with 98% enriched $^{18}O_2$ yielded an average (three trials) of 95% 1-adamantanol-^{18}O.

The investigation into the adamantane hydroxylation was continued in an attempt to determine the significance of the induction period. Heating a solution of 0.25 mmol of adamantane with 0.1 mol % of $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ in 0.5 mL of 1,2-dichloroethane under argon for 12 h followed by addition of oxygen led to no change in the induction period required for hydroxylation. On the other hand, heating a solution of 0.25 μmol of $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ in 0.5 mL of 1,2-dichloroethane under 1 atm of oxygen for 12 h followed by addition of 0.25 mmol of adamantane led after 5 h to formation of 6.5 mol % of 1-adamantanol versus 6.8 mol % in a reaction run for 17 h with all components present. These results clearly indicate that the induction period is related to the catalyst activation by dioxygen. This activation is strongly a function of temperature and more weakly a function of the oxygen pressure. The induction period is reasonably connected to the oxidation of the inactive original precursor ruthenium(III)-substituted polyoxometalate to an active form of a higher oxidation state, e.g. ruthenium(IV).

Since it was known from the literature in the ruthenium porphyrin case[7] that the Ru(II)/Ru(IV)/Ru(VI) manifold is operating in the activation of dioxygen whereas the Ru(III)/Ru(V) manifold is inactive, a similar situation was hypothesized for this ruthenium polyoxometalate catalyzed reaction.[12] Indeed, as stated above, reduction of the initial ruthenium(III) polyoxometalate with zinc or sodium ascorbate to a ruthenium(II) analogue followed by addition of molecular oxygen led to immediate adamantane hydroxylation at postinduction rates. Other indirect evidence pointing to a Ru(II)/Ru(IV) rather than a Ru(III)/Ru(V) manifold was obtained by addition of aqueous sodium periodate to a solution of 0.25 mmol of adamantane and 0.25 μmol of $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ in 0.5 mL of 1,2-dichloroethane. Sodium periodate has been shown to oxidize Ru(III) to Ru(V) under these conditions.[13] Addition of 1 atm of molecular oxygen showed no catalytic activity for such an oxidized ruthenium species even after 3 days. Further evidence for a Ru(II)/Ru(IV) manifold will be presented below.

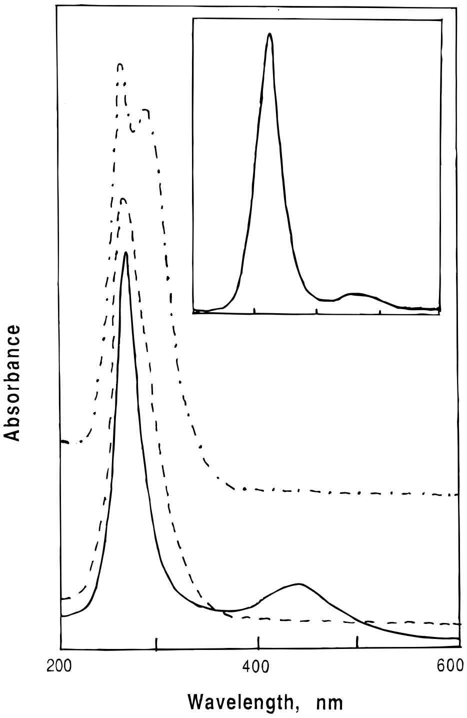


Figure 5. UV−vis spectra of $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$. All spectra were taken as 0.2 μM solutions and are offset for clarity. Key: (a) —, $K_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ in water; (b) - - -, $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ in 1,2-dichloroethane; (c) —•—, $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ in 1,2-dichloroethane after treatment with 1 atm of O_2 at 80 °C for 18 h. Insert: $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ in 1,2-dichloroethane after treatment with 1 atm of CO at 80 °C for 12 h.

Spectroscopic Studies and Coordination Chemistry. The kinetic and other studies connected with the selective hydroxylation of 1-adamantane presented above already indicated the formation of an active species formed upon mixing the ruthenium-substituted polyoxometalate and molecular oxygen. To further characterize the "activated species" formed during this interaction, UV−vis, IR, and ESR spectroscopy was used to understand the coordination chemistry between the ruthenium-substituted polyoxometalate and molecular oxygen. The UV−vis spectrum of K_{11}−**1** in water, Figure 5a, shows a W → O charge-transfer peak at 266 nm accompanied by an additional peak at 382 nm which we assigned to d−d transitions in the Ru(III)−aquo and/or Ru(III)−OH moiety. Dissolution the polyoxometalate in a 1,2-dichloroethane solution as Q_{11}−**1** (Q = tricaprylmethylammonium) under an ambient or an inert atmosphere changes the UV−vis spectrum, Figure 5b, so that only the peak at 266 nm remains. Upon "activation" of Q_{11}−**1** with molecular oxygen, the spectrum changes and an additional new peak appearing at 290 nm, Figure 5c, is observed. Spectral changes such as those observed here are known for polyoxometalates.[14] The change of the spectrum upon dissolution in an organic solvent can be attributed to the loss of the labile aquo and/or hydroxo ligand. The change upon addition of molecular oxygen can be attributed to a change in the oxidation state, e.g. Ru(III) → Ru(IV), the complexation of oxygen, and/or the formation of a ruthenium oxo or peroxo species. The ability of the ruthenium polyoxometalate to coordinate small molecules is not limited to molecular oxygen. For instance,

---

(11) Results were somewhat erratic in this regime due to experimental difficulties in exact measurement of conversions.

(12) Several ruthenium(IV) oxo and ruthenium(VI) dioxo compounds in addition to porphyrins[7] are known as oxygen transfer agents: (a) Che, C.-M.; Li, C.-K.; Tang, W.-T.; Yu, W.-Y. *J. Chem. Soc., Dalton Trans.* **1992**, 3153. (b) Stultz, L. K.; Binstead, R. A.; Reynolds, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 2520. (c) Leung, W.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8812. (d) Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 779. (e) Acquaye, J. H.; Muller, J. G.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 160. (f) Bailey, C. L.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1987**, 179.

(13) Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *112*, 6025.

(14) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

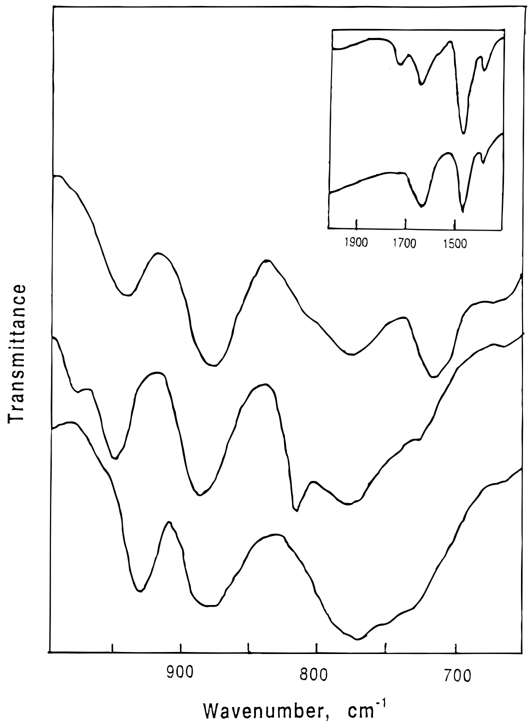


Figure 6. IR spectra of $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$. All spectra were taken after evaporation of a solution on a KBr plate and are stacked for clarity: (a, bottom) $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$; (b, middle) $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ after treatment with $^{16}O_2$; (c, top) $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ after treatment with $^{18}O_2$. Insert: $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ (bottom) before and (top) after treatment with CO. Where relevant, 0.5 mM solutions of $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ in 1,2-dichloroethane were treated with the relevant gas for 12 h at 80 °C.

treatment of Q_{11}−**1** in 1,2-dichloroethane with carbon monoxide, Figure 5 insert, also results in a dramatic change in the UV−vis spectrum with the appearance of an additional distinct peak at 420 nm.

The spectral changes vis-à-vis coordination chemistry observed in the UV−vis spectra can also be investigated by IR spectroscopy. The IR spectrum of untreated Q_{11}−**1**, Figure 6a, with peaks at 928, 881, and 765 cm^{-1} assigned to terminal W−O, corner-sharing W−O−W, and edge-sharing W−O−W moieties, changes, Figure 6b, upon activation with $^{16}O_2$ to yield a new peak at 805 cm^{-1}. The peak position leads to the possible assignment as a ruthenium peroxo or ruthenium oxo species but appears to eliminate a ruthenium dioxygen species expected to appear at ∼1100−1200 cm^{-1}.[15] Activation with $^{18}O_2$ leads to a significant 85 cm^{-1} shift in the observed IR spectrum, Figure 6c. This shift is higher than the theoretical 40 cm^{-1} shift expected but is attributed to a secondary effect of interaction with the polyoxotungstate "ligand" or matrix. A possible exchange of ^{16}O with ^{18}O within the polyoxometalate cannot be discounted. Evidence for the strong interaction between the proposed ruthenium oxo/peroxo species and the polyoxotungstate "ligand" can be observed by further comparison of the IR spectra. Thus, addition of $^{16}O_2$ leaves the peak at 765 cm^{-1} unchanged, but the peak a 881 cm^{-1} is slightly shifted to 888 cm^{-1}. The shift of the peak at 928 cm^{-1} to 945 cm^{-1} is much more dramatic. Significantly, the shifts of the peaks at 881 and 928 cm^{-1} upon activation with $^{18}O_2$ to higher energies are less than what is observed for activation with $^{16}O_2$ as would be expected. Thus, the peak at 881 cm^{-1} is essentially unchanged and the peak at 928 cm^{-1} is shifted only slightly to 933 cm^{-1}. The use of IR spectroscopy also allowed confirmation of carbon monoxide coordination. Thus, treatment of Q_{11}−**1**, with CO at 100 °C for 2 days clearly showed the formation of a peak at 1738 cm^{-1} clearly indicative of a carbon monoxide complexation, Figure 6 insert.

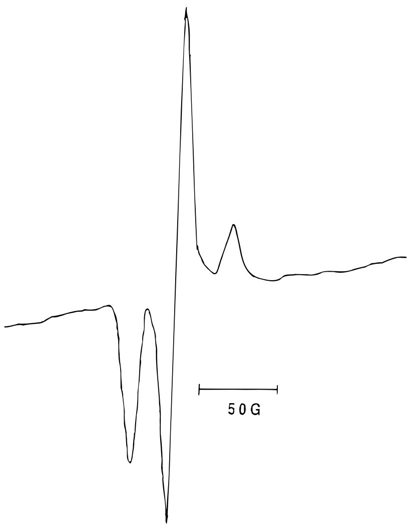


Figure 7. ESR spectrum of $Q_{11}WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$ after addition of a spin trap. The spectrum (X-band, $n = 9.185$ GHz) was measured at 120 K after 0.25 mmol of adamantane, 0.25 μmol of Q_{11}-$WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2$, 0.5 mL of 1,2-dichloroethane, and 1 atm of oxygen were mixed at 80 °C for 14 h and 1 μmol of 2-methyl-2-nitrosopropane (spin trap) was added. Addition of 5,5-dimethyl-1-pyrroline *N*-oxide gave identical results. Solutions before addition of either spin trap or solutions with adamantane after addition of either spin trap were "silent".

Further investigations of the ruthenium-substituted polyoxometalate, its oxidation state, and the effect of molecular oxygen were carried out using ESR spectroscopy. The ESR spectrum of the original paramagnetic $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ species shows a typical spectrum for an anisotropic ruthenium(III) species in an octahedral coordination.[9b] Dissolution of Q_{11}−**1** in 1,2-dichloroethane and treatment with molecular oxygen or with molecular oxygen and adamantane as substrate yield an ESR-silent solution pointing toward a diamagnetic or an antiferromagnetically coupled ruthenium intermediate. Attempts to change the oxidation state by addition of spin traps, both 2-methyl-2-nitrosopropane (MNP) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), yielded the following results. In the case of Q_{11}−**1** treated only with molecular oxygen, addition of either spin trap had essentially no effect.[16] On the other hand, addition of a spin trap to a solution where Q_{11}−**1** was treated with molecular oxygen and adamantane yielded a very clean spectrum, Figure 7, with $g_1 = 1.96$ and $g_2 = 2.01$. No formation of an organic radical was observed, and importantly the ESR spectra were identical for both spin traps. In our interpretation of the results, in the sample of Q_{11}−**1** treated with molecular oxygen, a diamagnetic ruthenium(IV) oxo or a magnetically coupled ruthenium(III) μ-peroxo species (see also below) was unaffected by the addition of the spin trap because the ruthenium center was coordinatively saturated and interaction of the ruthenium center with the spin trap was inhibited. On the other hand, under adamantane hydroxylation reaction conditions, the polyoxometalate was partly not saturated coordinatively as in a diamagnetic ruthenium(II) species. In this case, addition of

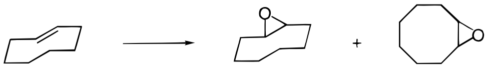
---

[15] Nakamoto, K. *Coord. Chem. Rev.* **1990**, *100*, 363.

[16] There was a very weak signal barely above the noise which appeared similar to that in the spectrum observed in Figure 7.

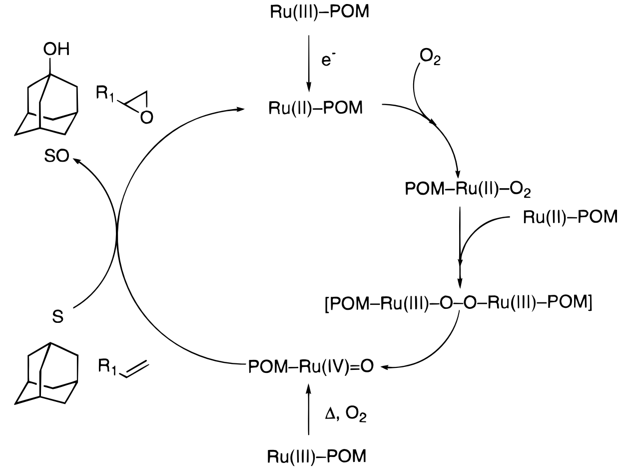
any spin trap led to the easy formation of a Ru(III) species with coordination of the spin trap at the previously noncoordinated site. The spectrum obtained is indeed clearly indicative of a low-spin, $S = {}^1/_2$, ruthenium(III) compound in an octahedral field.

Alkene Epoxidation. Original experiments designed to test the reactivity of alkenes were carried out by mixing 0.25 mmol of alkene and 0.25 μmol of Q_{11}−**1** in 0.5 mL of 1,2-dichloroethane under 1 atm of oxygen at 80 °C for 24 h. For a large series of alkenes (cyclohexene, *cis*-cyclooctene, styrene, 2,3-dimethyl-2-butene, 1-octene, and norbornene), no products were observed. Our interpretation of the results led to the conclusion that the alkenes inhibited binding of molecular oxygen to the ruthenium center necessary for its activation. Support for this conclusion was obtained by using adamantane and cyclooctene as cosubstrates under the reaction conditions described above. The experiment conclusively showed that the presence of cyclooctene prevented the normal hydroxylation of adamantane. Alkenes can, however, still be oxidized using the $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ polyoxometalate in one of three ways. First, a solution of Q_{11}−**1** (1−50 mM) in 1,2-dichloroethane may be treated with molecular oxygen at 80 °C for 12 h followed by removal of excess oxygen and addition of an alkene. Further reaction at room temperature for 2 h yielded epoxides in higher than 99% selectivity.[8] Second, use of high oxygen pressure compared to lower alkene concentration can increase the likelihood of molecular oxygen coordination to the ruthenium active site and decrease the tendency for inhibition by the alkene. Thus, a reaction carried out by mixing 0.25 mmol of *cis*-cyclooctene and 0.25 μmol of Q_{11}−**1** in 0.5 mL of 1,2-dichloroethane under 5 atm of oxygen at 80 °C for 24 h yielded 5% (50 turnovers) *cis*-cyclooctene oxide versus no reaction at 1 atm. A control experiment without catalyst under identical conditions also yielded no epoxide; therefore, this is indeed a catalytic reaction. A third possibility is to use a sterically hindered but active alkene which would be less likely to inhibit molecular oxygen coordination and activation. *trans*-Cyclooctene was chosen to test this hypothesis, eq 4. A reaction of 0.25 mmol of *trans*-cyclooctene and 0.25 μmol of Q_{11}−**1** in 0.5 mL of 1,2-dichloroethane under 1 atm of oxygen at 80 °C for 24 h gave 12.5 mol % (125 turnovers) of cyclooctene oxide at a *trans*:*cis* ratio of 20:1. In addition to proving that catalytic epoxidations are indeed possible, this experiment gave important additional proof that the reaction proceeding via the proposed ruthenium oxo species is not of a free radical nature, because the trans-cyclooctene substrate acts as a free radical clock ($k_{\text{isomerization}} = 10^9\ s^{-1}$).[17] Therefore, under typical autoxidation conditions, only *cis*-cyclooctene oxide was formed whereas with reactions that are not of a free radical nature, e.g. epoxidation with dioxirane[18] or with a porphyrin iron oxo intermediate,[19] *trans*-cyclooctene oxide was the major product as in this case.



(4)

Scheme 1. Proposed Catalytic Cycle for Dioxygen Activation and Substrate Oxygenation



Mechanistic Proposal. On the basis of the results observed for the hydroxylation of adamantane, including those of the kinetics studies and the UV−vis, IR, and ESR spectroscopic studies of the ruthenium coordination chemistry, and the results of the alkene epoxidation experiments, a dioxygenase type catalytic cycle is proposed, Scheme 1. There is now a large amount of evidence indicating the catalytic oxidation of hydrocarbons catalyzed by $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ is not a free radical reaction. This evidence includes (a) a substrate (adamantane):dioxygen reaction stoichiometry of 2:1, (b) the product selectivity observed in *trans*-cyclooctene and adamantane epoxidation and hydroxylation, respectively, (c) the fact that free radical scavengers do not inhibit catalytic hydroxylation of adamantane, (d) the kinetic isotope effect observed in 1,3-adamantane-d_2 hydroxylation, (e) the lack of reactivity of alkylaromatics such as cumene, (f) the absence of $H_2{}^{18}O$ formation when $^{18}O_2$ is used as the oxidant, and (g) the isolation of a ruthenium oxo or peroxo species, its identification by IR, and its use in the stoichiometric epoxidation of alkenes. To the contrary, we have amassed a significant body of information indicating that the $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ polyoxometalate catalyzes hydrocarbon oxidation via a dioxygenase type mechanism in a Ru(II)/Ru(IV) type manifold as described in Scheme 1. Much of the evidence that contradicts the metal-catalyzed autoxidation also supports the dioxygenase type mechanism. The key points favoring the dioxygenase mechanism are the adamantane:dioxygen reaction stoichiometry and the formation of a ruthenium oxo or peroxo intermediate without formation of water. The intermediate was isolated, identified by IR (supported also by UV−vis) spectroscopy, and used as a stoichiometric epoxidizing agent. Additionally, concerning the ruthenium oxidation states, the ESR experiments show that the active intermediate is diamagnetic, i.e. Ru(II), Ru(IV), or Ru(VI), or is a magnetically coupled Ru(III) μ-peroxo species. As stated above, the fact that solution after the addition of a spin trap to a mixture of polyoxometalate and oxygen only shows no ESR signal indicates the presence of a coordinatively saturated ruthenium species, POM−Ru(IV)=O or POM−Ru(III)−O−O−Ru(III)−POM. On the other hand, in the presence of substrate and oxygen, some POM−Ru(II) species is present. This may react with a spin trap (ST) to yield a ST−Ru(III)−POM compound with very indicative spectrum, typical of low-spin $S = {}^1/_2$ compounds in an octahedral field.

The formulation of the mechanism as presented in Scheme 1 is also strongly supported by the kinetic studies of the adamantane hydroxylation. According to the mechanistic scheme, the interaction of the ruthenium-substituted polyoxo-

---

(17) Shea, K. J.; Kim, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 3044.

(18) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Shulz, M.; Smerz, A. K.; Veloza, L. A.; Weinkötz, S.; Winde, R. *Chem.—Eur. J.* **1997**, *3*, 104.

(19) Traylor, T. G.; Iamamoto, Y.; Nakano, T. *J. Am. Chem. Soc.* **1986**, *108*, 3529.

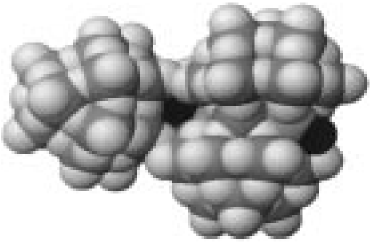


Figure 8. CPK model of the stipulated μ-peroxo dimer intermediate. Each black sphere represents peroxo bridge and a terminal oxo attached to a ruthenium center.

metalate may be also be described as in eq 5. Under the reasonable assumption that the formation of the Ru(III)−peroxo dimer is the rate-determining step,[20] eq 6 can be derived. The derived rate equation indeed predicts, as was experimentally observed, that the reaction should be second order in the polyoxometalate. Analysis of the oxygen dependence shows that when dioxygen is in limiting concentrations relative to the polyoxometalate, ($K_1[O_2] < 1$; experimentally at $P_{O_2} = 0.2$ atm) but not to the organic substrate, the reaction is dependent on the molecular oxygen pressure. Upon an increase in the oxygen pressure ($K_1[O_2]$ becomes ≥ 1), the rate at first increases but the dependency on the oxygen pressure also decreases (experimentally at $P_{O_2} = \sim 0.8$ to ~ 1.5 atm). After a further increase in oxygen pressure, for example at $P_{O2} = 3$ atm and $K_1[O_2] \gg 1$, it was observed that the rate decreased (Figure 4; k_{obs} decreased). This can be explained by a saturation effect, whereby if $K_1 \gg 1$ there are fewer free Ru(II) moieties. Analytically, the k_{obs} decreases from somewhat less than k_2K_1 to $\sim k_2/K_1$. The reaction approaches inverse first order in O_2. A CPK model of a proposed intermediate is given in Figure 8. The strong steric constraints regarding the formation of a POM−Ru(III)−O−O−Ru(III)−POM species, which may be inferred from Figure 8, nicely explain the low entropy of activation observed in this reaction and support the assumption that its formation is rate determining. Although the IR and ESR spectra certainly support such a POM−Ru(III)−O−O−Ru(III)−POM intermediate, other possibilities may also be entertained.

$$\mathrm{Ru^{II}POM + O_2 \overset{K_1}{\rightleftharpoons} Ru^{II}POM{-}O_2}$$

$$\mathrm{Ru^{II}POM{-}O_2 + Ru^{II}POM \xrightarrow[\text{rds}]{k_2} Ru^{III}POM{-}O{-}O{-}Ru^{III}POM}$$

$$\mathrm{Ru^{III}POM{-}O{-}O{-}Ru^{III}POM \rightarrow 2Ru^{IV}{=}O} \qquad (5)$$

$$\mathrm{d}P/\mathrm{d}t = k_2[\mathrm{Ru(II)}][\mathrm{RuO_2}] = k_2K_1[\mathrm{Ru(II)}]^2[\mathrm{O_2}] \quad (\text{where } K_1 = [\mathrm{RuO_2}]/[\mathrm{Ru(II)}][\mathrm{O_2}])$$

$$[\mathrm{Ru_T}] = [\mathrm{Ru(II)}] + [\mathrm{RuO_2}] = [\mathrm{Ru(II)}] + K_1[\mathrm{Ru(II)}][\mathrm{O_2}] = [\mathrm{Ru(II)}](1 + K_1[\mathrm{O_2}]) \quad (6)$$

$$\therefore \quad [\mathrm{Ru(II)}] = \frac{[\mathrm{Ru_T}]}{1 + K_1[\mathrm{O_2}]} \quad \text{and} \quad \frac{\mathrm{d}P}{\mathrm{d}t} = k_2K_1\frac{[\mathrm{Ru_T}]^2[\mathrm{O_2}]}{(1 + K_1[\mathrm{O_2}])^2}$$

Some comments are also in order to explain the initiation of the catalytic cycle from the ruthenium(III) precursor. The transfer of the $[\mathrm{WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2}]^{11-}$ polyoxometalate into the organic phase in our minds leads to formation of ruthenium(III) sites of tetragonal coordination. The formation of such five-coordinate metal sites upon transfer of alkali metal salts of polyoxometalates into apolar organic media with quaternary ammonium halides is well documented.[21] In the most straightforward manner, the catalytic reaction can be initiated by the addition of a reducing agent leading to formation of the ruthenium(II) species. More complicated appears to be the initiation with heating under an oxygen atmosphere. In this case, there is an induction period where presumably ruthenium(III) is oxidized to a ruthenium(IV) oxo species. In the future, the mechanistics of this process will still need to be explored.

Conclusion

In this paper, the results on the activation of molecular oxygen using a "sandwich" type ruthenium-substituted polyoxometalate have been described. Studies on the hydroxylation of adamantane showed an adamantane:dioxygen stoichiometry of 2:1. This finding, together with a kinetic study of the adamantane hydroxylation, the use of UV−vis, IR, and ESR spectroscopy to study the molecular oxygen coordination and oxidation states of the polyoxometalate, and the study of alkene epoxidation, including the observation of retention of conformation in the catalytic oxidation of *trans*-cyclooctene, has led to us to propose a dioxygenase type mechanism as outlined in Scheme 1. It would have been of course helpful to observe the various intermediate species by ^{183}W NMR; however, all our attempts at these measurements failed due to insufficient solubility of Q_{11}−**1** in organic phases.

Experimental Section

Materials. Organic substrates of highest available purity (Aldrich and Fluka) were purified prior to use by passing the compounds over a neutral alumina column. Adamantane was an exception and was used without treatment. *trans*-Cylooctene was prepared by the known literature procedure.[17] 1,2-Dichloroethane (Frutarom) was treated with H_2SO_4 and $SnCl_2$ to remove stabilizers and peroxides, respectively, and then distilled under ambient conditions prior to use. $^{18}O_2$ (98% isotopic enrichment) was obtained from Enritech. Polyoxometalates, $[\mathrm{WZn(M1)_2(ZnW_9O_{34})_2}]^{q-}$ (M1 = Ru(III), Mn (II), Co(II), Ni(II), Cu(II), Zn (II), Rh(III), Pt(II), Pd(II), Fe(III), were prepared as alkali metal salts by the published literature procedures.[9,22] $\mathrm{K_{11}[WCoRu^{III}_2(CoW_9O_{34})_2]\cdot 21H_2O}$ was prepared from $\mathrm{Na_{12}[WCo_3(CoW_9O_{34})_2]\cdot 47H_2O}$[22a] by dissolving 23 g (3.9 mmol) of $\mathrm{Na_{12}[WCo_3(CoW_9O_{34})_2]\cdot 47H_2O}$ in 10 mL of water at 90 °C under an inert argon atmosphere. $\mathrm{Ru^{II}(DMSO)_4Cl_2}$, 4 g (12.2 mmol), was added, and the solution was kept at 90 °C under argon for 18 h. After cooling and addition of excess KCl, the $\mathrm{K_{11}[WCoRu^{III}_2(CoW_9O_{34})_2]\cdot 21H_2O}$ product was filtered off and recrystallized as green-brown needles (yield 46%). Anal. Found (calcd): K, 7.21 (7.48); W, 60.0 (60.78); Co, 2.93 (3.08); Ru, 3.3 (3.54). $\mathrm{K_{11}[WZnRu^{III}_2(CoW_9O_{34})_2]\cdot 23H_2O}$ was prepared from $\mathrm{Na_{12}[WZn_3(CoW_9O_{34})_2]\cdot 45H_2O}$ in an identical procedure.[23]

The alkali metal cations of the polyoxometalates were exchanged with a quaternary ammonium salt by a metathesis reaction. Typically, 1 mmol (5.75 g) of $\mathrm{K_{11}[WZnRu^{III}_2(ZnW_9O_{34})_2]}$ dissolved in a minimal amount of water was reacted with 11 mmol of trioctylmethylammonium chloride dissolved in dichloromethane. After completion of the transfer

---

[20] This assumption is based on the fact that a very low entropy of activation, $\Delta S^{\ddagger}_{25} = -54.9$ cal/(mol K), was observed. This is most consistent with the associative formation of a peroxo dimer in the rate-determining step as opposed to a more dissociative transition state and significantly higher $\Delta S^{\ddagger}_{25}$ expected if the formation of $\mathrm{Ru^{IV}{=}O}$ from the peroxo dimer was the rate-determining step.

[21] (a) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737. (b) Neumann, R.; Gara, M. *J. Am. Chem. Soc.* **1995**, *117*, 5066.

[22] (a) Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143. (b) Neumann, R.; Khenkin, A. M. *J. Mol. Catal.* **1996**, *114*, 169.

[23] Feldberg, L.; Khenkin, A. M.; Neumann, R. Manuscript in preparation.

reaction easily observable by UV−vis and transfer of the colored polyoxometalate, phases were separated, the organic phase was dried with Na_2SO_4, and the solvent was removed by evaporation. Yields were essentially quantitative, and the $Q_{11}[WZnRu^{III}_2(ZnW_9O_{34})_2]$ catalyst was used as a stock solution in 1,2-dichloroethane.

Kinetic Studies−Adamantane Hydroxylation. The kinetic studies of adamantane hydroxylation were carried out in ∼25 mL pressure tubes (Ace Glass). In a typical procedure, 2.5 mmol of adamantane, 2.5 μmol of $Q_{11}[WZnRu^{III}_2(ZnW_9O_{34})_2]$, and 5 mL of 1,2-dichloroethane were placed in the glass tube with a Teflon stirrer. Dioxygen, >99% purity, was introduced into the reaction mixture at the required temperature and pressure after a series of three pump−thaw operations. The tube was immersed in a temperature-controlled oil bath equipped with a magnetic stirrer. Aliquots of the reaction mixture were taken at the desired time intervals and directly injected into a gas chromatograph (HP 5890, FID detector, He carrier gas) fitted with a capillary methyl silicone bonded phase column (RTX-1, length 30 m, i.d. 032 mm, coating thickness 0.25 μm). Reactions at less than 1 atm of dioxygen were carried out using the appropriate dioxygen/nitrogen mixtures. The adamantane:dioxygen stoichiometry was measured by introducing ∼1 atm of dioxygen into a 5 mL vial containing 0.25 mmol of adamantane and 0.25 μmol of $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ in 0.5 mL of 1,2-dichloroethane. The pressure was measured exactly using a mercury manometer and the valve closed. After reaction at 80 °C for 2 days, the reaction vial was cooled and the amount of oxygen consumed measured by reopening the reaction vial attached to the manometer.

Spectroscopic Studies. UV−vis spectra were measured on a diode array spectrometer (HP 8452) using 1 cm quartz cuvettes. Solutions, 20 μM, were prepared by dissolving $Q_{11}[WZnRu^{III}_2(ZnW_9O_{34})_2]$ in 1,2-dichloroethane or $K_{11}[WZnRu^{III}_2(ZnW_9O_{34})_2]$ in water. For polyoxometalate treated with O_2 or CO, the solution was placed in a glass pressure tube and O_2 or CO was added as described above. After 18 h at 80 °C, the tube was opened, the solution was transferred to the cuvette, and the spectrum was recorded immediately. IR spectra were measured on a Nicolet 510M FTIR instrument. In this case, 0.5 mM solutions were prepared and treated as above. After 12 h at 80 °C, a few drops of a solution was placed on a KBr plate, the solvent was quickly evaporated under a stream of oxygen, and the the spectrum was recorded. ESR spectra were measured with a Varian E-12 spectrometer at 120 K (frequency 9.185 GHz, scan range 400 G, time constant 0.3 s, modulation amplitude 8 G at 100 kHz, and microwave power 80 mW). Solutions of 2.5 μmol of $Q_{11}[WZnRu^{III}_2(ZnW_9O_{34})_2]$ in 0.5 mL of 1,2-dichloroethane in 10 mL pressure tubes with or without 2.5 mmol of adamantane were treated with dioxygen for 14 h at 80 °C. Aliquots of the solutions were transferred to 4 mm quartz ESR tubes, and where indicated, 0.1 mmol spin trap samples (2-methyl-2-nitrosopropane or 5,5-dimethyl-1-pyrroline *N*-oxide) were added and the reactions were quenched by cooling with liquid nitrogen.

Acknowledgment. This research was supported by the Israel Science Foundation founded by the Israel Academy of Science and Humanities. Dr. Alex Khenkin is thanked for the oxygen consumption measurements.

JA974243B