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Mechanism and Dynamics in the $H_3[PW_{12}O_{40}]$-Catalyzed Selective Epoxidation of Terminal Olefins by H_2O_2. Formation, Reactivity, and Stability of $\{PO_4[WO(O_2)_2]_4\}^{3-}$

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Abstract: The highly selective catalytic epoxidation of terminal alkenes by the complex $W^{VI}/P^{V}/H_2O_2/CHCl_3/PTC$ (PTC = phase transfer catalyst) system (Ishii−Venturello chemistry) has been extensively investigated by groups in several countries and recently commercialized, yet little is known with certainty about the mechanism. The substrate conversions and epoxide selectivities observed under biphasic conditions, aqueous H_2O_2/alkene in $CHCl_3$, with 21 polyoxometalates (cetylpyridinium chloride as the phase-transfer catalyst, PTC) including the Ishii precursor complex, $[PW_{12}O_{40}]^{3-}$, clearly indicate that only $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$, which both rapidly form $\{PO_4[WO(O_2)_2]_4\}^{3-}$, **1**, are effective. Simultaneous monitoring of organic oxygenated products and gaseous products (nearly all O_2) with several of these polyoxometalates confirm that H_2O_2 disproportionation is by far the dominant side reaction with several d-electron transition metal-substituted polyoxometalate catalyst precursors. Analysis of the $^2J_{W-P}$ coupling satellites in the ^{31}P NMR spectra of the polytungstophosphate products from the stoichiometric reaction of **1** with alkene substrates as a function of cation, solvent, field strength, and time indicates that both a PW_4 and a PW_3 specie are formed initially and one PW_2 specie subsequently. Several lines of kinetic and spectroscopic evidence indicate that two processes dominate over all others during Ishii−Venturello epoxidation: a slow epoxidation, **1** (PW_4) + alkene → PW_4, PW_3, and PW_2 (henceforth called "subsequent peroxo species" or **SPS**) + epoxide, followed by a rapid regeneration of **1** with H_2O_2. First, little epoxidation is observed until **1** is in appreciable concentration. Second, the rate law for epoxidation of 1-octene by the Arquad salt of **1**, Arq**1** (Arquad = $[(C_{18}H_{37})_{75\%} + (C_{16}H_{33})_{25\%}]_2[CH_3]_2N$), in $CHCl_3$ at 23 °C is $v_0 = k[\mathbf{1}][\text{1-octene}]$. Third, **1** is the dominant polytungstophosphate present under steady state turnover conditions. Fourth, the ratio of the initial rates of epoxidation is $v_{0(\text{Arq}\mathbf{SPS})}/v_{0(\text{Arq}\mathbf{1})} = 0.13 \pm 0.01$. Fifth, the dominant inorganic product in the formation of **1**, $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$, is two orders of magnitude slower in alkene epoxidation than Arq**1** under identical conditions at both 23 and 60 °C. Additional ^{31}P NMR studies address both ion pairing effects and dynamic exchange in **1** and the **SPS** PW_4. A linear correlation was found between the change in both chemical shift and $^2J_{W-P}$ coupling constant for the **SPS** PW_4 specie but not the **SPS** PW_2 or the **SPS** PW_3 species as a function of reaction time. This is consistent with the **SPS** PW_4 specie undergoing rapid dynamic exchange on the ^{31}P NMR time scale. Addition of 1 equiv of 1,2-epoxybutane to tetra-*n*-hexylammonium **SPS** (THA**SPS**) does shift the **SPS** PW_4 resonance to high field with a larger $^2J_{W-P}$ coupling constant in accord with the correlation. Consequently, the dynamics of **SPS** PW_4 may reflect exchange of epoxide product. Rapid catalyst inactivation despite being one of two success limiting features of Ishii−Venturello epoxidation was not addressed in any previous work. Under the typical biphasic reaction conditions, catalysis nearly stops after 500 turnovers. The effects of alkene, H_2O, and epoxide product on epoxidation rates and polytungstophosphate speciation monitored by ^{31}P NMR establish that epoxide, but apparently neither alkene nor H_2O, leads to irreversible catalyst inactivation.

Introduction

Polyoxometalates have been used as homogeneous catalysts for a wide variety of thermal organic substrate oxidations.[1−28] Systems have been designed which utilize the terminal oxidants alkyl hydroperoxide[6−11] and iodosylbenzene[7,10−12] as well as the more environmentally and economically significant oxidants

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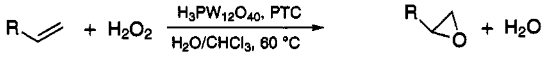
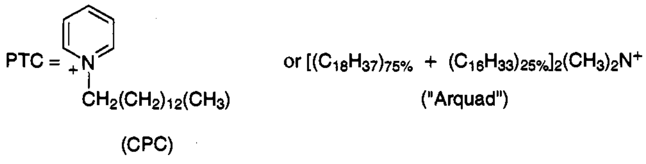
dioxygen[13−16] and hydrogen peroxide.[17−39] One process developed by Ishii and co-workers is of particular interest. This involves the epoxidation of relatively electron poor terminal olefins by H_2O_2 and heteropolyacids, principally $H_3[PW_{12}O_{40}]$, using a phase transfer catalyst (PTC) such as cetylpyridinium chloride (CPC) or "Arquad" (eq 1).[24,25,26e] This and closely related reactions, which have been examined by several academic and industrial research groups in the U.S., Europe, and Japan proceed with high conversion and selectivity for epoxide and are now used commercially. Several patents have also been filed.[26]

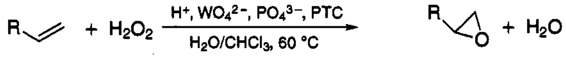


(1)

>85% conversion, 95% selectivity



The transformation in eq 1 is similar operationally and mechanistically to chemistry primarily associated with Venturello and co-workers, eq 2.[29−33] Here, biphasic H_2O_2-based epoxidations of terminal olefins are effected by the presence of tungstate and phosphate. Similar results are obtained if tungstate is replaced with tungstic acid, $WO_3{\cdot}H_2O$.[34,35a] Under noncatalytic conditions very similar to those in eq 2, the polyperoxometalate $\{PO_4[WO(O_2)_2]_4\}^{3-}$, **1**, was isolated and characterized crystallographically (Figure 1).[31] This tetranuclear species was postulated to be the active oxygen transfer agent in eq 2 based on its ability, as an isolated complex, to effect the selective epoxidation of terminal olefins.[27−29] Recent studies of the Ishii−Venturello chemistry by French[35] and British[36] groups include spectral characterizations of several peroxotungstates including the title compound **1**, a dinuclear metal peroxo species, $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$, and three new peroxophosphotungstates of composition PW_nO_x, where $n = 2$, 3, and 4. All five of these species derive from $H_3[PW_{12}O_{40}]$ and excess aqueous H_2O_2 without organic substrate. It has not yet been established whether any of these species are intermediates derived from the epoxidation of alkene. Although organic product distributions from stoichiometric epoxidations by some of these species have been reported, little or no kinetics data have been published. In particular, the British group reported the spectral characterization of the three new peroxophosphotungstates *in aqueous media without organic substrate present.*[36] This was followed by a more complete spectral characterization of these species under similar conditions (including an X-ray crystal structure of $\{HPO_4[WO(O_2)_2]_2\}^{2-}$) by the French group while this manuscript was being reviewed.[35b] Although the reported plots of epoxide versus time for both **1** and the PW_2 species, $\{HPO_4[WO(O_2)_2]_2\}^{2-}$, show similar behavior, no attempt was made to determine the importance, if any, of the peroxotungstate intermediates generated directly from the stoichiometric epoxidation of alkene. Both the French and British groups have thoroughly characterized the Mo analog of **1**, $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, and reported similar static spectroscopic studies and organic product distributions ($\{PO_4[MoO(O_2)_2]_4\}^{3-}$ stoichiometrically or catalytically, using aqueous H_2O_2, epoxidizes alkenes).[36,37] While previous studies hypothesize that **1** is the active epoxidizing species, the evidence for this is tenuous. Most dynamic processes involved in Ishii−Venturello epoxidation are poorly understood at best as almost no kinetics data are yet available. Recent studies by an Italian group did report rate laws and rate constants for the stoichiometric oxidation of alkenes, sulfides, and sulfoxides by $\{PO_4[MoO(O_2)_2]_4\}^{3-}$.[38]



(2)

(95% conversion and selectivity)

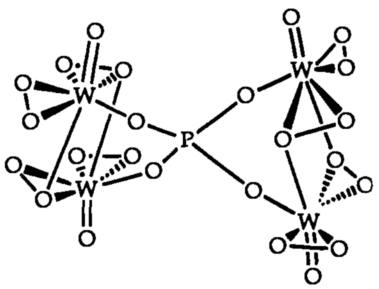


Figure 1. Molecular structure of $\{PO_4[WO(O_2)_2]_4\}^{3-}$, **1**.

The studies reported here were undertaken for three reasons. First, the thermodynamics and speciation of the $W^{VI}/P^{V}/H^+/H_2O_2/CHCl_3$ biphasic system and the related Mo^{VI} system coupled with the underlying catalytic behavior have not been investigated simultaneously but they are clearly more complicated than implied by all the published studies of the Ishii−Venturello chemistry.[35−37] To date there are X-ray crystal structures for 27 mononuclear[39−55] and 16 polynuclear[37,39,56−64]

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peroxo Mo^{VI} complexes, with four of the latter containing non-terminal peroxo moieties,[58,60,64,65] and 8 mononuclear[66–73] and 8 polynuclear[35b,74–79] peroxo W^{VI} complexes. Only two of the latter contain non-terminal peroxo moieties.[31,37] The synthetic conditions used in a majority of the preparations are similar to the conditions in Ishii–Venturello catalytic epoxidation. Second, transition metal species isolated from catalytic reactions are seldom the true catalysts, which by definition are usually too reactive and short lived to be isolable. Isolated species usually represent kinetic cul-de-sacs including less active forms of the catalyst or catalyst precursor. Kinetic studies must be conducted to unambiguously identify catalytically relevant species. The third and most general motivation for this study is the inherent challenge defined by a homogeneous catalytic chemistry that is simultaneously as mechanistically complex and practically useful as Ishii–Venturello chemistry. A variety of kinetics, product distribution, and spectroscopic experiments in this paper clarify many features of Ishii–Venturello chemistry.

Experimental Section

Materials. The solvents chloroform and methylene chloride (Burdick & Jackson) were used as received. High-purity 1-octene (Fluka), 1,2-epoxyoctane (Wiley), bromobenzene (Kodak), *m*-dibromobenzene (Kodak), and 1,2-octanediol (Fisher) were purchased and used as received. Deuterated solvents (CD_3CN and $CDCl_3$) were purchased from Cambridge Isotope Labs. Cetylpyridinium chloride (CPC), 1,2-epoxybutane, tetra-*n*-hexylammonium chloride (THACl), and tetra-*n*-pentylammonium iodide were obtained from Aldrich and used as received. Hydrogen peroxide (35% w/w aqueous solution) supplied by Interox Corp. was used in all experiments. The tetra-*n*-alkylammonium phase transfer agent $\{[(C_{18}H_{37})_{75\%} + (C_{16}H_{33})_{25\%}]_2[CH_3]_2N\}$-Cl (Arquad 2HT (Arquad)) was supplied by Akzo and was purified by repeated washings with acetone. Tungstic acid, formulated as $WO_3 \cdot H_2O$, was purchased from Aldrich. Prepurified argon was obtained from Linde. The polyoxometalates $H_3[PW_{12}O_{40}]$,[80] $H_3[PMo_{12}O_{40}]$,[80] $H_4[SiW_{12}O_{40}]$,[81,82] and $K_7[PW_{11}O_{39}]$[81,82] and transition metal-substituted[83–86] and silylated[87] derivatives $K_{(10-n)}[X^{n+}TM^{II}W_{11}O_{39}]$ (where X^{n+} = B(III), Si(IV), P(V), and TM = d-electron transition metal) and $(Me_4N)_4[(C_6H_5Si)_2OSiW_{11}O_{39}]$, respectively, were prepared and characterized by literature procedures.

Methods. A Bruker WP200SY or a General Electric GN-500 nuclear magnetic resonance spectrometer equipped with a broadband probe was utilized for the ^{31}P NMR experiments (^{31}P: 81.015 and 202.443 MHz, respectively). ^{183}W spectra were recorded on the Bruker instrument with a probe specifically designed for ^{183}W using 15-mm o.d. tubes (^{183}W: 8.331 MHz). Phosphorus spectra were referenced to 0.1% trimethyl phosphate (TMP) in $CDCl_3$ or CD_3CN, as an external standard. The chemical shifts were not corrected for bulk magnetic susceptibility. Tungsten spectra were referenced by sample exchange to a 2 M $Na_2WO_4 \cdot 2H_2O$ solution in D_2O using a 1 M solution of $H_4[SiW_{12}O_{40}]$ in D_2O as a secondary reference. For both ^{31}P and ^{183}W, upfield shifts are reported as negative values.

Infrared spectra were obtained on a Nicolet model 510 FT-IR spectrophotometer using 2–4% w/w KBr pellets. Infrared samples were prepared both by manual grinding using a mortar and pestle and mechanical mixing by a "Wig-L-Bug". In our hands, the latter procedure led to significantly more decomposition of the polyperoxometalate compounds, as defined by the alteration of major bands in the spectrum, than did the former. For these experiments, the manual procedure was used.

Organic products were identified by gas chromatography–mass spectroscopy (GC–MS) using a Hewlett–Packard 5990 gas chromatograph equipped with a 25-m × 0.2-mm (o.d.) 5% phenyl methyl silicone capillary column and interfaced with a Hewlett-Packard 5971A mass spectrometer. Helium was used as the carrier gas. A similarly equipped Hewlett-Packard 5890 gas chromatograph using nitrogen as the carrier gas and a flame ionization detector was used for organic product quantification. Gaseous products were identified and quantified using the Hewlett-Packard 5890 chromatograph equipped with a 5 Å (900–1000 mesh) 5-ft × 0.5-in. molecular sieve column and a thermal conductivity detector. Argon was used as the carrier gas for quantification of both organic and gaseous products. Internal standard techniques were used.

Preparation of Polyperoxometalates. The Arquad salt of the tetranuclear polyperoxometalate compound, $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (Arq**1**), was prepared by both the reaction of H_2O_2 with tungstic acid in the presence of phosphate[31] and the peroxide mediated decomposition of $H_3[PW_{12}O_{40}]$.[31,35] The latter method consistently gave higher yields and better reproducibility than the former, including the preparation of Arq**1** in gram quantities, and was the procedure of choice in these

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experiments. To a solution of 16.5 g (6 mmol) of $H_3[PW_{12}O_{40}]$ in 10 mL of H_2O was added, with vigorous stirring, 100 mL of 35% w/w aqueous H_2O_2 (~1 mol; 170 equiv based on $[PW_{12}O_{40}]^{3-}$). After the solution was stirred for 30 min, 70 mL of a $CHCl_3$ solution containing 9.1 g of Arquad was added, and the resulting biphasic mixture was thorougly stirred for 30 min. The $CHCl_3$ layer was then concentrated on a rotary evaporator to produce 13.3 g of a white, flaky compound (yield ~80%). This procedure yields primarily **Arq1** and the dinuclear polyperoxometalate, $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$. The latter can be isolated as the potassium salt from the aqueous phase of the reaction mixture. Characterization of the white material from the $CHCl_3$ layer showed it to be **Arq1** free of polyoxotungstates. It is soluble in chlorocarbon solvents and insoluble in CH_3CN. Chemical shift values for ^{31}P and ^{183}W NMR in $CDCl_3$ were in accord with literature values: ^{31}P NMR, 0.65 ppm; ^{183}W NMR, two resonances, −584, −588 ppm.[31,35] The FTIR data also agreed with the literature values: 1087 (s) and 1057 (s) (P=O); 984 (m) and 971 (m) (W=O); 845(s) (O−O); 590 (m) and 523 (m) $(W(O_2)_{s,as})$; other bands, 721 (w), 651 (m), 575 (m), 548 (m), 444 (w).[31,35] The tetra-*n*-hexylammonium salt, **THA1**, was prepared by the literature method[31] and characterized by ^{31}P NMR in both $CDCl_3$ (δ = 0.37 ppm) and CD_3CN (δ = 0.80 ppm).

The dinuclear compound $(Ph_4P)_2\{[WO(O_2)_2(H_2O)]_2O\}$ was prepared and characterized by literature procedures.[65] ^{183}W NMR: −567 ppm. FT-IR: 964 (m) (W=O); 839 (m) (O−O); 616 (w) $(W_2{-}O)_{as}$; 573 (m) and 562 (m) $(W(O_2)_2)_{s,as}$; other band, 779 (m).

Biphasic Catalytic Epoxidation of 1-Octene by Heteropolyoxometalates with H_2O_2 at 60 °C (Table 1). A 20-mL round-bottomed Schlenk flask was charged with polyoxometalate (5.2 × 10^{-3} mmol), H_2O_2 (1.96 mmol), 3 mL of $CHCl_3$, the appropriate number of equivalents of CPC (e.g., 0.016 mmol for $H_3[PW_{12}O_{40}]$), and a stir bar. The reaction vessel was purged with argon and then capped with a rubber septum stopper. The reaction was initiated by the addition of 1.3 mmol (250 equiv per equiv of polyoxometalate) of olefin via syringe. The Schlenk flask was then placed in a hot oil bath at 60 °C and stirred magnetically for 3 h. The reaction mixture remained biphasic throughout the duration of the reaction and each phase was homogeneous. Following the reaction, the Schlenk flask was allowed to cool to room temperature while the aqueous and organic phases separated, and then 0.03 mmol of bromobenzene internal standard was added. Aliquots were removed from the $CHCl_3$ layer and analyzed by GC. The epoxide was identified and quantified by GC-MS and GC.

Quantification of O_2, H_2O_2, and Organic Oxidation Products in a Single Reaction (Table 2). Some of the heteropolyoxometalate reactions were analyzed for O_2 generation. These reactions were prepared by degassing the $CHCl_3$ solution several times prior to olefin addition. Following the reaction, the head space atmosphere was analyzed by withdrawing gas aliquots via a gas-tight syringe. Oxygen was identified by coinjection of an authentic sample. Oxygen was quantified using nitrogen from air as an internal standard (subtracting the corresponding moles of O_2 in air). Analysis of the head space prior to olefin addition confirmed that no oxygen contamination was present. Immediately following analysis of the gaseous products, bromobenzene (0.07 mmol) was added and the aqueous H_2O_2 was extracted with three aliquots of H_2O (6 mL) and analyzed by iodometric titration.[88] The products in the remaining organic layer were then analyzed by GC. Other conditions are given in the Table 2 footnotes.

^{31}P NMR of Inorganic Products Derived from the Stoichiometric Epoxidation of 1-Octene by Arq1 at 60 °C. A 10-mL round-bottomed Schlenk flask was charged with **Arq1** (0.19 mmol), $CDCl_3$ (5 mL), the internal standard *m*-dibromobenzene (0.09 mmol), and a stir bar. The reaction vessel was purged with Ar and then capped with a rubber septum stopper. The reaction was initiated by the addition of 4 equiv of olefin (0.74 mmol) via syringe and the Schlenk flask was then placed in a hot oil bath at 60 °C for 3 h. After being cooled to room temperature, the reaction mixture was analyzed by GC and ^{31}P NMR.

Titration of $H_3[PW_{12}O_{40}]$ with H_2O_2 Monitored by Epoxidation Kinetics and ^{31}P NMR. To 0.5 mL of an aqueous solution of $H_3[PW_{12}O_{40}]$ (0.5 g, 0.17 mmol) was added varying quantities of hydrogen peroxide. Each reaction was stirred for 15 min, then 3 mL of a $CDCl_3$ solution of Arquad (0.3 g, 0.53 mmol) was added. This biphasic mixture was stirred for 15 min and then the phases were allowed to separate. The organic layer was transferred to a 10-mm o.d. NMR tube and immediately evaluated by ^{31}P NMR. The total time for NMR sample preparation and analysis was ~60 min in all cases. The product distributions formed upon addition of a specific number of equivalents of H_2O_2 to the $H_3[PW_{12}O_{40}]$ were all run in duplicate and agreement was good in all cases. Several of the NMR samples (10, 20, and 50 equiv of H_2O_2 relative to $H_3[PW_{12}O_{40}]$) were remeasured over a period of 2 weeks to evaluate time dependent changes in the product distribution.

To measure the rate of epoxide formation as a function of added H_2O_2, the $CHCl_3$ layers of samples prepared identically to those in the NMR experiments were placed in 10-mL round-bottomed flasks and to each was added 0.09 mmol of *m*-dibromobenzene. 1-Octene (2.23 mmol) was added to initiate the reaction and the rate of epoxide formation was monitored by GC. The various samples contained 2, 5, 10, 15, 20, 25, and 50 equiv of H_2O_2. Reaction rates were determined using the initial rate method.

Hydrolytic Stability of Arq1 Monitored by ^{31}P NMR. Experiments were also performed to determine the effect of H_2O and H_2O_2 on **Arq1**. **Arq1** (0.5 g) was added to each of three vials containing 3 mL of $CDCl_3$. To the first vial nothing additional was added. To the second vial 1.5 mL of H_2O was added. To the third vial 50 equiv of H_2O_2 were added (final volume of the aqueous component was 1.5 mL). Each vial was stirred for 1 h at room temperature and then the chlorocarbon layer was analyzed by ^{31}P NMR.

Kinetics of Epoxide Formation by Arq1 at 23 °C in $CHCl_3$. Because of the slow thermal decomposition of **Arq1**, only fresh samples of the complex were used in the kinetic experiments. Furthermore, the complex was routinely analyzed by ^{31}P NMR to ensure that no decomposition had occurred. A 45 mM solution of **Arq1** in $CHCl_3$ (4 mL) and *m*-dibromobenzene internal standard (0.09 mmol) were added to a 5-mL round-bottomed Schlenk flask under argon. The flask was purged for ~30 s and capped with a rubber septum stopper; the reaction was then initiated by the addition of the olefin substrate via syringe. A continual slow argon purge was maintained via a needle inserted through the septum stopper. The needle was not submerged in the liquid since peroxide-based oxidation and dissolution of the metal needle to form small amounts of transition metal species competent to catalyze disproportionation of H_2O_2 was a concern.

At appropriate time intervals, the septum was removed and under argon purge, a 0.3−0.5 mL aliquot of the reaction was taken using a graduated glass serological pipet (Fisher). The reaction was quenched by quickly transferring the aliquot to a vial containing 0.3 mmol of tetra-*n*-pentylammonium iodide, $(n\text{-}C_5H_{11})_4NI$. This reagent was found to be the most successful for the efficient and rapid reduction of the peroxidic moieties of **Arq1**. Quenching of **Arq1** by aqueous solutions of KI, NaBr, Na_2SO_3, $NaHSO_3$, or $Na_2S_2O_4$ was too slow to be of utility in these reactions. Tetra-*n*-heptylammonium bromide rapidly and efficiently quenched the reaction, but the generated Br_2 reacted quickly with the olefin substrate and the epoxide product. Zinc dust (Fisher) was too unreactive.

The septum stopper was replaced after sampling and the reaction was kept under argon for the duration of the kinetic run. Aliquots were withdrawn at times of 0.5, 1.0, 1.5, 2.0, 5.0, 10.0, 15.0, and 25.0 min. Epoxide formation was then quantified in the individual samples by GC. All reactions were conducted at 23 °C. Control reactions confirmed that neither I_2 nor the oxygenated products reacted with the olefin or epoxide in the kinetic time frame under these experimental conditions.

Studies with "Subsequent Peroxo Species", SPS. These species are generated by allowing **Arq1** (0.18 mmol) in $CDCl_3$ (3 mL) to react, with 1 equiv of 1-octene at 60 °C for 75 min. A similar reaction with **THA1** in $CDCl_3$ or CD_3CN produced **THASPS**. Both solutions were investigated by ^{31}P NMR spectroscopy.

In addition, two key experiments were performed with Arq**SPS**. The first involved the regeneration of **Arq1** from Arq**SPS**. The second compared the reactivity of Arq**SPS** versus **Arq1** for epoxidation of 1-octene. In the first experiment, Arq**SPS** was generated and allowed

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[88] Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; John Wiley and Sons: New York, 1989.

to react with 1 or 50 equiv of H_2O_2 for 30 min at 60 °C. In the second experiment, ArqSPS was produced and allowed to react with 20 equiv of 1-octene under N_2. Aliquots (0.3–0.5 mL) were withdrawn at 0-, 1.0-, 2.0-, 3.0-, 4.0-, and 15.0-min intervals and added to vials containing 0.125 g of tetra-*n*-pentylammonium iodide. The aliquots were analyzed by GC; *m*-dibromobenzene was used as the internal standard.

Comparison of the Reactivity of Arq1 versus $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$ in CH_2Cl_2. Only fresh samples of the polyperoxometalates, Arq1 or $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$, were used. To a 5-mL round-bottomed Schlenk flask purged and then filled with argon was added 0.16 mmol of the polyperoxometalate, 4 mL of CH_2Cl_2, 0.09 mmol of *m*-dibromobenzene (internal standard), and a stir bar. Kinetic runs were conducted at both 23 and 60 °C. The reactions performed at 60 °C were temperature controlled by placing the reaction vessel in a hot-oil bath. The reaction was initiated by the addition of 3.5 mmol of 1-octene (20 equiv based on initial concentration of polyperoxometalate). The formation of epoxide was followed by removing aliquots with a syringe and analyzing by GC.

Catalytic Inactivation in Ishii–Venturello Epoxidation. Three experiments were performed. The first was a turnover experiment where 0.02 mmol of Arq1 was added to a Schlenk flask followed by 15 mmol of H_2O_2 (35%) and 3 mL of $CDCl_3$. The vessel was degassed with Ar and heated to 60 °C. Two millimoles of 1-octene was added to initiate the reaction and the progress was monitored by GC. More substrate was added as needed until epoxide formation was negligible (22 h total time). *m*-Dibromobenzene (0.1 mmol) was added. Organic and phosphorus-containing products were analyzed by GC and ^{31}P NMR, respectively. Furthermore, in an attempt to regenerate the catalyst, 15 mmol of H_2O_2 was added and the mixture was stirred for 14 h. The $CDCl_3$ layer was then analyzed by ^{31}P NMR.

The second experiment addressed the degradation of catalyst in 1,2-epoxybutane and its epoxidizing ability in that solvent. Arq1 (0.18 mmol) was added to 3 mL of epoxide and monitored over time by ^{31}P NMR using a coaxial tube containing D_2O to lock the signal. To a Schlenk flask was added 0.01 mol of Arq1 followed by 3 mL of epoxide solvent and then 1.5 mmol of H_2O_2 (35%). The vessel was degassed and 1 mmol of 1-octene was added. The solution was run for 22 h at 60 °C. The internal standard, *m*-dibromobenzene (0.1 mmol), was added and the products were analyzed by GC.

In the third experiment, 2 equiv of 1,2-epoxybutane were added to ArqSPS under N_2 for incubation periods of 2.0 and 5.0 min followed by addition of 20 equiv of 1-octene. Aliquots were removed, quenched as in previous ArqSPS kinetic experiments (*vide infra*), and analyzed by GC.

Results

Epoxidation of 1-Octene by H_2O_2 Catalyzed by Polyoxometalates. The oxidation of 1-octene by H_2O_2 was examined in the presence of a variety of heteropolyacids and transition metal-substituted and silylated polyoxometalates. As the commercially available 35% w/w aqueous H_2O_2 was used in all cases, all reactions were run under conventional two-phase conditions using a phase transfer agent. Water soluble forms of the polyoxometalates and the phase transfer catalyst, cetylpyridinium chloride (CPC), were used in all cases. The results from these reactions are summarized in Table 1. The heteropolyacid $H_3[PW_{12}O_{40}]$ was the most successful polyoxometalate evaluated in terms of both olefin conversion and epoxide selectivity. The lacunary form of the polytungstophosphate was also quite reactive. In contrast, the Zn(II)-substituted polytungstophosphate, $[PZn^{II}W_{11}O_{39}]^{5-}$, had a modest activity, the polymolybdophosphate, $H_3[PMo_{12}O_{40}]$, had a low activity, and the rest of the surveyed polyoxometalates a lower activity still. No epoxide was formed if either the H_2O_2 or the polyoxometalate catalyst was omitted from any of these systems.

Quantification of O_2, H_2O_2, and Organic Oxidation Products in a Single Reaction. Transition metal-catalyzed dismutation of hydrogen peroxide (eq 3)is usually the single

$$2H_2O_2 \xrightarrow[\text{complex catalyst}]{\text{transition metal}} 2H_2O + O_2 \qquad (3)$$

most significant side reaction in transition metal-catalyzed hydrogen peroxide based oxygenation of organic substrates.[89] For this reason and since the degree of catalyzed dismutation was not adequately addressed in previous studies of Ishii–Venturello chemistry, we chose to quantify both dismutation and olefin oxygenation (epoxidation) under competitive conditions in the same reaction for several catalysts (Table 2). While non-productive dismutation of active oxygen is substantial for most of the species (the V-, Mn-, Co-, and Zn-substituted polyanions) and even for $H_3[PW_{12}O_{40}]$, it is relatively less so for the Fe-containing compound. This is consistent with the oxidation process in Haber–Weiss peroxide chain breakdown and/or other oxidative processes, and not reductive ones, being

Table 1. Epoxidation of 1-Octene by H_2O_2 Catalyzed by Various Polyoxometalates in $CHCl_3$ at 60 °C[a]

polyoxometalate	% conversion[b]	% selectivity[c]
1. $H_3[PW_{12}O_{40}]$	78	>98
2. $H_4[SiW_{12}O_{40}]$	<0.1[d]	
3. $H_3[PMo_{12}O_{40}]$	2.5	67
4. $Na_7[PW_{11}O_{39}]$	66	95
5. $K_5[PTiW_{11}O_{40}]$	<0.1[d]	
6. $K_4[PVW_{11}O_{40}]$	0.7	55
7. $K_5[PMn^{II}W_{11}O_{39}]$	0.6	50
8. $K_5[PFe^{II}W_{11}O_{39}]$	0.8	50
9. $K_5[PCo^{II}W_{11}O_{39}]$	0.4	45
10. $K_5[PZn^{II}W_{11}O_{39}]$	10.4	90
11. $K_7[PTi_2W_{10}O_{40}]$	<0.1[d]	
12. $H_5[PV_2Mo_{10}O_{39}]$	1.1	37
13. $K_8[SiW_{11}O_{39}]$	0.7	50
14. $K_6[SiTiW_{11}O_{40}]$	<0.1[d]	
15. $K_6[SiMn^{II}W_{11}O_{39}]$	<0.1[d]	
16. $K_6[SiFe^{II}W_{11}O_{39}]$	<0.1[d]	
17. $K_6[SiCo^{II}W_{11}O_{39}]$	0.7	30
18. $K_7[BMn^{II}W_{11}O_{39}]$	0.8	36
19. $K_7[BCo^{II}W_{11}O_{39}]$	0.8	38
20. $K_6[BCo^{III}W_{11}O_{39}]$	1.0	50
21. $(Me_4N)_4[(C_6H_5Si)_2OSiW_{11}O_{39}]$	<0.1[d]	

[a] All reactions run at 60 °C in a biphasic system of 3.0 mL of $CHCl_3$ and ~0.13 mL of H_2O. Reactions contained 5.2×10^{-3} mmol of polyoxometalate, the *n* equivalents of CPC (*n* = charge on polyanion), 1.3 mmol of 1-octene, and 1.96 mmol of H_2O_2. [b] Moles of organic products/initial moles of olefin. [c] Moles of epoxide/moles of total organic products. [d] Below the GC detection limits.

Table 2. Fate of Active Oxygen—Substrate Oxidation versus Dismutation[a]

	% active oxygen		
polyoxometalate	O_2[b]	organic products[c]	H_2O_2[d]
1. $H_3[PW_{12}O_{40}]$	52	34.2	1.7
2. $K_4[PVW_{11}O_{40}]$	97	0.7	2.5
3. $K_5[PFe^{II}W_{11}O_{39}]$	22	0.3	62.4
4. $K_5[PMn^{II}W_{11}O_{39}]$	89	0.5	0.8
5. $K_5[PZn^{II}W_{11}O_{39}]$	83	3.0	0.5
6. $K_5[PCo^{II}W_{11}O_{39}]$	105	1.0	0.1

[a] All reactions run at 60 °C in a biphasic system of 3.0 mL of $CHCl_3$ and ~0.13 mL of H_2O under Ar. Reactions contained 5.2×10^{-3} mmol of polyoxometalate, the appropriate number of equivalents of CPC, 1.3 mmol of 1-octene, and 1.96 mmol of H_2O_2. [b] Determined by GC; defined as (2 × moles of O_2/initial moles of H_2O_2)(100). [c] Defined as (moles of oxygen incorporated into organic products/initial moles of H_2O_2)(100). The organic products include the epoxide, *n*-alcohol, and octanoic acid. [d] Defined as (moles of unreacted H_2O_2/initial moles of H_2O_2)(100).

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(89) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

rate limiting in the transition metal-catalyzed dismutation.[90] The effectiveness of $H_3[PW_{12}O_{40}]$ in epoxide formation derives principally from the facility with which it breaks down into **1** and other effective catalytic species for epoxidation (*vide infra*).

Spectral Monitoring and Titration Kinetics of $H_3[PW_{12}O_{40}]$ with H_2O_2. The purpose of this experiment was to reveal the relationship between catalytic activity and complex speciation in an effort to identify those species requisite for olefin epoxidation. Previously the French group had evaluated speciation in the $[H_2O_2]/H_3[PW_{12}O_{40}]$ system by UV−vis, NMR, and Raman spectroscopy and in this case the complexes were transferred to and evaluated in organic media.[35a] We also observed complex time-dependent distributions of polytungstophosphates where the particular distribution depends on the ratio $[H_2O_2]_o/[H_3[PW_{12}O_{40}]]_o$.[91] An exemplary experiment using ^{31}P NMR is illustrated in Figure 2. In this study $H_3[PW_{12}O_{40}]$ was incubated with the indicated number of H_2O_2 equivalents. These solutions were then extracted immediately into $CDCl_3$ using the phase transfer agent Arquad and the ^{31}P NMR spectrum of the $CDCl_3$ phase obtained. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases (60 min). The addition of H_2O_2 leads initially to the gradual conversion of $[H_3[PW_{12}O_{40}]$ to a number of unidentified species. On the basis of preliminary Raman and ^{183}W NMR data the French group assign these as intermediate peroxo species $[P_mW_nO_o(O_2)_p]^{x-}$.[35a] However, more work needs to be done in this area to clarify the nature of these complexes. After 25 equiv of H_2O_2, some Arq**1** is present along with two unidentified phosphorus-containing species with single ^{31}P NMR resonances at −11.8 and 4.4 ppm, respectively. After the addition of 50 equiv, the transformation to Arq**1** is complete and virtually quantitative. Analysis of the two reactions with 10 and 20 equiv of H_2O_2 over a 2-week period showed no formation of Arq**1**. However, analysis of the sample with 50 equiv of H_2O_2 showed first the formation of Arq**1** and then, within 1 h, the conversion of Arq**1** to a roughly equal mixture of the species with resonances at −11.8 and 4.4 ppm.

In order to correlate oxidation ability with the species in the above $[H_2O_2]/H_3[PW_{12}O_{40}]$ solutions, olefin was added to samples prepared identically to those used in the ^{31}P NMR experiments in Figure 2 and the formation of epoxide was monitored with time. Exemplary results are shown in Figure 3. *Epoxide is not generated in any substantial amount until Arq1 is in appreciable concentration.* Furthermore, epoxide is formed very slowly upon addition of olefin to the mixture containing the two species with resonances at −11.8 and 4.4 ppm that results from aging of the $CDCl_3$ solution of Arq**1** (50 equiv of H_2O_2).

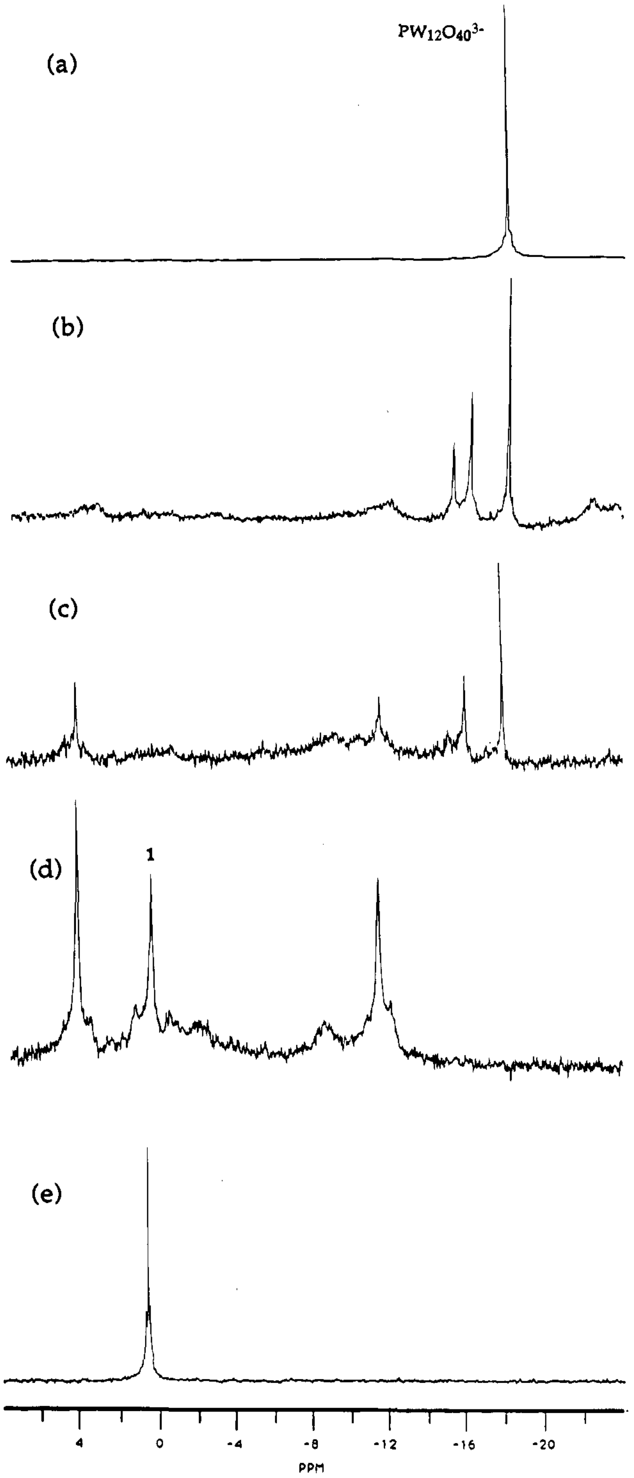

Figure 2. ^{31}P NMR spectra of $H_3[PW_{12}O_{40}]$ titration with *n* equivalents of H_2O_2, followed by extraction of the inorganic products into $CDCl_3$ (see Experimental Section), where *n* = (a) 2, (b) 10, (c) 15, (d) 25, (e) 50. The spectra with *n* = 5 and 20 have been omitted for clarity. Spectra are referenced to 0.1% TMP in $CDCl_3$ by the sample exchange method. The incubation and NMR data acquisition times are constant in all cases (60 min).

In a control experiment the thermal hydrolytic stability of Arq**1** was evaluated in the absence of excess H_2O_2. A $CDCl_3/H_2O$ biphasic solution of Arq**1** analyzed by ^{31}P NMR showed it to degrade to five phosphorus-containing species. In contrast, Arq**1** in the presence of H_2O_2, but under otherwise identical conditions, showed little change in the spectrum over the same time interval.

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[90] The oxidative process (eq i; M_{ox} and M_{red} = the oxidized and reduced forms of the one-electron redox couple in transition metal complexes) in Haber−Weiss peroxide chain breakdown (eqs i and ii) is often rate limiting and

$$M_{ox} + H_2O_2 \rightarrow M_{red} + HOO^{\bullet} + H^+ \quad (i)$$

$$M_{red} + H_2O_2 \rightarrow M_{ox} + HO^- + HO^{\bullet} \quad (ii)$$

correlates with redox potentials, cf.: Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 3. Pertinent potentials vis-à-vis the TMSP complexes in Table 2 are $Fe^{III/II}$ (E_0 = +0.771 V), $Co^{III/II}$ (E_0 = +1.83V), and $Mn^{III/II}$ (E_0 = +1.54 V), cf.: *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; Section 8−16. The anomalously high rate of H_2O_2 dismutation by $[P(Zn^{II})W_{11}O_{39}]^{5-}$ is not clear but this complex demetalates quite readily.

[91] A recent paper by Brégeault and co-workers (see ref 35b) describes the preparation of three peroxophosphotungstate species of composition $[PW_xO_y]^{\omega-}$ *in aqueous media* where this ratio, $[H_2O_2]_0/[H_3[PW_{12}O_{40}]]_0$, is 84. In our titration experiments we did not exceed a ratio of 50 and consequently we did not observe these species.

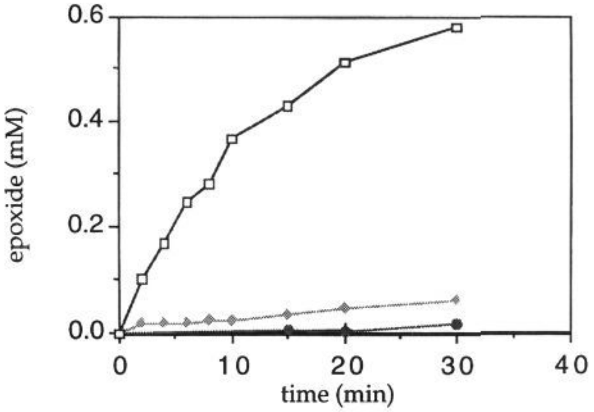

Figure 3. Formation of 1,2-epoxyoctane as a function of the number of equivalents (n) of H_2O_2 and time: $n = 50$ (□), 25 (◇), 20 (●). The reactions with $n = 15$, 10, 5, and 2 equiv have been omitted for clarity.

Stoichiometric Epoxidation of 1-Octene by 1. Arq**1** efficiently oxidizes 1-octene to the epoxide in $CHCl_3$ at 60 °C. Every equivalent of Arq**1** produces ~3.5 equiv of epoxide, consistent with the presence of 4 equiv of active oxygen in Arq**1**. Quantitative regeneration of Arq**1** was effected by addition of H_2O_2 (*vide infra*). These results are in agreement with similar experiments by the French[35] and English[36] groups using the corresponding tetra-*n*-butylammonium salt of **1**. The conversion is ~85% based on the initial concentration of 1-octene and selectivity for epoxide is >95%. The ^{31}P NMR spectrum of the reaction mixture is very complex, consistent with the presence of a considerable number of phosphorus-containing species. Several of the product peaks have chemical shifts identical with those observed in Figure 2.

Kinetics of Epoxide Formation by Arq1 in $CHCl_3$ at 23 °C. With the results in the previous section available, we turned to further kinetic experiments to probe the mechanism of epoxidation by Arq**1**. The reaction at 60 °C proved to be too rapid for precise quantification, and even at room temperature (23 °C), the rate of epoxide formation was too fast to obtain satisfactory initial rate data. However, tetra-*n*-pentylammonium iodide was found to quickly quench the reaction by reducing the peroxidic moieties of Arq**1** via eq 4,[92] permitting reproducible initial rates to be obtained.

$$O_2^{2-} + 4H^+ + 2I^- \rightarrow 2H_2O + I_2 \tag{4}$$

An exemplary rate profile plot is shown in Figure 4. Epoxidation was determined to be approximately first order in Arq**1** and first order in olefin (Figures 5 and 6, respectively).

Kinetics of Epoxide Formation by Polyperoxometalates in CH_2Cl_2. Inasmuch as the μ-oxo ditungsten tetraperoxy complex, $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$, is also formed by the decomposition of $H_3[PW_{12}O_{40}]$ by H_2O_2,[35a] the kinetics of its reaction with 1-octene was also examined. The epoxidation of several olefins, including 1-octene in CH_2Cl_2 by $[(Ph)_3(C_6H_5\text{-}CH_2)P]_2\{[WO(O_2)_2(H_2O)]_2O\}$ has been reported.[93] Whereas the $(Ph)_4P^+$ salt of the dinuclear compound failed to dissolve whatsoever in $CHCl_3$, even at 60 °C in a closed Schlenk flask for 2 h, both Arq**1** and the dinuclear compound were sufficiently soluble in CH_2Cl_2 to allow a comparison of epoxidation rates. At both 23 and 60 °C, the rate of epoxide formation by $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$ was found to be at least two orders of magnitude slower than that observed for Arq**1**.

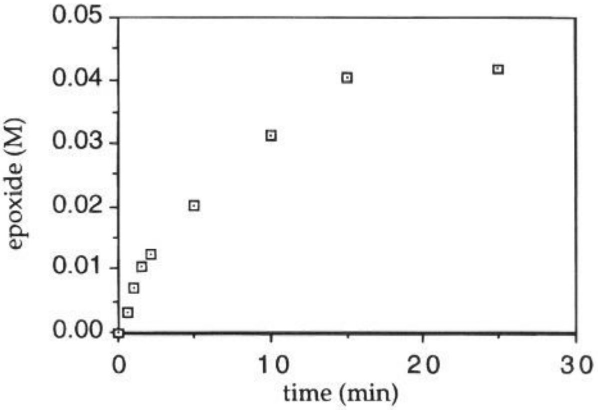

Figure 4. Kinetic profile of 1-octene epoxidation reaction by Arq**1**, where [**1**] = 45 mM, and [olefin] = 0.88 M in 4 mL of $CHCl_3$ under Ar at 23 °C. Aliquots were removed at times of 0.5, 1.0, 1.5, 2.0, 5.0, 10.0, 15.0, and 25.0 min and were quenched via reaction with $[(n\text{-}C_5H_{11})_4N]I$ (see Experimental Section).

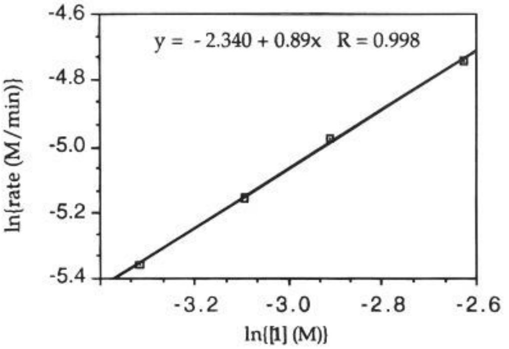

Figure 5. Initial rate dependence of 1,2-epoxyoctane formation on initial concentration of Arq**1** (0.88 M 1-octene in 4 mL of $CHCl_3$ at 23 °C under Ar). The aliquots were quenched with $[(n\text{-}C_5H_{11})_4N]I$ (see Experimental Section).

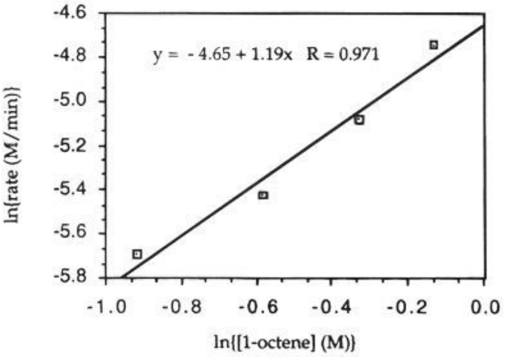

Figure 6. Initial rate dependence of 1,2-epoxyoctane formation on initial concentration of olefin (0.073 M Arq**1** in 4 mL of $CHCl_3$ at 23 °C under Ar). The aliquots were quenched with $[(n\text{-}C_5H_{11})_4N]I$ (see Experimental Section).

Studies with "Subsequent Peroxo Species", SPS. What are likely key species under conditions of catalytic turnover in Ishii–Venturello epoxidation are those formed upon reaction of Arq**1** with 1 equiv of olefin. Given that Arq**1** formally contains 8 equiv of peroxide (Figure 1), the specie(s) formed upon transfer of 1 equiv of active oxygen is likely to be not only epoxidation competent but also optimally situated to regenerate Arq**1** in the presence of H_2O_2. Stoichiometric reaction of Arq**1** in $CDCl_3$ with 1 equiv of a representative

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(92) Day, R. A.; Underwood, A. L. *Quantitative Analysis*, 4th ed.; Prentice hall: Englewood Cliffs, 1985.

(93) Prandi, J.; Kagan, H. B.; Mimoun, H. *Tetrahedron Lett.* **1986**, *27*, 2617.

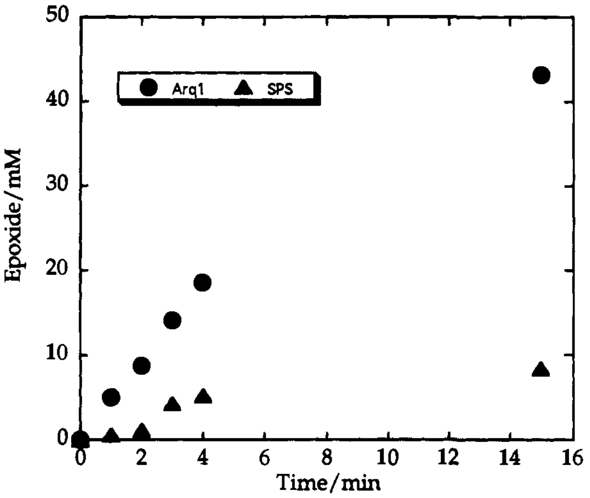

Figure 7. Kinetic profiles of 1-octene epoxidation by Arq**1** vs Arq**SPS**. [Arq**1**] = [Arq**SPS**] = 50 mM, [olefin] = 0.88 M in 5 mL of $CHCl_3$ under Ar at 23 °C. Aliquots were removed at times of 1.0, 2.0, 3.0, 4.0, and 15.0 min and were quenched with $[(n\text{-}C_5H_{11})_4N]I$.

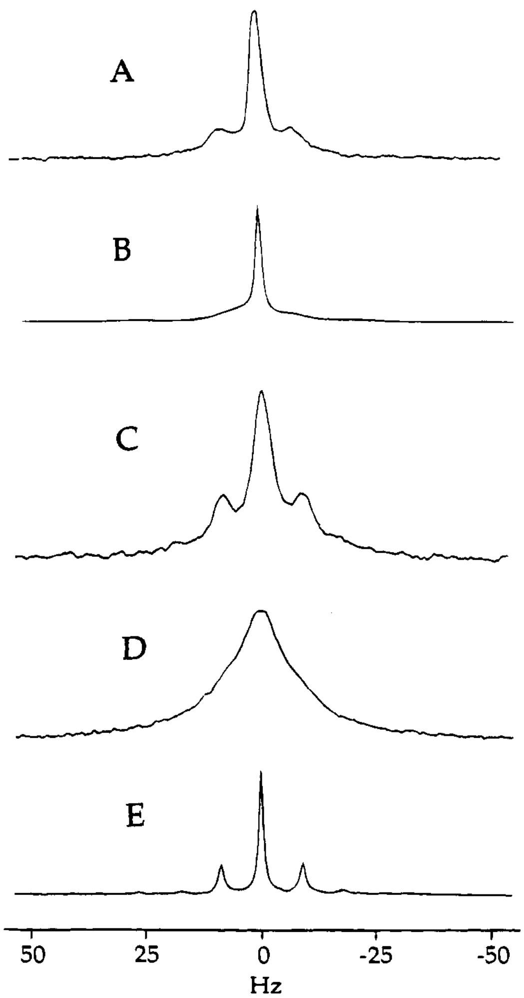

Figure 8. Cation, solvent, and magnetic field dependence on the $^2J_{W-P}$ satellite line widths in the ^{31}P NMR spectra of **1**: (**A**) Arq**1** in $CDCl_3$ at 81 MHz (4.70 T), $\delta = +0.60$ ppm; (**B**) Arq**1** in $CDCl_3$ at 202 MHz (11.7 T), $\delta = +0.60$ ppm; (**C**) THA**1** in $CDCl_3$ at 81 MHz (4.70 T), $\delta = +0.37$ ppm; (**D**) THA**1** in $CDCl_3$ at 202 MHz (11.7 T), $\delta = +0.37$ ppm; (**E**) THA**1** in CD_3CN at 202 MHz (11.7 T), $\delta = +0.80$ ppm. All spectra were centered to reflect more clearly the variation in line widths. Spectral parameters and FID apodization (0.6 Hz exponential line broadening) are constant in all spectra.

Ishii–Venturello alkene substrate, the terminal olefin 1-octene, does not cleanly produce one inorganic product. The reaction generates three resonances in the ^{31}P NMR (−0.30, −3.0, and −8.4 ppm relative to TMP/$CDCl_3$), none of which are characteristic of known Keggin derived polytungstophosphates. A peak at +0.60 ppm due to unreacted Arq**1** persists in these solutions. This mixture, which we will refer to henceforth as "subsequent peroxo species" or Arq**SPS**, reacts with 1 equiv of H_2O_2 to partially regenerate Arq**1** and with 50 equiv of H_2O_2 to completely regenerate Arq**1**. This result implies that the three new phosphorus resonances found in Arq**SPS** are polytungstophosphates and there is no irreversible process involving phosphorus-containing species that proceeds in appreciable or ^{31}P NMR detectable yield upon epoxidation. In a second experiment, the mixture Arq**SPS** was demonstrated to be kinetically competent to epoxidize 1-octene. As seen from Figure 7, reaction of Arq**SPS** undergoes an induction period of 2.0 min. Furthermore, the initial rates during this induction period were evaluated and Arq**SPS** epoxidized about 13% as quickly as Arq**1** ($v_{o(SPS+octene)}/v_{o(1+octene)} = 0.13 \pm 0.01$). Similar behavior was observed for the tetra-*n*-hexylammonium salts, THA**1** and THA**SPS**; however, THA**1** reacted at a reproducibly slower rate than Arq**1**, $k_{THA1}/k_{Arq1} = 0.20 \pm 0.01$.

Further structural and dynamic information on both **1** and the **SPS** was obtained from analyses of the $^2J_{W-P}$ coupling satellites that were readily discernible in the ^{31}P NMR spectra of these complexes under appropriate conditions. The Arq**SPS** in $CDCl_3$ did not provide sufficient resolution of the $^2J_{W-P}$ satellites to permit an unambiguous assignment of PW_n speciation. A study of the effect of counterion, solvent, concentration, and field strength on the $^2J_{W-P}$ satellite resolution enabled the PW_n stoichiometries of the various **SPS** components to be obtained. In $CDCl_3$, it was found that these $^2J_{W-P}$ satellites have narrower lines for both THA**1** and THT**SPS** at low field (4.70 T) than for the corresponding Arq compounds (Figure 8: A and C); however, at high field (11.75 T) the central line of the THA**1** specie is severely broadened, implicating a dynamic process (Figure 8: C and D). Satellite line narrowing is also observed for THA**1** and THT**SPS** in CD_3CN relative to $CDCl_3$ at both high and low fields under otherwise identical conditions (Figure 8: C, D, and E).[94] In addition, the $^2J_{W-P}$ satellite line widths depend on the magnetic field strength; that is, at higher field the satellite lines are broadened (Figure 8: A, B, C, and D). Furthermore, the δ for THA**1** and Arq**1** is concentration dependent in $CDCl_3$ but not so in CD_3CN. In $CDCl_3$, as the concentration increases from 4 to 40 mM the chemical shift changes from +0.46 to +0.37 ppm.

Since the coordination number of W is 7 (distorted pentagonal bipyramid) in **1** and probably also in **SPS**, ^{183}W relaxation is expected to be dominated by the chemical shift anisotropy mechanism at high fields. As a consequence, if ^{183}W is scalar coupled to ^{31}P, then by scalar relaxation of the second kind, the ^{31}P satellites will appear broadened at higher field.[95] Therefore, in order to determine *n* for a given specie PW_n, the best possible spectra are obtained with the THA compounds in CD_3CN at low field. Figure 9 shows the spectrum obtained on reacting 1 equiv of 1-octene with THA**1** in $CDCl_3$ followed by

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[94] Two figures reported in ref 35a indicate similar behavior (Arq**1** in $CDCl_3$ gives very broad $^2J_{W-P}$ satellites compared with the tetra-*n*-butylammonium salt of **1** in 9:1 (v:v) CH_3CN:$CDCl_3$); however, no explanation is offered for this behavior.

[95] Conversely, a field-dependent line width variation of the central resonance suggests a dynamic process which is fast at low field and intermediate at high field since it is not expected for ^{31}P to be dominated by the chemical shift anisotropy relaxation mechanism. See: Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; The Bath Press: Avon, 1986; Chapter 5.

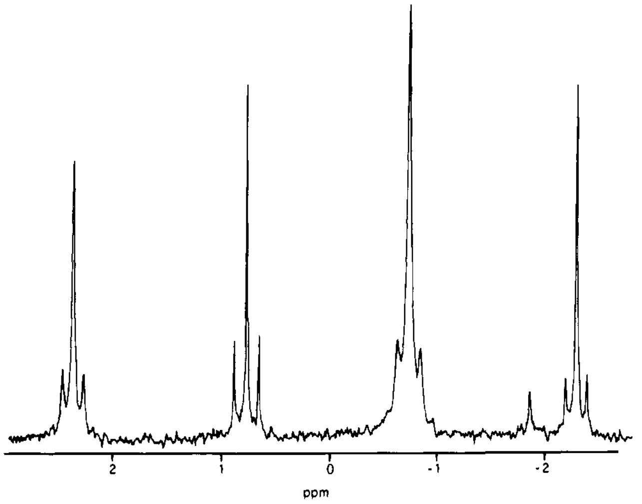


Figure 9. ^{31}P NMR spectrum of the tetra-*n*-hexylammonium (THA) salts of the subsequent peroxo species, THA**SPS**, prepared via reaction of THA**1** with 1 equiv of 1-octene in $CDCl_3$ at 74 °C for 1 h. The $CDCl_3$ solvent was then removed on a vacuum line and replaced with CD_3CN. NMR parameters: pulse width = 10 μs (30°); relaxation delay = 5.0 s; spectral width = 3355.7 Hz; block size = 16K; acquisition time = 2.44 s.; line broadening = 0.6 Hz; number of scans = 128.

solvent removal on a vacuum line and then addition of CD_3CN. This spectrum allowed for an unambiguous assignment of PW_n for the three observed phosphorus-containing reaction products based on the relative heights of the satellites with respect to the main line. The assignments are as follows: +2.39 (PW_4), −0.72 (PW_3), and −2.26 ppm (PW_2). The resonance persisting at +0.80 ppm is that due to unreacted THA**1**. Note that the chemical shifts for THA**SPS** are different from those observed in Arq**SPS**.

In a number of experiments in both $CDCl_3$ and CD_3CN, the reaction of 1-octene with THA**1** shows variability in both chemical shift (+2.10 to +3.00 ppm) and $^2J_{W-P}$ coupling constant (16.6 to 14.4 Hz) for the THT**SPS** PW_4 resonance as a function of the extent of reaction. Here a linear correlation is observed between $\Delta\delta$ and Δ^2J_{W-P} (Figure 10); analysis of the $^2J_{W-P}$ satellites indicates retention of PW_4 stoichiometry. Addition of 1 equiv of 1,2-epoxybutane to THA**SPS** in $CDCl_3$ shifted the PW_4 resonance to higher field with a larger $^2J_{W-P}$ coupling constant in agreement with the correlation. No change was observed on adding 2 equiv of tetra-*n*-hexylammonium chloride to THA**SPS** in $CDCl_3$. The PW_3 resonance upfield of THA**1** shows a slight variability in chemical shift (−0.69 to −0.90 ppm) and coupling constant (16.7 to 17.4 Hz); however, no relationship between Δ^2J_{W-P} and $\Delta\delta$ is apparent for this resonance within experimental error. In general, both the THA**SPS** PW_4 and PW_3 peaks appear together at early times and grow at the expense of THA**1**. Only later does the line due to PW_2 appear.

Catalytic Inactivation in Ishii−Venturello Epoxidation. The inactivation of the catalyst in Ishii−Venturello epoxidation, although an important and possibly a success-limiting feature of the chemistry, has not been addressed in previous work. Catalyst inactivation is, in fact, quite dependent upon product concentration. Turnover experiments indicate that the maximum turnover is ~500 (mol of epoxide)/(mol of catalyst). Analysis by ^{31}P NMR shows that the final inorganic product(s) is not Arq**1**. Reaction using 1,2-epoxybutane as the organic solvent instead of $CHCl_3$, under otherwise identical conditions, yields less than 2 equiv of 1,2-epoxyoctane per equivalent of Arq**1**. The solution of Arq**1** in the epoxide solvent monitored by ^{31}P NMR shows that catalyst degradation occurs within hours. The new phosphorus-containing species cannot be regenerated with excess H_2O_2. However, when 2.0 equiv of 1,2-epoxybutane were added to Arq**SPS**, there was no change in the kinetic behavior compared to Arq**SPS** when no epoxide was added.

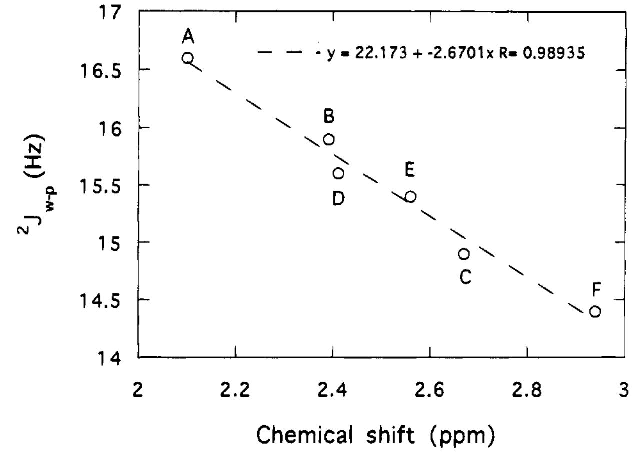


Figure 10. Plot of $^2J_{W-P}$ vs chemical shift for the **SPS** PW_4 resonance observed under different conditions: (A) THA**1** in $CDCl_3$ with 1 equiv of 1-octene maintained at 74 °C for 1 h; (B) sample A followed by removal of $CDCl_3$ on a vacuum line and replacement with CD_3CN; (C) THA**1** in CD_3CN with 1 equiv of 1-octene maintained at 70 °C for 1 h; (D) sample C after sitting for 1 week at ambient temperature; (E) THA**1** in CD_3CN with 1 equiv of 1-octene maintained at 72 °C for 2 h; (F) THA**1** in CD_3CN without substrate maintained at 72 °C for 2 h. The experimental error in the $^2J_{W-P}$ and chemical shift values are no less than 0.2 Hz and 0.005 ppm, respectively.

Discussion

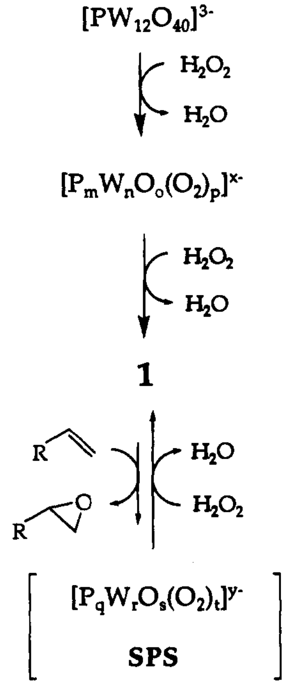
General Characteristics of the $W^{VI}/P^V/H_2O_2/CHCl_3/PTC$ (Ishii−Venturello) Epoxidation System. The only catalyst precursors of the common Keggin class that lead to effective epoxidation (reasonable turnover and high selectivity for epoxidation) are $[PW_{12}O_{40}]^{3-}$ and its lacunary derivative, $[PW_{11}O_{39}]^{7-}$ (Table 1). Two dominant factors explain the behavior. First, while all the Keggin-type catalyst precursors are labile and degrade in aqueous H_2O_2, the d-electron-metal-free polytungstophosphates are the most labile and form the active epoxidizing agents including **1** most readily. The rates of epoxidation using the Keggin catalyst precursors in Table 1 qualitatively correlate directly with the rates of degradation of these complexes in aqueous H_2O_2. Second, the epoxide yields based on H_2O_2 will be decreased proportional to the ability of a particular complex to catalyze the dominant side reaction, H_2O_2 dismutation (Table 2). The observed differences in H_2O_2 dismutation activity in the Fe, Mn, and Co TMSP complexes are consistent with the oxidative process in Haber−Weiss peroxide chain breakdown and/or other substrate oxidation-metal reduction processes being rate limiting.[90] $H_3PMo_{12}O_{40}$ is catalytically active for epoxidation of 1-octene, albeit at a lower level of reactivity than its tungsten analog. Polymolybdophosphate analogs of **1** have been prepared and were shown to be less active for olefin epoxidation than **1**.[35−37] The lack of reactivity by $H_4[SiW_{12}O_{40}]$ may reflect either the known lower rate of degradation of this complex by aqueous peroxide and the lower lability in general relative to $H_3[PW_{12}O_{40}]$[1] or the related point that the silicon analog of **1** does not form in appreciable concentration under Ishii−Venturello conditions. Importantly, it should be noted that TMSP complexes of structural classes other than the Keggin type in Table 1 have dramatically different stabilities in aqueous H_2O_2, ratios of epoxidation to dismutation, and epoxidation selectivities. The complexes of formula $[(\mathrm{TM\text{-}solvent})_2(\mathrm{TM})_2(\mathrm{XW_9O_{34}})_2]^{x-}$, where TM is usually a d-electron transition metal and X is a d or p block "heteroatom", are particularly promising in this regard.[96,97]

Speciation of Active Epoxidizing Agents in the $W^{VI}/P^{V}/H_2O_2/CHCl_3$/PTC (Ishii−Venturello) System. Several groups have studied this system but little is known about the mechanism. While rate laws have been reported for the stoichiometric oxidation of alkenes, sulfides, and sulfoxides by the molybdenum analog of **1**, $\{PO_4[MoO(O_2)_2]_4\}^{3-}$,[38] no comparable data are available on Ishii−Venturello epoxidation. Mechanistically valuable information available for the latter has been limited to product studies, spectroscopic characterization of **1** and other peroxotungstate/peroxophosphotungstate species obtained either under non-turnover conditions[36] or without the presence of substrate,[35] and epoxide concentration−time curves for stoichiometric oxidation of (*R*)-(+)-limonene by **1**, $\{HPO_4[WO(O_2)_2]_2\}^{2-}$, and $\{PO_4[MoO(O_2)_2]_4\}^{3-}$.[35,37]

Compound **1** has been suggested to be the catalytically important species in eq 1 based on some of the indirect information enumerated above and based on isolation of **1** from reactions of H_2O_2 and $H_3[PW_{12}O_{40}]$.[24−37] Without supporting kinetics data, however, this is a speculation. Facile turnover usually precludes isolation of intermediate species that lie along the principal reaction coordinate, that is, the true catalyst(s). Such species are short lived and usually present in low concentration. By extension, species that are isolable are usually not the true catalyst(s) but represent kinetic repositories of species in equilibrium with the true catalysts or byproducts that are irrelevant to the catalysis.

Seven lines of evidence speak to the active epoxidizing agents in the $W^{VI}/P^{V}/H_2O_2/CHCl_3$/PTC system and their dynamic behavior under turnover conditions. The dominant general processes starting with the Ishii precursor complex, $H_3[PW_{12}O_{40}]$, consistent with the following data, are summarized in Scheme 1. None of the processes illustrated in Scheme 1 necessarily implies a detailed mechanism; some clearly represent several steps. First, the rate law for stoichiometric epoxidation by **1** is $v_0 = k[\mathbf{1}][\text{alkene}]$, which rules out unimolecular formation of some active epoxidizing agent from **1**. It does not rule out formation of such an intermediate induced by the association of one molecule of alkene with one molecule of **1**. Second, monitoring both the epoxide concentration and complex speciation as a function of H_2O_2 added to $H_3[PW_{12}O_{40}]$ under biphasic conditions clearly shows little formation of epoxide product until **1** is in appreciable concentration. Third, ^{31}P NMR spectra clearly indicate that both the PW_4 and PW_3 "subsequent peroxo species", **SPS**, are formed subsequent to transfer of oxygen from **1** to alkene. PW_2 species are clearly generated only subsequent to formation of PW_3. Thus the **SPS** are predominantly PW_4 and PW_3 compounds (the subscript "*r*" in the **SPS** formula in Scheme 1 is primarily 4 and 3 and to a lesser extent 2). Fourth, ^{31}P NMR spectra further indicate that the PW_4, PW_3, and PW_2 **SPS** readily convert back to **1** under turnover conditions (biphasic with aqueous peroxide present) and that **1** is by far the dominant polytungstophosphate present under such conditions. The necessary implication of this is that reoxygenation of PW_4, PW_3, and PW_2 by H_2O_2 is faster than epoxidation by **1**. These relative rates are indicated as different sized arrows in Scheme 1. Fifth, rate data coupled with PW_n speciation abundance data from ^{31}P NMR establish key points about the dominant epoxidizing agent. Brégeault and coworkers had reported a [limonene oxide] versus time curve indicating a somewhat faster rate of epoxide formation with **1** than with the PW_2 complex, $\{HPO_4[WO(O_2)_2]_2\}^{2-}$, but no further analysis of the complex rate behavior implied with this plot was provided including a rate law.[35b,37] We have measured the relative rates of epoxidation by **1** and the **SPS** (raw data in Figures 4 and 7) giving the following calculated value, $v_{0(\mathbf{SPS}+\text{octene})}/v_{0(\mathbf{1}+\text{octene})} = 0.13 \pm 0.01$. This coupled with the low steady state concentrations of **SPS** PW_n, $n \le 4$, species by ^{31}P NMR indicate that the latter species are not very important during turnover. As a consequence, they have not been added to Scheme 1. Thus while **1** is clearly not the only epoxiding agent in Ishii−Venturello epoxidation it is the kinetically significant one. Sixth, the observed rate for alkene epoxidation at both 23 and 60 °C in CH_2Cl_2 by $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$, a dominant inorganic byproduct in the formation of **1** from the Ishii precursor Keggin polytungstate, $H_3[PW_{12}O_{40}]$, was found to be two orders of magnitude slower than Arq**1** under identical conditions. Consequently, epoxidation by $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$ under turnover conditions is not kinetically significant and therefore has not been added to Scheme 1. The kinetics and spectroscopic data imply that the dominant processes in Ishii−Venturello catalytic epoxidation are those at the bottom of Scheme 1 (**1** $\rightleftharpoons$ **SPS**).

Scheme 1. Dominant Processes in Ishii−Venturello Homogeneous Catalytic Epoxidation[a]



[a] Processes of finite, measurable but minor importance are not shown and processes that are shown are general and do not imply detailed mechanism (see text).

More detailed NMR studies indicate further key features of the dynamic properties of **1** and **SPS**. Four lines of evidence indicate that ion pairing may occur in $CDCl_3$.[98] First, the chemical shifts of both the THA and Arq salts of **1** are concentration dependent in $CDCl_3$; however, the chemical shift for THA**1** is not concentration dependent in CD_3CN (Arq**1** is not soluble in CD_3CN). This is consistent with a greater degree

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[96] Hill, C. L.; Khenkin, A. M. *Mendeleev Commun.* **1993**, 140−142.

[97] Hill, C. L.; Khenkin, A. M. Research submitted for publication and unpublished.

[98] Ion pairing of polyanion salts in organic media has been addressed by Finke and co-workers and by other groups albeit to a limited extent: Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1787−1789 and references cited therein.

of dissociation in the higher dielectric solvent CD_3CN relative to $CDCl_3$. Second, the satellite line widths of Arq**1** are substantially larger than those of THA**1** in $CDCl_3$ (see Figure 8). This is consistent with a longer rotational correlation time for the Arq salt due to the larger size of the cation. Third, the satellite line widths for the THA salts of both **1** and **SPS** are reduced in CD_3CN relative to $CDCl_3$. This is also consistent with a reduced rotational correlation time in CD_3CN due to a greater degree of dissociation in this solvent. One caveat with regard to points two and three is that the differences in line width may simply reflect variations in sample viscosity; however, the marked improvements in resolving the $^2J_{W-P}$ satellites with the THA salts over the Arq analogues in the same solvent would seem to discount this possibility. Fourth, the large chemical shift differences reported for **1** in D_2O (−1.36 ppm) relative to THA**1** in $CDCl_3$ (+3.47 ppm) using 85% H_3PO_4 as the external standard argue for the existence of ion pairing as such large changes in chemical shift cannot be easily attributed to solvent effects.[36] Furthermore, Brégeault and co-workers also note this fourth point and similarly concluded that ion pairing may be operative here.[35b] The substantial and reproducible differences in the chemical shifts observed for Arq**SPS** vs THA**SPS** could also be attributed to greater ion pairing in the former; however, the possibility that these species are different from those in THA**SPS**, although unlikely, cannot be ruled out.

The linear correlation found between $\Delta\delta$ and Δ^2J_{W-P} for the **SPS** PW_4 resonance as a function of the extent of reaction (see Figure 10) is consistent with fast exchange on the ^{31}P NMR time scale between two or more PW_4 species that contribute to this resonance. Changes in the relative populations of these **SPS** PW_4 species as the reaction proceeds lead to variability in both the averaged chemical shift and averaged coupling constant. Since the $^2J_{W-P}$ coupling is well-resolved, it follows that the observed dynamic behavior is not due to PO−W bond making and breaking as clearly this process is slower than the ^{31}P NMR time scale. It is expected in the case of the **SPS** PW_4 species that three of the tungsten sites remain seven coordinate and the fourth does not. This latter site must find a ligand in the reaction mixture in order to obtain coordinate saturation. The observed NMR spectra as a function of variability in the concentrations of the available ligands (olefin, epoxide, solvent, etc.) are consistent with this picture. Addition of 1 equiv of 1,2-epoxybutane to THA**SPS** in $CDCl_3$ shifts the resonance to high field with a larger $^2J_{W-P}$ coupling constant in accord with the correlation shown in Figure 10. This behavior is consistent with epoxide ligation of THA**SPS** in $CDCl_3$ at the negative end of the chemical shift range (+3.00 to +2.10 ppm) and perhaps CD_3CN ligation at the positive end of the range. Interestingly, a recent paper by Griffith and co-workers reported the structural characterization of two pyridine *N*-oxide peroxometalate complexes, $[WO(O_2)_2(pyO)_2]$ and $[MoO(O_2)_2(pyO)_2]$, prepared by the oxidation of pyridine in the presence of H_2O_2 and the corresponding metal oxide, $MO_3{\cdot}H_2O$.[99] The reaction in $CDCl_3$ gives the most upfield chemical shift for this resonance, consistent with the inability of $CDCl_3$ to compete with epoxide for ligation. All other points in the plot derive from reactions in CD_3CN which may compete with epoxide for binding. Here the shift to less positive chemical shifts tracks with increasing reaction time. Furthermore, the most positive chemical shift is observed in the thermal decomposition of **1** without substrate in CD_3CN.

Of interest to note here is a paper recently published by Brégeault and co-workers while this paper was under review.[35b] Here the authors report the synthesis and *in situ* characterization of three PW_n species with $n = 2$, 3, and 4 ($n = 2$ was isolated as $Q_2H[PO_4\{WO(O_2)_2\}_2]$ and structurally characterized) generated from the decomposition of $H_3PW_{12}O_{40}$ by H_2O_2 *in aqueous media without organic substrate* ($[H_2O_2]/[H_3PW_{12}O_{40}] = 84$). Their results are complementary to ours since *our PW_n species are generated directly from the epoxidation of alkene substrates in nonaqueous media*. Whether the species we report here are identical in composition to those prepared by Brégeault and co-workers is clouded by the aforementioned "effect" of solvent on the ^{31}P NMR chemical shifts. The difference in chemical shifts between their isolated $Q_2H[PO_4\{WO(O_2)_2\}_2]$ complex (4:1 CH_3CN:$CDCl_3$) and our PW_2 complex (CD_3CN) may be due to lack of protonation in our system. On correcting for the different chemical shift references[100] their chemical shift is more positive by 1.48 ppm in accord with this hypothesis.

Limitations in Ishii−Venturello Epoxidation. Solvent Compatibility and Catalyst Inactivation. There are two factors above all others that limit the potential value of Ishii−Venturello catalytic epoxidation. First, toxic and carcinogenic chlorocarbon solvents are required. While alternative solvents have been examined, none approach chlorocarbons with respect to both rate and epoxide selectivity at high conversion. The use of chlorocarbons largely defeats the significant environmental and economic advantages of using H_2O_2 as the oxidant. Second, catalysis stops after a modest number of turnovers: very little activity persists after 500 turnovers and rate decreases are noted well before that. This crucial inactivation of the system has not been addressed by any of the previous investigations. Rate and spectroscopic data in this study clearly indicate that while Arq**1** decomposes in the presence of both alkene and H_2O, it is unlikely that either of these species is primarily responsible for irreversible inactivation of the catalytic system. Experiments with epoxide solvent (1,2-epoxybutane), however, show that the catalyst is irreversibly decomposed at high concentrations of epoxide. The inorganic species formed upon reaction with epoxide under Ishii−Venturello conditions do not react with H_2O_2 to regenerate **1** or PW_n, $n < 4$ species. A clear implication is that if epoxide could be removed as it formed during turnover, the catalytic reaction would last significantly longer.

Acknowledgment. This research was supported by Interox Corp. and the National Science Foundation. We also thank Dr. Mark Weeks for the preparation of several of the d-electron transition metal-substituted polyoxometalates.

JA940941+

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(99) Griffith, W. P.; Slawin, A. M. Z.; Thompson, K. M.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 569−570.

(100) The chemical shifts reported both here and in ref 35b are not corrected for bulk magnetic susceptibility.