Polyoxoanion-Supported, Atomically Dispersed Transition Metals: The Catalytic Oxidation of Cyclohexene with Dioxygen by the Catalyst Precursors [(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-COD)Ir•P$_2$W$_{15}$Nb$_3$O$_{62}$], [(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-COD)Rh•P$_2$W$_{15}$Nb$_3$O$_{62}$], and [(n-C$_4$H$_9$)$_4$N]$_{4.5}$Na$_{2.5}$[(C$_6$H$_6$)Ru•P$_2$W$_{15}$Nb$_3$O$_{62}$]

NORITAKA MIZUNO,[1] DAVID K. LYON, AND RICHARD G. FINKE[2]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1210

[(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-COD)Ir•P$_2$W$_{15}$Nb$_3$O$_{62}$], **1**, [(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-COD)Rh•P$_2$W$_{15}$Nb$_3$O$_{62}$], and [(n-C$_4$H$_9$)$_4$N]$_{4.5}$Na$_{2.5}$[(C$_6$H$_6$)Ru•P$_2$W$_{15}$Nb$_3$O$_{62}$] have been shown to catalyze the oxygenation of cyclohexene with molecular oxygen. The polyoxoanion-supported iridium(I) complex, **1**, shows the highest activity of this group with a turnover frequency of 2.9 h^{-1} at 38°C in CH$_2$Cl$_2$ (540 total turnovers), which is 100-fold greater than its parent iridium compound, [(1,5-COD)IrCl]$_2$. Additional experiments using H$_2$/O$_2$ mixtures and H$_2$O$_2$ are also discussed. The apparent rate law for the oxidation of cyclohexene by O$_2$ by **1** is -d[cyclohexene]/dt = k_2 obsd · [**1**]^1[cyclohexene]^{1}P(O$_2$)$^{1\rightarrow0}$. These compounds constitute the first examples of oxygenation catalysis using molecular oxygen and a polyoxoanion-*supported* transition-metal precatalyst. © 1991 Academic Press, Inc.

INTRODUCTION

Polyoxoanion-supported organometallics[3] offer new and exciting opportunities to explore the catalytic properties and mechanisms of oxide-supported, atomically dispersed transition metals. A key point is that the composition and structure of the active site can be fully established at the atomic level for such soluble systems (Fig. 1). Such compositional, structural, and mechanistic information is central to the rational design of improved catalysts. These discrete analogs of solid oxide-supported heterogeneous systems also generally present only one type of active site, i.e., homogeneity in their active sites. For these reasons polyoxoanion-supported organometallics, and demonstration of catalysis by a polyoxoanion-supported metal, are of interest. Oxidation chemistry with polyoxoanion-supported metals is of special interest because the polyoxoanion is highly oxidation resistant, if not inert.

Our overall goal is to develop the needed paradigm for polyoxoanion-supported catalysis. Recently we described the first example of *reductive* catalysis (cyclohexene hydrogenation) (*2, 3*) by a polyoxoanion-*supported* metal, work which employed the supported catalyst precursor [(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-COD)Ir•P$_2$W$_{15}$Nb$_3$O$_{62}$], **1**. Herein, we describe the first example[4] of *oxidative catalysis*, while surveying three different polyoxoanion-supported catalyst precursors. The results also demonstrate that the preferred catalyst precursor is again **1**,

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[1] Present address: Catalysis Research Center, Hokkaido University, Sapporo, Japan.

[2] To whom correspondence should be addressed.

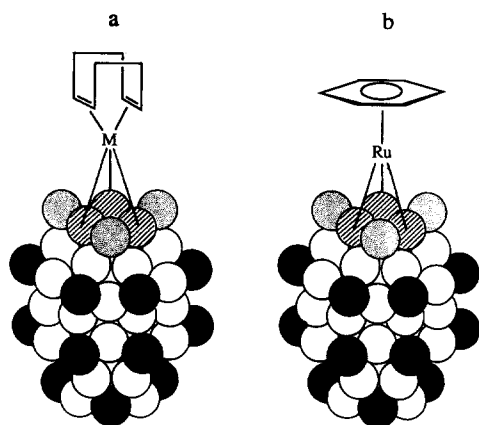[3] See Ref (*1*) for earlier papers in a series.

[4] The *stoichiometric* reaction of O$_2$ with the trimetaphosphate organometallic complex [(1,5-COD)Ir•P$_3$O$_9$]$^{2-}$ has been recently reported in an elegant x-ray crystallographic study by Klemperer and co-workers (*9*).

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a b

FIG. 1. Space filling representations of the proposed structures of (a) $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)M\cdot P_2W_{15}Nb_3O_{62}]$ $(M = Ir, Rh)$ and (b) $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]$ based on ^1H, ^{13}C, ^{31}P, and ^{183}W NMR spectroscopic data $(3, 18, 19)$. The black circles represent terminal oxygens and the white circles represent bridging oxygens. The grey circles are terminal oxygens attached to the niobium (Nb–O) and the hatched circles are oxygens bridging two niobiums (Nb–O–Nb). The key is that regiospecific support of the organometallic cations occurs on the more basic "$Nb_3O_9^{3-}$" end of $P_2W_{15}Nb_3O_{62}^{9-}$ $[= "(PO_4)_2^{6-}(W_{15}Nb_3O_{54})^{3-}"]$. Further details about the synthesis and the structures are available $(3, 18, 19)$. Note Added in Proof: Recent ^{17}O NMR studies demonstrate that, in the Ir(I) complex 1, the iridium is bonded to two Nb-O-Nb (hatched) oxygens and to one Nb-O terminal (grey) oxygen.

which contains both iridium and the very basic $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion.

We note that classical types of heteropolyanions (4) mediate the catalytic oxidation of organic substrates with molecular oxygen $(5–7)$ and there is one report of organometallic cations plus isopolyanion clusters catalyzing $t\text{-}BuOOH$ oxidation of cyclohexene (8). It is important not to confuse the present, novel polyoxoanion-supported metals and their different chemistry (primarily due to cis-coordination sites, possible mobility on the oxide surface, and possible dissociation of one of the three oxide ligands leading to a coordinatively unsaturated and thus reactive site on the metal) with the more common situation of polyoxoanion framework-incorporated metals (such as the

Nb^{5+} in $P_2W_{15}Nb_3O_{62}^{9-}$ or the V^{5+} in $P_2W_{15}V_3O_{62}^{9-}$, where the Nb^{5+} or V^{5+} metal is rigidly fixed in the framework, without mobility and without the ability to dissociate oxide ligands to generate a site of coordinative unsaturation). This important conceptual point is discussed in further detail elsewhere $(34$, footnote 1f).

The catalytic oxygenation of substrates by molecular oxygen is of particular interest (10) and oxygenations of various cycloalkenes with molecular oxygen and Ir, Rh, or Ru organometallic complexes to yield 2-cyclohexen-1-one, 2-cyclohexen-1-ol, and cyclohexene epoxide are among those that have been examined $(11–16)$. However, even in the best examples of the oxygenation of cycloolefins with dioxygen catalyzed by Ir, low rates (0.02–0.5 turnovers/h) $(11, 12)$ and few total turnovers (3 to 14 (15) turnovers) $(12, 15)$ have been the rule. Mixed-metal systems containing Ir/Mo and Rh/Nb, have been shown to lead to enhanced rates and turnovers in a classic paper in the area of allylic oxidation (17). However, the study reported below is novel in comparison to all previous work. It is worth noting that a key to each of the catalysts described herein is the novel, basic oxide polyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$, whose niobium oxide groups approach the basicity of CH_3O^-. (Note the difference between the custom-made, basic $P_2W_{15}Nb_3O_{62}^{9-}$ and the commercially available, well-known polyoxoanions $PW_{12}O_{40}^{3-}$ or $P_2W_{18}O_{62}^{6-}$ which parallel ClO_4^- in their conjugate acid strengths.)

EXPERIMENTAL

The synthesis and expecially the unequivocal characterization of pure polyoxoanion-supported organometallics is a key and time-consuming aspect of this work as detailed in separate publications $(3, 18, 19)$. $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$, 1, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh\cdot P_2W_{15}Nb_3O_{62}]$, and $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]$ were prepared, from $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ and $[1,5\text{-}$

COD)$MCl]_2$ (M = Ir, Rh) or [$(C_6H_6)RuCl_2]_2$, in a ≤ 1 ppm O_2 concentration Vacuum Atmospheres dry box according to our detailed procedures (*3, 18, 19*). Several modifications have been made as these preparations have been improved over several years, especially in the synthesis of the precursor material [(n-$C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (*3, 18*). All three compounds are O_2-sensitive materials and thus were stored under a N_2 atmosphere. ([(n-$C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$, **1**, and [($n$-$C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh\cdot P_2W_{15}Nb_3O_{62}]$ are *highly* O_2-sensitive and require storage in the dry box). Dichloromethane (from CaH_2), 1,2-dichloroethane (from CaH_2), acetone (from K_2CO_3), acetonitrile (from CaH_2), N,N-dimethylacetamide (from K_2CO_3), and dimethylsulfoxide (from 3 Å mol sieves) were distilled under dry N_2 or under a partial vacuum. Cyclohexene was distilled from Na under dry N_2 to remove contaminating alkylhydroperoxides. After distillation, the liquids were dispensed into glassware that had been thoroughly cleansed, dried at 200°C, and cooled under a dry N_2 flow. The solvents were then stored in the dry box for the duration of the study.

A typical reaction was performed as follows: In the dry box, the catalyst (25 mg, 4.41 $\times$ 10^{-3} mmol in the case of **1**) was dissolved in a sealable glass vial (16 or 100 mL) containing a magnetic stir bar and 3.0 ml of the appropriate solvent. Freshly distilled cyclohexene (0.5 ml, 4.94 mmol) was added to the solution, and the vial was sealed and brought immediately out of the dry box. The glass vial was then attached to a vacuum line, cooled to 77 K (liquid N_2 trap), and degassed by three freeze–pump–thaw cycles. The vial was allowed to warm to 195 K (dry-ice ethanol bath) and 1 atm of O_2 gas was introduced to the system. The reaction vessel was then placed at 38°C (P_{total} = 1.6 atm) and vigorously stirred. The reaction vessel was removed from the bath every 4 h to refill the tube with 1 atm O_2. The reaction solution was periodically sampled by syringe and analyzed by gas chroma-
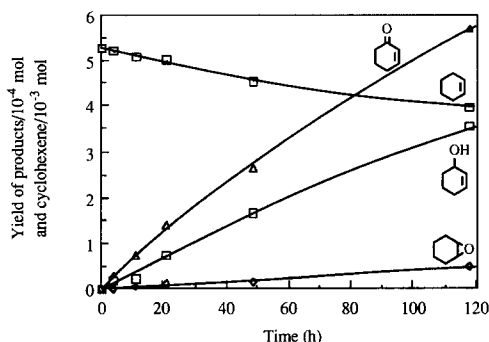

FIG. 2. The time course of cyclohexene oxygenation in the presence of O_2 (at a partial pressure $P(O_2)$ of 1 atm) and [(n-$C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ in CH_2Cl_2 at 38°C.

tography on a carbowax capillary column. The amount of each product was calculated by comparison to a calibration curve for authentic material under identical conditions. Tests for active-oxidant products by iodometry (*20*) (for example peroxides like cyclohexene hydroperoxide) proved negative ($\leq 1 \times 10^{-6}$ mol in CH_2Cl_2).

RESULTS AND DISCUSSION

The time course of cyclohexene oxidation, in the presence of the iridium(I) complex **1** and O_2 and under conditions of low cyclohexene conversion, is shown in Fig. 2, during which time the light-yellow-brown solution changed to a deep-yellow-brown and remained visibly homogeneous.[5] The ratio of the primary allylic oxidation products, 2-cyclohexen-1-ol and 2-cyclohexenone, showed little change with time and the number of turnovers after 330 h totaled approximately 540. Preliminary kinetic studies show reasonable first-order plots for the loss of [cyclohexene] (Fig. 3) and indicate that the rate of decrease of cyclohexene is $-d[\text{cyclohexene}]/dt = k_{2,\text{obsd}}\cdot[\textbf{1}]^1[\text{cyclohexene}]^1\{P(O_2)\}^{1\rightarrow 0}$ (Figs. 4–6) in the con-

[5] After the reaction is allowed to proceed for 118 h a small amount of precipitated material is observed. This may be caused by the catalyst's insolubility in the H_2O formed during the reaction.
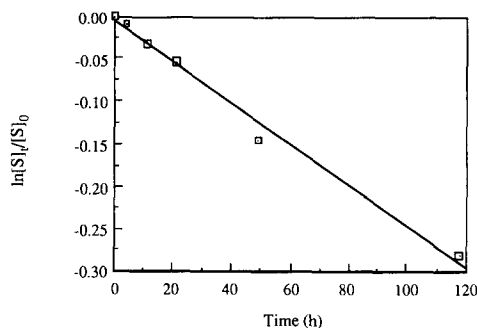
FIG. 3. First-order plot of cyclohexene disappearance (S = cyclohexene) due to its oxygenation in the presence of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ at 38°C. Solvent: CH_2Cl_2 (3.0 ml); [cyclohexene]: 1.5 M; $[[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]]$: 1.3 m$M$. Given the rate law under these conditions of $-d[\text{cyclohexene}]/dt = k_{2,\text{obsd}} \cdot [\mathbf{1}]^1[\text{cyclohexene}]^1\{P(O_2)\}^0$, the slope is the pseudo-first-order rate constant, $k_{1,\text{obsd}}(= k_{2,\text{obsd}}\cdot[\mathbf{1}]^1)$.
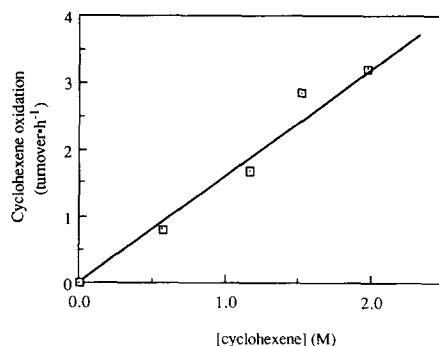

FIG. 5. Cyclohexene oxidation (pseudo-first-order rate constant) as a function of the concentration of cyclohexene in CH_2Cl_2. Temperature, 38°C; partial pressure $P(O_2)$, 1 atm; $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$, 1.3 m$M$. Additional kinetic studies, such as the (cyclohexene) dependence at low partial pressure of O_2, are of interest (33).

centration ranges of **1**, cyclohexene, and oxygen partial pressure $[P(O_2)]$ from 1.3×10^{-3} to 4.0×10^{-3} M, 0 to 2 M, and from 0 to 760 mm Hg, respectively (a partial pressure $\{P(O_2)\}^0$ dependence, that is, saturation kinetics, is reached by a oxygen partial pressure of $P(O_2) = 760$ mm Hg). The initial turnover frequency (TOF)$_i$, which was calculated from the slope of the first-order plots and normalized to the concentration of the catalyst, yielded (TOF)$_i = 2.9$ h^{-1} at 38°C

$[(\text{TOF})_i = k_{2,\text{obsd}} \cdot [\text{cyclohexene}]_i]$. This value is 100-fold larger than that for $[(1,5\text{-}COD)IrCl]_2$ (21) examined under identical conditions as a part of this work. That is, as a ligand, $P_2W_{15}Nb_3O_{62}^{9-}$ gives rise to a 100-fold rate increase in comparison to Cl$^-$. The (TOF)$_i$ for **1** is also larger than the literature reports for $Ir(CO)(PPh_3)_2Cl(O_2)$ (0.39 h^{-1}, 65°C, neat cyclohexene), $Ir(CO)(PPh_3)_2Cl$ (0.44 h^{-1}, 65°C, neat cyclohexene), and $[Ir HCl_2(1,5\text{-}COD)]_2$ ($\approx$0.08 h^{-1} (15), 5°C, N,N-

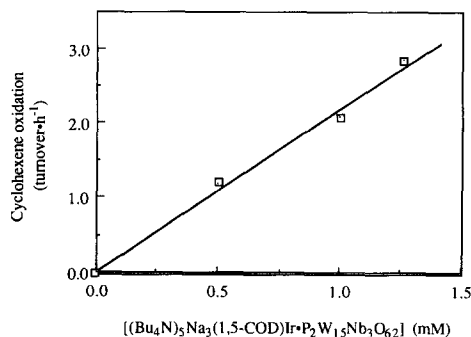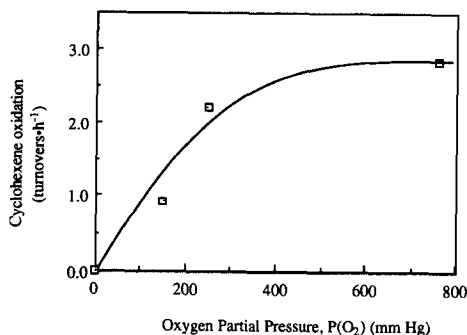FIG. 4. Cyclohexene oxidation (pseudo-first-order rate constant) as a function of the concentration of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ in CH_2Cl_2. Temperature, 38°C; partial pressure $P(O_2)$, 1 atm; [cyclohexene], 1.5 M.
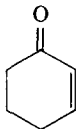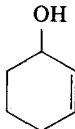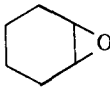

FIG. 6. Cyclohexene oxidation (pseudo-first-order rate order constant) as a function of the pressure of the oxygen partial pressure in CH_2Cl_2. Temperature, 38°C; [cyclohexene], 1.5 M; $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]$, 1.3 m$M$. Additional studies to augment the preliminary kinetic data shown are in progress (33).

TABLE 1

The Oxidation of Cyclohexene Using Molecular Oxygen in CH_2Cl_2 at 38°C

Precatalyst	% Conversion	Selectivity[a] (%)		
		O	OH	
$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]^{b}$	4.2	62	32	5
$[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru \cdot P_2W_{15}Nb_3O_{62}]^{c}$	1.2	46	49	5
$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]^{b,d}$	0.2	80	20	Trace
$[(1,5\text{-}COD)IrCl]_2$	0.04	85	15	0
$[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (Control reaction)	0	—	—	—
	Reaction with H_2O_2			
$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]^{b,e}$	2.8	84	16	Trace
	Reaction with $O_2 + H_2$			
$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]^{b,f}$	5.6	57	38	5

Note. [Precatalyst], 1.3 mM, 0.65 mM for $[(1,5\text{-}COD)IrCl]_2$; [cyclohexene], 1.5 M; partial pressure $P(O_2)$, 1 atm.

[a] After 20 h.

[b] The fate of the 1,5-COD has not been determined, but will likely follow the precedent in Refs. (9, 15).

[c] The fate of the C_6H_6 is under investigation as benzene oxidation to phenols is of interest.

[d] This result was confirmed by increasing the precatalyst concentration to 52 mM.

[e] In the presence of 0.61 ml of 30% H_2O_2 ($5.4 = 10^{-4}$ mol) under a N_2 atmosphere.

[f] In the presence of 1 : 2 oxygen : hydrogen mixture, P_{total} = 1 atm. CAUTION: $H_2 : O_2$ mixtures are an explosion hazard over a broad range (ca. 5 to 95% H_2 in O_2).

dimethylacetamide) (12, 15), although the different conditions make the comparisons less meaningful.
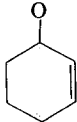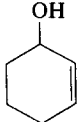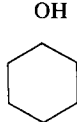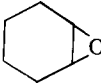
The catalytic oxygenations of cyclohexene in the presence of various catalysts and O_2 are shown in Table 1. The activity of the $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$-supported Ir, Rh, and Ru compounds decreased as follows: $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]$ > $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6))Ru \cdot P_2W_{15}Nb_3O_{62}]$ > $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]$. (A control (no Ir) using just $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (22) shows no activity (Table 1, Entry 5), hence the iridium is required for catalysis.) However, the product selectivity did not change significantly in this series. Furthermore, the selectivities are reminiscent of those observed for H_2O_2 (Table 1, second

to last entry) under identical conditions. In preliminary experiments (Table 1, last entry), further enhancement of the catalytic oxygenation reaction was observed for the mixed 1 : 2 oxygen : hydrogen system, similar to that reported by James and co-workers (15).

Table 2 summarizes the results of the oxygenation of cyclohexene with dioxygen in the presence of the preferred catalyst precursor $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]$, 1. The rate constants for oxidation are solvent dependent decreasing as follows: CH_2Cl_2 > 1,2-dichloroethane > acetone > acetonitrile $\gg$ N,N-dimethylacetamide $\approx$ dimethylsulfoxide, with relative rates of 6 : 4.25 : 2.75 : 1 : 0 : 0, respectively. In all solvents, the primary products were the allylic oxidation products 2-cyclohexen-

TABLE 2

The Solvent Dependence of the Oxygenation of Cyclohexene by Molecular Oxygen and
$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\bullet P_2W_{15}Nb_3O_{62}]$

Solvents	Rate constants $(10^{-3}\ h^{-1})$	% Conversion	Selectivity[a] (%)			
			O	OH	OH	O (epoxide)
CH_2Cl_2	2.4	5.1	62	32	0	5
$1,2\text{-}C_2H_4Cl_2$	1.7	3.9	73	27	0	Trace
$(CH_3)_2CO$	1.1^b	2.2	56^b	29^b	13^b	1^b
CH_3CN	0.4	0.07	71	29	0	Trace
$CH_3CON(CH_3)_2$	0	0	—	—	—	—
$(CH_3)_2SO$	0	0	—	—	—	—

Note. Temperature, 38°C; $[[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\bullet P_2W_{15}Nb_3O_{62}]]$, 1.3 m$M$; [cyclohexene], 1.5 M; partial pressure $P(O_2)$, 1 atm.

[a] After 20 h; error bars are ±10%.

[b] Rate constants and selectivity to oxygenated products only. 1,3-cyclohexadiene (15%) and benzene (2%) were also formed (see footnote 6).

1-ol and 2-cyclohexen-1-one,[6] with a carbon (mass) balance greater than 85%.

The results prove that the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion in **1** enhances the rate of catalytic oxidations 100-fold in comparison to the Cl^- ligands in $[(1,5\text{-}COD)IrCl]_2$; this result in turn strongly suggests (but does not prove) that polyoxoanion-supported iridium is the actual catalyst resulting from the catalyst precursor, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\bullet P_2W_{15}Nb_3O_{62}]$, **1**. The fact that the rate law is cleanly first order in the supported-complex **1** is consistent with (but also not proof of) this conclusion. Furthermore, our recent demonstration (2, 3) that the Ir(I)•polyoxoanion bonds in **1** survive *even under reductive* (H_2 + *cyclohexene*) *conditions* makes it highly probable that these bonds, and thus polyoxoanion-supported iridium, is present under the catalytic conditions where iridium is oxidized by O_2

[6] The formation of 1,3-cyclohexadiene and benzene due to hydrogen transfer was observed for the reaction in acetone. The selectivities to 1,3-cyclohexadiene and benzene were 15 and 2%, respectively. The values listed in Table 1 are only for oxygenated products and do not include these values.

leading to even greater $Ir^{1+n}\bullet P_2W_{15}Nb_3$ O_{62}^{9-} electrostatic bonding. However, additional mechanistic studies, of the type that we have done for our polyoxoanion-supported reductive catalysis (2, 3), are needed to substantiate this point. We expect such studies to confirm that the present work is only the second example of polyoxoanion-supported catalysis of any type.

Other important mechanistic questions raised by this initial study include: (i) Are polyoxoanion-supported $[Ir(III)O_2]^+$, or possibly $[Ir(V)(=O)_2]^+$ and related species (23–25), involved in *initiation* of allylic oxidation (note that no induction periods are detected)? Alternatively, is the observed allylic oxidation simply well-known autoxidation involving RO_2H intermediates and their Haber–Weiss (26) decomposition? And (ii) is there a way to change the selectivity, while still using O_2 as the oxidant, primarily to expoxidation rather than allylic oxidation products?

CONCLUSIONS

To summarize, the results herein demonstrate: (1) The first example of a catalyst for

oxidation chemistry with molecular oxygen starting from a polyoxoanion-supported catalyst precursor; (2) that the preferred catalyst precursor, among the three tested (Ir, Rh, Ru), is the iridium(I) complex, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$; (3) that the presence of the oxidation-resistant basic oxide $P_2W_{15}Nb_3O_{62}{}^{9-}$ enhances the catalytic rate 100-fold for allylic oxidation of cyclohexene, in comparison to the Cl^- anions in $[(1,5\text{-}COD)IrCl]$, to yield turnover rates 5–120 higher than those previously observed with Ir catalysts; and (4) that the preferred $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ system exhibits a total turnover number of 540 turnovers after 330 h, a value 39-fold higher than previously reported for Ir complexes. The additional kinetic, mechanistic, inhibitor studies (3, 6, 7, 27–31) and other work needed to answer the questions raised by this initial study or by other relevant literature (26–32) are in progress (33) and will be reported in due course.

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