



Kinetic studies on phenylphosphopolyperoxotungstates catalyzed epoxidation of olefins with hydrogen peroxide

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ABSTRACT

Kinetic studies on the catalytic activity of phenylphosphopolyperoxotungstate complexes $[C_{21}H_{37}N]_2[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2H_2O\}]$ (**A**) and $[C_{21}H_{37}N]_2[(p-NO_2Ph(O)PO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2H_2O\}]$ (**B**) in the epoxidation of olefins with hydrogen peroxide as the oxidizing agent were carried out in CH_3CN/H_2O solvent mixtures. The nitro-substituted catalyst, **B**, was shown to be more active than **A**. However, the higher acidity of **B** enhances more epoxide ring-opening to yield 1,2-diol. Under biphasic conditions, the epoxide ring-opening is reduced, and in most cases the 1,2-diol products do not form. Under homogeneous conditions, the reaction is first-order with respect to the catalyst and the olefin, and between zero- and first-order with respect to the H_2O_2 concentration. The rate of the reaction increases with the olefin nucleophilicity. The epoxidation rate constants of para and meta substituted styrenes are correlated with σ^+ according to the Hammett equation. The reaction constants ($\rho \sim -0.9$) and the reaction stereoselectivity suggest a mechanism, which involves an external nucleophilic attack of the π -system of the olefin on the electropositive oxygen of the W-peroxo group. A catalytic cycle involving a fast (pre-equilibrium) reaction between H_2O_2 and the catalyst followed by the oxygen-transfer step (rate-determining) is proposed.

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1. Introduction

Homogeneous catalytic oxidations of organic substrates by environmentally safe oxidants, such as H_2O_2 , have been of growing interest due to recent environmental concerns [1]. Hydrogen peroxide is among the best and most atom efficient oxidants (second only to molecular oxygen). The major benefit of using H_2O_2 is that it is environmental well accepted since the only by-product from the oxidation is water, eliminating the need for expensive disposal treatments [1c,2]. In addition, H_2O_2 has a high oxygen content (47%), exists in high purity, and can be safely stored and used [3,4]. Hydrogen peroxide is a much more reactive oxidant than molecular oxygen. Due to its amphoteric nature, it can be activated by both acidic and basic transition metal catalysts both under homogeneous [5] and heterogeneous [6–8] conditions.

The search for effective and recyclable catalysts to activate H_2O_2 for the oxidation of organic compounds is the focus of many

researchers in both academic and industry [9]. Catalyst activity, stability and cost are the major concerns for applying effective catalysts in an industrial scale [10]. Polyoxometalates, POMs, (or polyperoxometalates, PPMs) meet both stability and cost criteria. Some of them have shown high catalytic turnovers, and are recyclable for further use [11–13]. Organophosphate PPM derivatives of Mo and W, such as $[NR_4]_2[(PhPO_3)\{MO(O_2)_2\}_2\{MO(O_2)_2(H_2O)\}]$; (M = Mo and W) have been prepared a decade ago [14]. The W-PPMs have shown higher activities than the Mo analogous toward oxidations with H_2O_2 including epoxidation [11]. In addition, the activation of H_2O_2 by $[NR_4]_2[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]$ (**A**) in oxidation reactions has been examined, and **A** was found to be an effective catalyst for the oxidation of numerous organic substrates, such as sulfides, alcohols, amines and olefins [15–17]. Recently, we have prepared a new PPW; $[C_{21}H_{37}N]_2[(p-NO_2Ph(O)-PO_3)-\{WO(O_2)_2\}_2\{WO(O_2)_2H_2O\}]$ (**B**) as a modified form of **A** by introducing a nitro group into the phenyl moiety. Kinetic studies on the oxidation of organic sulfides by H_2O_2 catalyzed by **A** and **B** have shown that **B** is more active and selective for the conversion of sulfides to the corresponding sulfoxides [18].

In this study, we have investigated the activities of the above-described tungsten catalysts in the epoxidation of olefins by H_2O_2 . The presence of a phenyl group and a large organic counter-cation (cetylpyridinium) were shown to enhance the catalyst solubility

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in organic solvents where homogeneous catalytic reactions can be studied. Detail kinetic studies on the epoxidation of olefins and styrenes by H_2O_2 catalyzed by **A** and **B** are presented. The reactions were carried out under homogeneous conditions in mixed organic/aqueous solutions.

2. Experimental

2.1. Materials and methods

Water was purified by a Milipore-Q deionization system. H_2O_2 (35%, Fischer) was used as received. Acetonitrile, diethyl ether and methanol (HPLC grade, Aldrich) were used without further purification. All the alkenes, tungsten trioxide monohydrated [$\text{WO}_3 \cdot \text{H}_2\text{O}$], sodium tungstate dihydrate [$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$], phenylphosphonic acid [$\text{C}_6\text{H}_5\text{P}(\text{O})(\text{OH})_2$], (4-nitrophenyl)-phosphoryldichloride [$4\text{-O}_2\text{NC}_6\text{H}_4\text{OP}(\text{O})(\text{Cl})_2$], and cetylpyridinium chloride [$\text{C}_{21}\text{H}_{37}\text{NCl}$] were used as purchased from Aldrich. Stock solutions of hydrogen peroxide were prepared in deionized water by diluting commercial samples of H_2O_2 (35%). The diluted stock solutions were standardized daily by the iodometric method [19].

IR spectra were measured with a JASCO FT-IR-460 Plus spectrometer using KBr pellets. NMR spectra were measured applying a JEOL 400 and 400-MHz Bruker Avance DPX-400 Spectrometer (^{31}P , 162 MHz, using external H_3PO_4 as reference; ^1H , 400 MHz, TMS). The UV spectra were measured on JASCO UV-vis V-550 and Shimadzu UV-2401 Spectrophotometers.

2.2. Synthesis of the catalysts

$[\text{C}_{21}\text{H}_{37}\text{N}]_2[(\text{PhPO}_3)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2\text{H}_2\text{O}\}]$, **A**, was prepared as previously described [14], with cetylpyridinium chloride instead of NMe_4Cl . When 2.5 g (10 mmol) of $\text{WO}_3 \cdot \text{H}_2\text{O}$ was used, the yield was 3.3 g (2.1 mmol, 63%). The product was identified by UV-vis, IR and NMR spectroscopic methods.

$[\text{C}_{21}\text{H}_{37}\text{N}]_2[(p\text{-NO}_2\text{Ph}(\text{O})\text{-PO}_3)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2\text{H}_2\text{O}\}]$, **B**, was prepared as previously described [18]. When 2.5 g (10 mmol) of $\text{WO}_3 \cdot \text{H}_2\text{O}$ was used, the yield was 3.2 g (2.1 mmol, 59%). The product was identified by UV-vis, IR and NMR spectroscopic methods [18].

2.3. Biphasic epoxidation

The catalyst (0.1 mmol) was dissolved in CHCl_3 (10 mL) and the olefin (20 mmol) was added. Aqueous hydrogen peroxide (30%, 10 mL) was added to the organic solution and the biphasic mixture was vigorously stirred for 12 h at 50 °C. The resulting organic layer was then analyzed with a gas chromatography.

2.4. Kinetic studies

Kinetic data were collected by using ^1H NMR and UV spectroscopic methods. For all reactions, the temperature was controlled within a temperature range of ± 0.5 °C. Reactions studied by ^1H NMR were carried out in CD_3CN in a total volume of 0.5–1.0 mL. The relative amounts of H_2O_2 , catalyst and olefin were chosen with a concern for the requirements of the kinetic analysis, which was carried out by a first-order or initial rate kinetic. The proton spectrum was recorded in 10–30 min intervals over the 6–12 h reaction time. Under pseudo-first-order conditions, the changes in the intensity (I) of the alkene signal(s) and/or the corresponding epoxide with time were fitted to a single exponential decay: $I_t = I_\infty + (I_0 - I_\infty) \exp(-k_p t)$. A spectrophotometric (UV) method was primarily used for the epoxidation of styrenes. In a typical experiment using $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1) as a solvent, reaction mixtures were prepared in the reaction cuvette (optical path = 1.0 cm, $V_T = 3.0$ mL) with the last component

added being the styrene. Some experiments were carried out in cuvettes with short optical paths, 0.1–0.2 cm, to allow direct measurement of the absorbance changes during the reaction when the catalyst or the styrene were varied because both have high molar absorptivities and contribute a large absorbance background at the wavelengths used. The data were obtained by following the loss of the styrene absorption in the range 250–275 nm. Initial rate and pseudo-first-order conditions applied in different protocols. In the latter case the pseudo-first-order rate constants were evaluated by nonlinear least-squares fitting of the absorbance-time curves to a single exponential equation, $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_p t)$.

3. Results and discussion

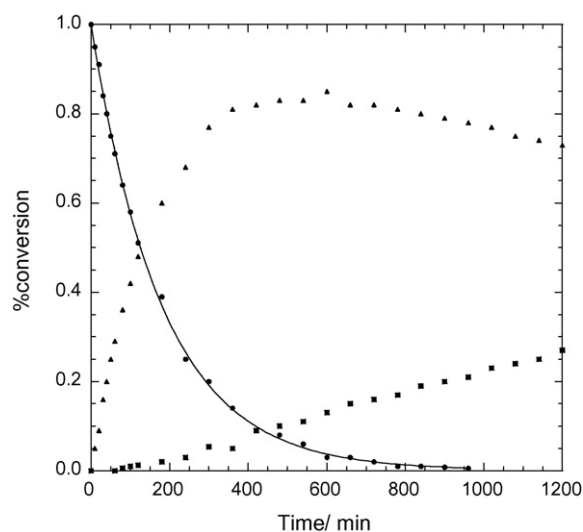
Epoxidations of open and cyclic alkenes, and of styrenes were carried out with aqueous H_2O_2 catalyzed by the polyperoxotungstates **A** and **B** under homogeneous conditions. Epoxidation did not occur without catalysts. These polyperoxotungstates do not activate organic hydroperoxides, such as *tert*-butylhydroperoxide, for epoxidation of olefins, being in agreement with literature reports that many tungsten compounds do not activate organic hydroperoxides for oxidation reactions [20]. On the other hand, polyperoxotungstates are active catalysts for oxidations with aqueous H_2O_2 , and show poor activity for the decomposition of H_2O_2 [15a].

3.1. Epoxidation and products

Methanol and acetonitrile were found to be good solvent to carry out the homogeneous catalytic epoxidation reactions. As shown in Table 1, the percent conversion of all olefins is higher in case of **B**. However, the epoxide ring-opening to 1,2-diol is also higher. The higher activity of **B** over **A** toward oxidation of nucleophilic substrates has been reported recently and was attributed to the higher electrophilicity of **B** as a result of the presence of an electron-withdrawing nitro group [18]. The epoxide ring-opening is also catalyzed by the W-catalyst and this ability is increasing with the catalyst's electrophilicity or acidity. High valent early transition metal catalysts, such as Re(VII) and Mo(VI) are known to catalyze this process due to their high acidity and oxygen affinity [5,24]. Increasing the water content in the solution leads to an increase in the oxidation rate. The epoxide ring-opening rate to 1,2-diol is also enhanced. Under biphasic conditions using $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ or $\text{CHCl}_3/\text{H}_2\text{O}$, the epoxide is more selectively obtained, and in most cases, 1,2-diol products are negligible, Table 1. Although epoxidation under biphasic conditions prevents or reduces the epoxide ring-opening, it employs high concentrations of H_2O_2 with low efficiency of the oxidant utilization and the reactions are significantly slower than when carried out under homogeneous conditions with the same catalysts and concentrations [15a]. The addition of 1–5 equivalents imidazole, *N*-methylimidazole, pyridine, 4-methylpyridine or 4-cyanopyridine with respect to the catalyst reduces the epoxidation rate and the percent conversion in acetonitrile, and the epoxide ring-opening is also inhibited. High epoxidation selectivities of numerous *cis* and *trans* isomers, such as *cis*- and *trans*-4-octene and β -methylstyrene, were observed. For example, epoxidation of *trans*- β -methylstyrene was converted to *trans*- β -methylstyrene oxide selectively. In the case of β -methoxystyrene, benzaldehyde was formed due to a C–C bond cleavage after the epoxidation takes place [16]. The epoxidation and the epoxide ring-opening rates are both enhanced by the olefin nucleophilicity. The effect of the electronic factor on the reaction rate is further investigated by using the Hammett correlation (see later). The steric factor had little effect on the epoxidation rate.

Table 1
Epoxidation of olefins by H₂O₂ catalyzed by **A** and **B**

Olefin	Medium	A			B		
		Conversion (%)	Epoxide (%)	Diol (%)	Conversion (%)	Epoxide (%)	Diol (%)
2,3-Dimethyl-2-butene	CH ₃ CN ^a	86	88	12	96	82	18
Cyclooctene	CH ₃ CN ^a	71	91	9	84	84	16
	Biph. ^b	49	99	–	64	99	–
Styrene	CH ₃ CN ^a	32	72	28	39	61	39
	Biph. ^b	21	94	6	31	92	8
<i>trans</i> -β-Methylstyrene	CH ₃ CN ^a	43	66	34	48	58	42
	Biph. ^b	33	92	8	41	91	9
β-Methoxystyrene	CH ₃ CN ^a	99	99 ^c	–	99	99 ^c	–
	Biph. ^b	91	99 ^c	–	98	99 ^c	–

^a The ratio cat:H₂O₂:olefin (1:200:10), in the presence of 10% H₂O at 40 °C for 12 h.^b In H₂O/CHCl₃ at 50 °C for 12 h.^c Benzaldehyde is the only product which is formed rapidly from the epoxide.**Fig. 1.** The changes in the relative peak intensities with time of 2,3-dimethyl-2-butene (●) at $\delta = 1.68$ ppm, and its oxidation products; the epoxide (▲) at $\delta = 1.36$ ppm and the 1,2-diol (■) at $\delta = 1.15$ ppm during the oxidation of 2,3-dimethyl-2-butene by H₂O₂ catalyzed by **B** in CD₃CN at 40 °C with [H₂O₂] = 1.0 M, [2,3-dimethyl-2-butene] = 0.04 M and [cat] = 5 mM.

3.2. Kinetics

The epoxidation of olefins with H₂O₂ catalyzed by phenylphosphopolyperoxy-tungstate catalysts (**A** or **B**) in CH₃CN/H₂O (9:1) at room temperature leads to the formation of epoxides. Epoxides undergo slow ring-opening by water leading to 1,2-diols. The ring-opening can also be catalyzed by **A** or **B**. A typical NMR experiment, which demonstrates the changes of the signal intensities with time during the epoxidation reaction is shown in Fig. 1. The active forms of the catalysts are proposed to be the peroxy forms shown in Scheme 1 [14–18].

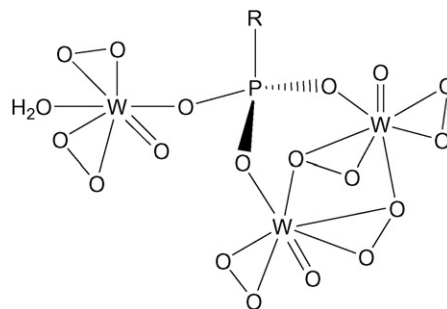
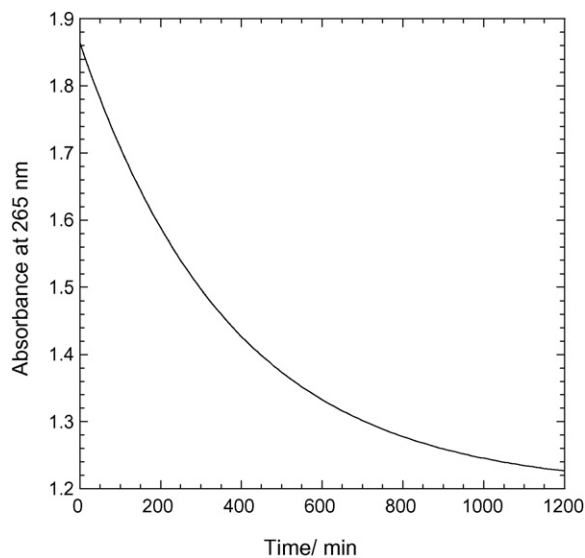
Compound **B**, [C₂₁H₃₇N]₂[(*p*-NO₂Ph(O)-PO₃)-{WO(O₂)₂}]₂{WO(O₂)₂H₂O}, has been prepared as a modified form of **A** by the introduction of a nitro group into the phenyl moiety.

3.2.1. The catalyzed rate

Kinetic experiments on the activity of each catalyst (**A** or **B**) in epoxidation of olefins (examined by NMR) and styrenes (examined by UV) were carried out in CD₃CN/D₂O (9:1 v/v) and in CH₃CN/H₂O (9:1 v/v), respectively, at 40 °C with large excess ([H₂O₂] = 1.0 M), and varied catalyst concentrations. Fig. 2 shows

the change in absorbance with time due to the consumption of β-methoxystyrene at 265 nm.

Under these conditions, the reaction rates were independent of H₂O₂ concentration, and the reactions follow a pseudo-first-order kinetic. The rate constants (k_p) were obtained by fitting the absorbance–time curves to a first-order exponential decay equation. The pseudo-first-order rate constants varied linearly with the concentration of the catalyst (Fig. 3), and the orders of the reactions

**Scheme 1.** The catalysts: R = C₆H₅ (**A**), *p*-NO₂-C₆H₅O (**B**).**Fig. 2.** The absorbance–time curve at 265 nm for the oxidation of β-methoxystyrene (4.0 mM) with H₂O₂ (1.0 M) catalyzed by **B** (1.0 mM) in CH₃CN/H₂O (9:1 v/v) at 40 °C.

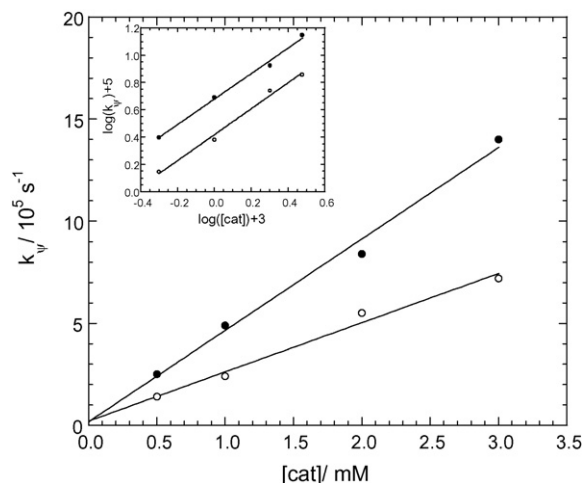
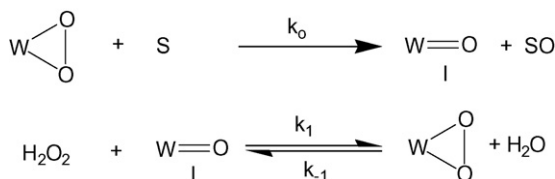


Fig. 3. Variation of the pseudo-first-order rate constants (k_{ψ}) with the catalyst (cat) concentrations for the oxidation of 1.0 mM β -methoxystyrene with H_2O_2 (1.0M) as catalyzed by **A** (○) and **B** (●). The slopes are the catalyzed second-order rate constants and the intercepts are the uncatalyzed rate constants. The inset shows the log plots.



Scheme 2.

with respect to the catalysts' concentrations were determined from plots of $\log(k_{\psi})$ against $\log[\text{catalyst}]$ and found to be 0.93 ± 0.05 and 0.95 ± 0.07 for **A** and **B**, respectively (Fig. 3 inset). These findings indicate that the reaction in both cases is first-order with respect to the catalyst concentration.

The slopes of the lines in Fig. 3 represent the catalyzed rate constants for the epoxidation of β -methoxystyrene by **A** ($k_A = 0.025 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$) and by **B** ($k_B = 0.045 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$). Similar experiments were carried out for the epoxidation of other olefins and the values of the catalyzed rate constants for reactions catalyzed by both catalysts (**A** and **B**) are listed in Table 2. The rate constants increase with the olefin nucleophilicity and are slightly affected by steric factors. The catalyzed rate constant for **B** is at least two times higher than that of **A** confirming the effect of the nitro group (in **B**) in enhancing the electrophilicity of the peroxy group(s) and of the activity toward oxidation of nucleophilic reductants, such as olefins. These activity trends indicate that the oxidation mechanism is similar for all olefins.

3.2.2. The rate law

It has been shown that oxidations by the catalytic systems $\text{H}_2\text{O}_2/\mathbf{A}$ and $\text{H}_2\text{O}_2/\mathbf{B}$ occur via transfer of an oxygen atom from the peroxy forms to a substrate (S) to form a peroxotungstate species (**I**) with one less peroxy group (as shown in Scheme 1) [18]. This species (**I**) reacts rapidly with H_2O_2 to regenerate the active species in a reversible step as depicted in Scheme 2.

The equilibrium constants and the rate constants (k_1 and k_{-1}) for the polyperoxotungstate catalysts, **A** and **B**, had been determined previously (in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$) [18] and had been found to be as follows:

Table 2

The rate constant for the epoxidation of different olefins by H_2O_2 catalyzed by **A** or **B**, in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1 v/v) at 40°C with $[\text{H}_2\text{O}_2] = 1.0 \text{ M}$, and $[\text{cat}]$ varied (0.5–5.0 mM)

Olefin	$k(\mathbf{A})$ ($10^2 \text{ M}^{-1} \text{ s}^{-1}$)	$k(\mathbf{B})$ ($10^2 \text{ M}^{-1} \text{ s}^{-1}$)
β -Methoxystyrene	2.5 ± 0.2	4.6 ± 0.3
Styrene	0.019 ± 0.004	0.039 ± 0.005
<i>m</i> -Methylstyrene	0.025 ± 0.003	0.055 ± 0.008
<i>p</i> -Methylstyrene	0.041 ± 0.004	0.072 ± 0.004
<i>p</i> -Methoxystyrene	0.092 ± 0.012	0.21 ± 0.02
α -Methylstyrene	0.069 ± 0.007	0.12 ± 0.02
<i>cis</i> - β -Methylstyrene	0.056 ± 0.006	0.11 ± 0.05
<i>trans</i> - β -Methylstyrene	0.052 ± 0.004	0.097 ± 0.008
<i>trans</i> -4-Octene	0.062 ± 0.006	0.13 ± 0.02
2,3-Dimethyl-2-butene	0.9 ± 0.1	2.2 ± 0.1
Cyclohexene	0.18 ± 0.02	0.43 ± 0.02
Cyclooctene	0.41 ± 0.03	0.95 ± 0.05

	A	B
k_1 ($\text{M}^{-1} \text{ s}^{-1}$)	0.5	1.5
k_{-1} (s^{-1})	0.004	0.007
K_{eq}	$\sim 1 \times 10^2$	$\sim 2 \times 10^2$

In general, alkenes are relatively weak nucleophiles and reductants. Therefore, the epoxidation step is expected to be much slower than the regeneration of the catalyst (the equilibrium step) especially in the presence of excess amounts of H_2O_2 . Using Scheme 2 as a general reaction sequence for the epoxidation of a styrene (namely β -methoxystyrene) by **A**/ H_2O_2 and **B**/ H_2O_2 , an *initial rate method* (see Section 2) was used to determine the rate law. The data obtained from the beginning of the reaction ($\Delta \text{Abs}_i \leq 5\%$) were used for kinetic analysis. This was intended to minimize the likelihood of the involvement of more than one form of the catalyst. The initial rate is calculated from the absorbance change with time using Eq. (1),

$$i.r. = - \left(\frac{1}{b \Delta \epsilon_{\lambda}} \right) \times \frac{\Delta \text{Abs}_i}{\Delta t} \quad (1)$$

where b is the optical path length and $\Delta \epsilon_{\lambda}$ is the total change in the molar absorptivity at λ , and ΔAbs_i is the initial change in the absorbance.

The rate due to the decrease in the styrene concentration with time can be expressed as follows:

$$\text{rate}(v) = \frac{-d[\text{styrene}]}{dt} = k_2[\text{WO}_2][\text{styrene}] \quad (2)$$

where the total concentration of the catalyst is $[\text{W}]_{\text{T}} = \text{WO}_2 + \text{WO}$.

At high H_2O_2 concentration ($\text{H}_2\text{O}_2 > 0.5 \text{ M}$), $[\text{W}]_{\text{T}}$ equals WO_2 ; i.e., WO is negligible because reacts rapidly with H_2O_2 to form WO_2 . Therefore, Eq. (2) can be expressed in terms of $[\text{W}]_{\text{T}}$ or using the initial concentration of the catalyst, $[\text{cat}]_i$.

$$\text{rate}(v) = \frac{-d[\text{styrene}]}{dt} = k_2[\text{W}]_{\text{T}}[\text{styrene}] \quad (2a)$$

Under these conditions, the values of k_A and k_B listed in Table 2 are actually the second-order rate constants (k_2) for the epoxidations of each olefin by **A** and **B**, respectively.

When H_2O_2 is present in lower concentrations ($< 200 \text{ mM}$), but still in greater concentration than styrene ($[\text{styrene}] < 0.5 \text{ mM}$), a rapid pre-equilibrium condition ($k_1[\text{H}_2\text{O}_2] + k_{-1} \gg k_2[\text{styrene}]$) can be applied. Under these conditions, the rate law can be expressed by Eq. (3), which is derived from Eq. (2) using the equilibrium expression and the mass balanced equations $[\text{W}]_{\text{T}} = \text{WO}_2 + \text{WO}$.

$$\text{rate}(v) = \frac{-d[\text{styrene}]}{dt} = \frac{K_1 k_2 [\text{W}]_{\text{T}} [\text{H}_2\text{O}_2] [\text{styrene}]}{1 + K_1 [\text{H}_2\text{O}_2]} \quad (3)$$

Variation of the initial rate with the initial concentration of H_2O_2 (in the range 2–200 mM) (see Fig. 4) and with the initial concentration of β -methoxystyrene (in the range 0.05–0.5 mM)

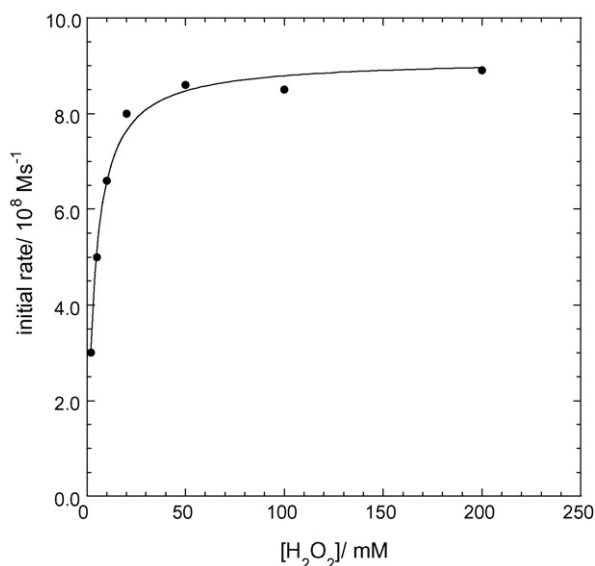


Fig. 4. A plot of the initial rate of oxidation of β -methoxystyrene (2.0 mM) by H_2O_2 catalyzed by the catalyst **B** (1.0 mM) against $[\text{H}_2\text{O}_2]$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1 v/v) at 40°C . The data fit to Eq. (3).

(see Fig. 5) is in agreement with Eq. (3). The kinetic data fit well to Eq. (3). Using the values of the second-order rate constants, $k_2(\mathbf{A})=0.025 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2(\mathbf{B})=0.046 \text{ M}^{-1} \text{ s}^{-1}$, obtained previously from the catalyst variation experiments, the equilibrium constants $K_1(\mathbf{A}) (= 1.9 \pm 0.5) \times 10^2$ and $K_1(\mathbf{B}) (= 2.6 \pm 0.3) \times 10^2$ were determined from the variation of the initial rate with the concentration of H_2O_2 according to Eq. (3). To confirm the validity of Eq. (3), the value of $k_2(\mathbf{B}) (= 0.038 \pm 0.003 \text{ M}^{-1} \text{ s}^{-1})$ was also determined from fitting the data in Fig. 5 to Eq. (3). The two values are in good agreement within the experimental errors associated with each measurement. Table 2 summarizes the values of k_2 for the epoxidation of different olefins by H_2O_2 as catalyzed by **A** and **B**.

3.2.3. Hammett correlation

The data in Table 2 show that the reactivity of the olefins increases with olefin nucleophilicity. Electron-donating group(s)

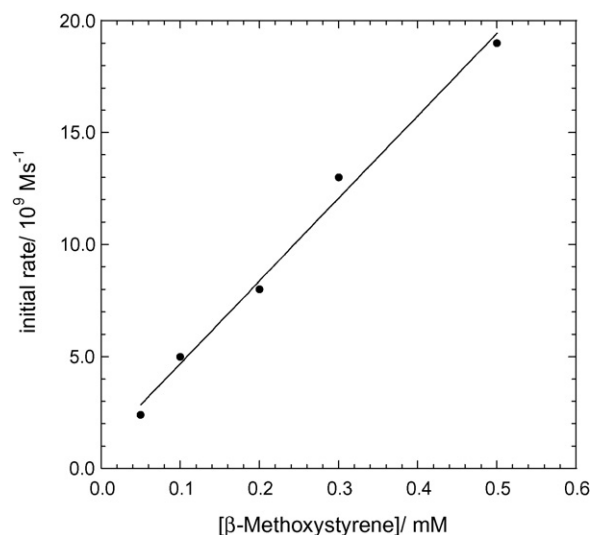


Fig. 5. The initial rate of oxidation of β -methoxystyrene by $[\text{H}_2\text{O}_2]$ (0.1 M) catalyzed by **B** (1.0 mM) varies linearly with $[\beta\text{-methoxystyrene}]$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1 v/v) at 40°C . The fit to Eq. (3) gave $k_2 = 0.038 \pm 0.003 \text{ M}^{-1} \text{ s}^{-1}$.

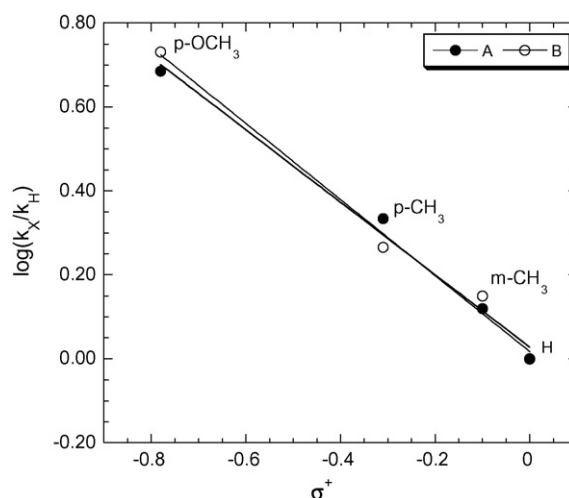
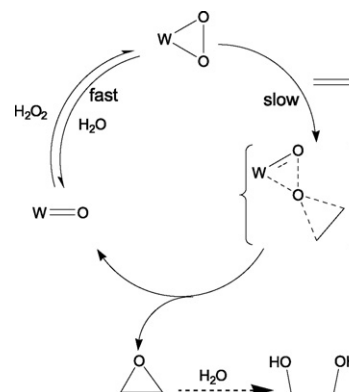


Fig. 6. The Hammett correlation of $k(\mathbf{A})$ and $k(\mathbf{B})$ for the oxidation of *meta* and *para* substituted styrenes by H_2O_2 as catalyzed by **A** (●) and **B** (○) against σ^+ . The reaction constants are $\rho(\mathbf{A}) = -0.86 \pm 0.06$ and $\rho(\mathbf{B}) = -0.91 \pm 0.07$.

on the phenyl or on the olefinic carbons increases the rate constant for the epoxidation of styrene by both catalytic systems in the same manner. Indeed, Hammett correlations of the rate constants of *p*- and *m*-substituted styrenes with σ^+ , $(\log(k_X/k_H)) = \rho\sigma^+$, were linear, and give the reaction constant values; $\rho(\mathbf{A}) = -0.86 \pm 0.06$ and $\rho(\mathbf{B}) = -0.91 \pm 0.07$ (Fig. 6). The linear correlation indicates that all the styrenes are oxidized via the same mechanism. The correlation with σ^+ implies a direct interaction through resonance between the substituent and the reaction site. Actually, the ρ values of both catalysts can be considered as (almost) equal. Similar negative values of ρ have been reported for the epoxidation of olefins by dimethyldioxirane and peracetic acid [21,22], and metal-peroxo catalysts of $\text{Mo}(\text{VI})$, and $\text{Re}(\text{VII})$ with H_2O_2 as the oxidant [5]. The relatively small negative value of ρ indicates the buildup of a partial positive charge on the olefinic carbons in the transition state. The epoxidation rate constants of styrenes with dimethyldioxirane ($\rho = -0.90$) [21] and $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ catalytic system ($\rho = -0.93$) [5d] are also correlated well with σ^+ . The first study proposed nucleophilic attack of one of the olefinic carbons (α or β) on the peroxy oxygen followed by an intramolecular attack of the same oxygen on the other olefinic carbon. In the case of $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ system, an external nucleophilic attack of the π -system of the olefin on the electropositive oxygen of the Re -peroxo group was proposed.

3.3. Proposed mechanism

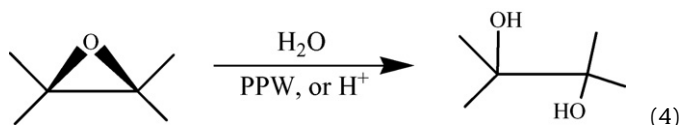
The kinetic results including the rate law, Hammett correlation and the epoxidation stereoselectivity suggest the following mechanism:



In the above-proposed mechanism, the nucleophilic olefin attacks the electrophilic oxygen of the W-peroxo group in a concerted oxygen-transfer step. This leads to the formation of a three-membered-ring transition state. The kinetic studies showed that the oxygen-transfer is the rate-determining step. This mechanism is consistent with the slight effect of steric factors on the rate constant since such an attack is less sensitive to steric hindrance. In addition, epoxidation by concerted oxygen-atom transfer is expected to be stereoselective as a C–C bond rotation is not possible. Absolute stereoselectivity was obtained for the epoxidation of *cis*- and *trans*-4-octene and β -methylstyrene. The Hammett correlation with σ^+ and the ρ value also agree with this mechanism. A similar three-membered-ring transition state has been proposed for the epoxidation of olefins by Mo(VI) and Re(VII) peroxo complexes. [23,5]

3.4. The epoxide ring-opening

Under homogeneous conditions, the epoxide ring-opening (Eq. (4)) is enhanced by the catalyst, the amount of water and the solution acidity. In fact, all these factors also increase the rate of the epoxidation reaction.



In the presence of 0.1 M HClO₄, the rates of the epoxidation and the 1,2-diol formation are increased and the epoxide ring-opening is almost independent of the catalyst (**A** or **B**) concentration. In neutral CH₃CN/H₂O (9:1), the rate of the epoxide ring-opening is increasing with increasing catalyst concentration. The order of the reaction with respect to the [catalyst] decreases with increasing the catalyst concentration. This may be attributed to the coordination of the epoxide (or the diol) to the metal center especially at high concentrations. Early transition metals (d⁰) have high oxygen affinity and form complexes with epoxides and diols [24]. Furthermore, these types of PPW are subjected to partial hydrolysis and/or decomposition especially in the later stages of the reaction. It has been reported that catalytic epoxidations with aqueous H₂O₂ using organophosphoruspolyperoxotungstate catalysts suffer from decomposition of the catalyst into phosphoric acid and polyperoxotungstates [15].

4. Conclusion

The phenylphosphate derivatives of polyperoxotungstate have been shown to be active POM catalysts for oxidations with H₂O₂ under homogeneous conditions. The relatively high stability and good solubility in organic solvents permit the use of these catalytic systems to oxidize a variety of organic substrates, such as olefins. Both the phenyl group and the phosphate group can be used to modify the catalyst for a better activity, selectivity, and solubility. This study presents a simple modification by introducing an electron-withdrawal group to enhance the electrophilicity of the PPW. Higher activities may be reached by applying PPW catalysts with more electron-deficient organophosphate group(s).

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