

Oxidation of Triarylphosphines and Aryl Methyl Sulfides with Hydrogen Peroxide Catalyzed by Dioxovanadium(V) Ion

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Although neither vanadium(V) ions nor hydrogen peroxide efficiently oxidize the title substrates, they do so in combination, with vanadium(V) as the catalyst in acidic aqueous acetonitrile. The kinetic data show that, of the two peroxovanadium species present, $OV(O_2)^+$ and $OV(O_2)_2^-$, only the latter reacts at a detectable rate. This unanticipated result can be attributed to the weaker O–O and V–O bonds in the diperoxo complex. The rate constants for both series of substrates follow the Hammett correlation, with $\rho_P = -1.35$ and $\rho_S = -0.83$. To analyze properly the kinetic data for the Ar_3P compounds, account must be taken of the protonation to Ar_3PH^+ in acidic solution. In retrospect, our earlier study [Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272–280] of phosphine oxidation catalyzed by $MeReO_3$ failed to do so, and the reaction constant must be corrected from the originally reported value to -1.56 .

Introduction

Vanadium is a biologically relevant element, present in a number of metalloenzymes including the haloperoxidases¹ that catalyze the oxidation of bromide to hypobromite and the nitrogenases that fix nitrogen.² Further interest stems from the finding that certain synthetic vanadium complexes can activate insulin-dependent physiological processes and can be regarded as potential insulin mimetics in the treatment of diabetes.³ Indeed, there has been a renewed interest recently, as demonstrated by the appearance of a number of reviews covering various aspects of the vanadium chemistry and biological chemistry.⁴

Numerous functional and structural model complexes for vanadium haloperoxidases have been prepared, many of which catalyze the oxidation of halides, just as the natural haloperoxidases do, as well as the oxidation of other substrates such as organic sulfides and olefins.⁴ The active oxidant in these systems is believed to be a peroxovanadium complex; this is analogous to the situation for the haloperoxidases.

Despite the volume of publications concerning the vanadium-catalyzed oxidation of a variety of substrates, the

mechanistic aspects of these reactions have not been fully resolved. Besides, the oxidation of phosphines with vanadium has not been investigated systematically, despite phosphine oxidation often providing a sound probe of mechanism. It is also of interest to compare the reactivity of the vanadium system with the MTO–hydrogen peroxide system, where MTO represents $MeReO_3$, methyltrioxorhenium(VII), which has been well studied.⁵ In this paper, we report the kinetic studies of the oxidation of triarylphosphines and methyl aryl sulfides with hydrogen peroxide catalyzed by dioxovanadium(V) in 1:1 MeCN:H₂O.

Experimental Section

Materials. The phosphines and sulfides were purchased commercially and used as received. Solutions of VO_2^+ were prepared by dissolving V_2O_5 in 1 mol L⁻¹ HClO₄. Solutions of hydrogen peroxide were diluted from 30% solution, and the concentration was determined spectrophotometrically by iodometric titration on the same day of usage. High-purity water was obtained by passing laboratory distilled water through a Millipore-Q water purification system. HPLC grade acetonitrile was used throughout.

Instrumentation. Shimadzu scanning spectrophotometers (UV-2101/3101 PC) were used to record the UV–vis spectra and to

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- (2) Liang, J.; Madden, M.; Shah, V. K.; Burris, R. H. *Biochemistry* **1990**, *29*, 8577–8581.
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- (4) (a) Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849–902. (b) Thompson, K. H.; Orvig, C. *Met. Ions Biol. Syst.* **2004**, *41*, 221–252. (c) Butler, A.; Carter-Franklin, J. N. *Nat. Prod. Rep.* **2004**, *21*, 180–188. (d) Redher, D. *Inorg. Chem. Commun.* **2003**, *6*, 604–617. (e) *Coord. Chem. Rev.* **2003**, *237*. This volume was dedicated to vanadium.
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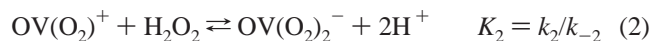
monitor the reaction progress. Quartz cuvettes with appropriate optical path lengths (0.1–1 cm) were used. The kinetics was studied at 25.0 ± 0.2 °C, maintained by either an electronic thermostatic holder or a circulating water thermostatic system. The NMR studies were carried out with a Bruker DRX-400 MHz spectrometer at 298 K.

Kinetics. The absorbance loss of the triarylphosphines and methyl aryl sulfides in the near UV region (250–280 nm) was recorded, except for *p*-NO₂C₆H₄SCH₃, where the absorbance change at 350 nm was followed. Methyl aryl sulfide oxidation can also be conveniently monitored by NMR spectroscopy in deuterated solvents, because sulfides and their oxidation products, sulfoxides and sulfones, gave distinctive methyl peaks. For example, the methyl signals of C₆H₅SCH₃, C₆H₅S(O)CH₃, and C₆H₅S(O)₂CH₃ resonate at δ 2.40, 2.72, and 3.08, respectively, in 1:1 D₂O–CD₃-CN mixture in the presence of 0.1 mol L⁻¹ DClO₄.

Under the conditions used for the oxidation of phosphines and sulfides, the reactions followed pseudo-first-order kinetics. The absorbance–time data were analyzed accordingly by nonlinear least-squares fitting using the program KaleidaGraph.

Results

Vanadium(V)–Peroxide Equilibria. The dioxovanadium(V) species, VO₂⁺ in aqueous solution, is the simplest model compound that functions as a haloperoxidase.⁶ The equilibria between vanadium(V) and hydrogen peroxide in acidic aqueous solutions can be described by the following two equations in which red monoperoxo OV(O₂)⁺ and yellow diperoxo OV(O₂)₂⁻ species form sequentially:



The different chemistry at each stage should be noted. Reaction 1 represents oxo group condensation, V=O + H₂O₂ → V(O₂) + H₂O. Reaction 2, on the other hand, is ligand (O₂²⁻) addition accompanied by proton loss. Thus, the diperoxo complex retains a V=O group with the formula shown, rather than being V(O₂)₂⁺; the actual diperoxo species reflects stabilization of V(V) by a metal–oxo multiple bond.

The equilibrium constants were determined spectrophotometrically to be $K_1 = 3.5 \times 10^4$ L mol⁻¹ and $K_2 = 1.3$ mol L⁻¹ at an ionic strength of 1.0 M.⁷ At an ionic strength of 0.3 mol L⁻¹, the equilibrium constants K_1 and K_2 are 3.7×10^4 L mol⁻¹ and 0.6 mol L⁻¹, respectively.⁸ With a different technique, ⁵¹V NMR spectroscopy, K_2 was determined to be 1.0 mol L⁻¹ at an ionic strength of 2.0 mol L⁻¹ (NaClO₄).⁶ Reactions 1 and 2 proceed to equilibrium rapidly; the second-order rate constants k_1 and k_2 in aqueous solution were reported to be ca. >3000 L mol⁻¹ s⁻¹ at 25 °C.⁷

The equilibrium constants were used to calculate the concentration of free hydrogen peroxide in solution, [H₂O₂], corrected from the formal concentration by the vanadium-coordinated H₂O₂ according to eqs 3–5:

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_{\text{T}} - [\text{OV}(\text{O}_2)^+] - 2[\text{OV}(\text{O}_2)_2^-] \quad (3)$$

where [H₂O₂]_T and [V]_T represent the formal concentrations

Table 1. Second-Order Rate Constants (L mol⁻¹ s⁻¹) for the Oxidation of Phosphines (*p*-X–C₆H₄)₃P by Hydrogen Peroxide in 1:1 CH₃CN/H₂O at 25 °C

X	3σ	k_u^a	k_u^b	k_4^b
OMe	-0.81	4.1 ± 0.1	0.82 ± 0.01	137 ± 6
Me	-0.51	2.98 ± 0.05	2.44 ± 0.03	374 ± 19
H	0	1.88 ± 0.03	2.52 ± 0.03	845 ± 25
Cl	0.69	1.06 ± 0.02	1.21 ± 0.02	672 ± 33
CF ₃	1.62	0.434 ± 0.003	0.597 ± 0.003	490 ± 20

^a No acid added. ^b [H⁺] = 0.10 mol L⁻¹.

of hydrogen peroxide and vanadium, respectively. In particular, [V]_T = [VO₂⁺] + [OV(O₂)⁺] + [OV(O₂)₂⁻]. Substitution from eqs 1 and 2 gives

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_{\text{T}} - \left\{ \frac{K_1[\text{H}_2\text{O}_2] + 2K_1K_2[\text{H}_2\text{O}_2]^2/[\text{H}^+]^2}{1 + K_1[\text{H}_2\text{O}_2] + K_1K_2[\text{H}_2\text{O}_2]^2/[\text{H}^+]^2} \right\} [\text{V}]_{\text{T}} \quad (4)$$

Given the values of the equilibrium constants and the concentration ranges, it can be shown that the concentration of VO₂⁺ itself is very low as compared to both of its peroxo complexes. Thus, eq 4 simplifies to this form,

$$[\text{H}_2\text{O}_2] \cong [\text{H}_2\text{O}_2]_{\text{T}} - \left\{ \frac{[\text{H}^+]^2 + 2K_2[\text{H}_2\text{O}_2]}{[\text{H}^+]^2 + K_2[\text{H}_2\text{O}_2]} \right\} [\text{V}]_{\text{T}} \quad (5)$$

To evaluate the actual concentration of free H₂O₂ in each experiment, its value on the right side of eq 5 was originally assigned as [H₂O₂]_T. The value of [H₂O₂] on the left was then calculated with K_2 taken as 1.0 mol L⁻¹. The resulting value of [H₂O₂] was applied to the right side iteratively until they converged. The correction from [H₂O₂]_T to the actual [H₂O₂] generally amounted to no more than 5% of the total hydrogen peroxide concentration, which translated into an even smaller effect on the rate constants.

Reactions between Phosphines and H₂O₂ without Vanadium. The reactions were carried out in a 1:1 v/v mixture of acetonitrile and water. This mixture ensures mutual solubility of the reagents and facilitates comparisons with MeReO₃ catalysis where it was also used.⁹ The uncatalyzed reaction between a phosphine and hydrogen peroxide has been reported previously.⁹ Here, a more systematic investigation was carried out to address a difficulty arising from the analysis of the vanadium-catalyzed reaction (see below). The rate constants for the uncatalyzed reaction were obtained under pseudo-first-order conditions with hydrogen peroxide in large excess. The results are collected in Table 1. For the reaction in the absence of an acid, the Hammett correlation of the second-order rate constants is evident, as the plot of log(k_u) versus 3σ gave a straight line with a slope = ρ = -0.40. This value of the reaction constant is consistent with nucleophilic attack of phosphine at a peroxo oxygen. However, in the reactions with 0.1 mol L⁻¹ HClO₄, a

(6) Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1995**, *117*, 3475–3484.

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(9) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272–280.

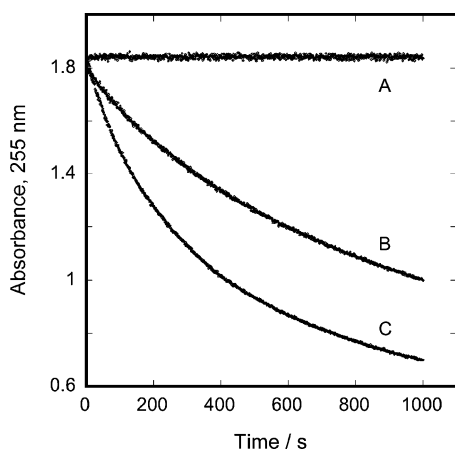


Figure 1. Absorbance–time traces for oxidations of PPh₃ by H₂O₂ in 1:1 CH₃CN–H₂O at 25 °C. Concentrations, mmol L⁻¹: 100 HClO₄, (A) 0.17 PPh₃, 0.16 VO₂⁺ (control); (B) 0.17 PPh₃, 0.39 H₂O₂; (C) 0.17 PPh₃, 0.16 VO₂⁺, 0.39 H₂O₂.

satisfactory Hammett correlation was not found. Protonation of phosphines, while a factor for the methoxy and methyl compounds especially, could not account for all of the effect. It appeared that besides the direct reaction between phosphine and hydrogen peroxide, there is a hydrogen ion-dependent pathway, similar to that in the reaction of PPh₃ with hydroperoxides.¹⁰ To confirm this point, the reactions of PPh₃ and (*p*-CF₃-C₆H₄)₃P, which is not a Bronsted base, were studied over a limited range of hydrogen ion concentration. The rate constants increased with increasing hydrogen ion concentration. The values determined in the presence of 0.10 mol L⁻¹ acid were used later in the analysis of catalytic reactions.

Oxidation of PPh₃. Preliminary Experiments. The possibility of direct oxygen atom transfer from VO₂⁺ to PPh₃ was studied with [PPh₃] and [VO₂⁺] on the order of 0.1 mmol L⁻¹. No reaction was evident; see trace A, Figure 1. In fact, even after 5 days, less than 10% spectral change could be recorded. Thus, it is safe to neglect this pathway in the present studies. Traces B and C demonstrate the catalytic effect of VO₂⁺ on the oxidation of PPh₃ by hydrogen peroxide. The presence of VO₂⁺ clearly accelerated the reaction, although the catalytic enhancement was apparently small considering the relatively high concentration of VO₂⁺. Actually, the catalytically active species is OV(O₂)₂⁻, which under the conditions used in the experiment depicted in Figure 1C is present in a small proportion, as will be shown later.

In preliminary studies, experiments were carried out with a large excess of [H₂O₂]_T (20.9 mmol L⁻¹) over PPh₃ (1.7 mmol L⁻¹) in which [V]_T was varied in the range 0.024–0.15 mmol L⁻¹. The data fit first-order kinetics. The plot of the *k*_{obs} versus [V]_T is shown in Figure 2, establishing that the catalyzed component of the reaction shows a first-order dependence on vanadium concentration. Seemingly this would afford a rate constant associated with a vanadium-containing reactive species. However, in another set of runs

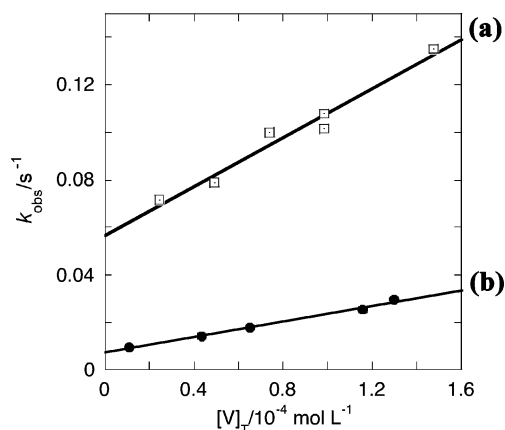


Figure 2. The plot of the pseudo-first-order rate constants against [V]_T for the oxidation of PPh₃ by H₂O₂ in 1:1 CH₃CN–H₂O at 25 °C. Concentrations, mmol L⁻¹: 100 HClO₄, (a) 1.7 PPh₃, 20.9 H₂O₂; (b) 0.30 PPh₃, 3.21 H₂O₂. The slopes are (a) 517 and (b) 163 L mol⁻¹ s⁻¹, respectively. The nonzero intercepts correspond to the uncatalyzed reaction between PPh₃ and hydrogen peroxide.

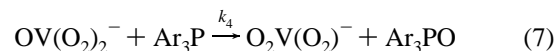
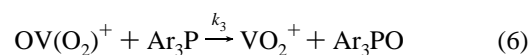
Table 2. Fitting of Kinetic Data for Vanadium(V)-Catalyzed PPh₃ Oxidation According to Eq 9

fit	fixed	<i>k</i> ₄ ^a	<i>k</i> ₃ ^a	<i>K</i> ₂ ^b
1	<i>K</i> ₂ = 1	887 ± 39	-46 ± 34	
2	<i>k</i> ₃ = 0	936 ± 101		0.8 ± 0.2
3	<i>k</i> ₃ = 0, <i>K</i> ₂ = 1	845 ± 25		
4	<i>k</i> ₄ = 0, <i>K</i> ₂ = 1		558 ± 94	

^a L mol⁻¹ s⁻¹. ^b mol L⁻¹.

with different concentrations of [H₂O₂]_T (3.21 mmol L⁻¹) and PPh₃ (0.30 mmol L⁻¹), a different slope was obtained, Figure 2.

Oxidation of PPh₃: Kinetic Model. As mentioned earlier, the reaction between VO₂⁺ and H₂O₂ reaches equilibrium very rapidly in 1:1 CH₃CN–H₂O. An instantaneous color change occurred upon mixing VO₂⁺ and H₂O₂ in 1:1 CH₃CN–H₂O media. Simulation showed that the equilibrium was reached within 0.5 s under most conditions used. The large excess of H₂O₂ over phosphines was used to maintain first-order kinetics for the uncatalyzed oxidation and to keep the concentrations of monoperoxo species OV(O₂)⁺ and diperoxo species OV(O₂)₂⁻ constant. It is conceivable that both peroxovanadium species are active reagents for oxygen transfer to phosphines (eqs 6 and 7), analogous to the MTO–H₂O₂ system. Neither of the peroxovanadium species could be neglected because in general they are present in comparable amounts in the beginning and the subsequent oxygen atom transfer reaction was not fast enough (see below). Thus, a prior equilibrium approximation seems reasonable when H₂O₂ is used in large excess over phosphines.



The total vanadium concentration can be expressed as [V]_T = [VO₂⁺]{1 + *K*₁[H₂O₂] + *K*₁*K*₂[H₂O₂]²/[H⁺]²}. Because VO₂⁺ itself shows no reactivity toward phosphine, the

(10) Hiatt, R.; McColeman, C. *Can. J. Chem.* **1971**, *49*, 1712–1715.

reaction rate could be written as eq 8, which gives rise to eq 9 considering that $1 \ll K_1[\text{H}_2\text{O}_2]$ (H_2O_2 is abbreviated as HP in eqs 8 and 9). Consequently, the reaction should follow pseudo-first-order kinetics, in agreement with the experimental results. The observed first-order rate constants were functions of both $[\text{H}_2\text{O}_2]$ and $[\text{V}]_{\text{T}}$ (eq 9). The data obtained were analyzed using software called Scientist.¹¹

$$\frac{d[\text{P}]}{dt} = k_u[\text{HP}][\text{P}] + \frac{k_3 K_1 [\text{HP}][\text{P}][\text{V}]_{\text{T}}}{1 + K_1[\text{HP}] + K_1 K_2 [\text{HP}]^2 / [\text{H}^+]^2} + \frac{k_4 K_1 K_2 [\text{P}][\text{V}]_{\text{T}} [\text{HP}]^2 / [\text{H}^+]^2}{1 + K_1[\text{HP}] + K_1 K_2 [\text{HP}]^2 / [\text{H}^+]^2} \quad (8)$$

$$-\frac{d[\text{P}]}{[\text{P}] dt} = k_{\text{obs}} = k_u[\text{HP}] + \left\{ \frac{k_3 + k_4 K_2 [\text{HP}] / [\text{H}^+]^2}{1 + K_2 [\text{HP}] / [\text{H}^+]^2} \right\} [\text{V}]_{\text{T}} \quad (9)$$

Oxidation of Phosphines. A detailed investigation was carried out with PPh_3 . The initial concentrations of H_2O_2 , PPh_3 , and VO_2^+ were varied over the range 1.4–20.9, 0.15–1.70, and 0.0073–0.15 mmol L^{-1} , respectively, such that $[\text{H}_2\text{O}_2] > 10 \times [\text{PPh}_3]$, while the reaction rate was still easily measurable. Values of k_{obs} were fitted to eq 9 to obtain k_3 and k_4 values with fixed $k_u = 2.52 \text{ L mol}^{-1} \text{ s}^{-1}$ at 0.1 $\text{mol L}^{-1} \text{ H}^+$ (Table 1). A number of plausible scenarios were explored, and the results are summarized in Table 2. With K_2 fixed at 1.0 mol L^{-1} and k_3 and k_4 allowed to float, fit 1, a negative value for k_3 was obtained, which made no sense. This suggests that the contribution of k_3 term is negligible as compared to k_4 . When k_3 was fixed at 0 and the values of k_4 and K_2 floated, fit 2, the resulting K_2 value fell in the range of the literature values, thus validating the assumption that $k_3 = 0$. Further, when k_4 was floated with $K_2 = 1.0 \text{ mol L}^{-1}$ and $k_3 = 0$, fit 3, a satisfactory result was obtained. The subsequent analyses were performed according to this fit. Note this does not mean k_3 is chemically zero, just that its value is so small relative to k_4 that even a small amount of diperoxo species would dominate the reaction under these conditions.

Figure 3 shows the relationship between the observed rate constants and the calculated ones from fit 3 under this model according to eq 9.

For the vanadium-catalyzed oxidation of a series of *para*-substituted triarylphosphines, (*p*-X-C₆H₄)₃P, similar treatment was applied. When both k_3 and k_4 were allowed to float, the fit of k_{obs} against $[\text{V}]_{\text{T}}$ and $[\text{H}_2\text{O}_2]$, with K_2 fixed at 1.0 mol L^{-1} , yielded a value of k_3 that was either negative or a small positive number with large standard deviations. In few cases when a seemingly reasonable number for k_3 was generated, for example, fit 4 in Table 2, the corresponding residual plots displayed nonrandom distribution. The best fitting, all PAR_3 substrates considered, was obtained with fixed $k_3 = 0$ and $K_2 = 1.0 \text{ mol L}^{-1}$. The resulting k_4 values are listed in Table 1.

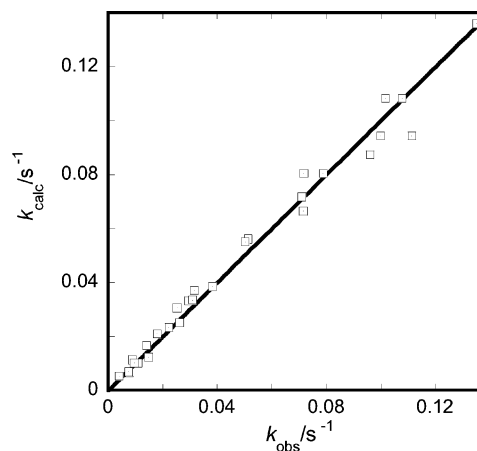


Figure 3. The relationship between the observed and calculated rate constants for the oxidation of PPh_3 from eq 9 with $k_u = 2.52 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_3 = 0$, and $K_2 = 1.0 \text{ mol L}^{-1}$, fit 3 from Table 2. The fitted parameter k_4 is $845 \pm 25 \text{ L mol}^{-1} \text{ s}^{-1}$. The line shown is the theoretical $y = x$ line.

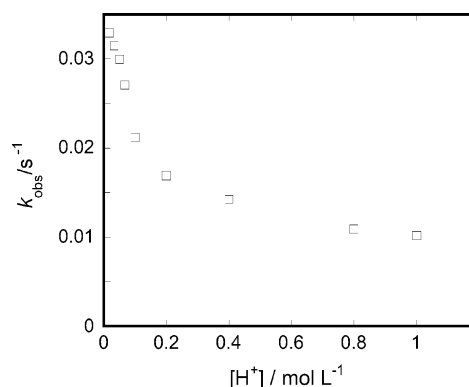


Figure 4. Plot of the observed rate constant k_{obs} of the oxidation of PPh_3 as a function of the concentration of acid at 25 °C and $\mu = 1.0 \text{ mol L}^{-1}$ (LiClO_4). Concentrations (mmol L^{-1}): 2.3 H_2O_2 , 0.16 PPh_3 , and 0.073 V_{T} .

As can be seen from eqs 1 and 2, the actual concentration of $\text{OV}(\text{O}_2)_2^-$ in solution depends on $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$. Under conditions shown in Figure 1C, the concentration of free H_2O_2 is low and the actual concentration of $\text{OV}(\text{O}_2)_2^-$ is only ~2% of the total vanadium; thus, the catalytic effect was relatively small. It was also expected that increasing $[\text{H}^+]$ would decrease $[\text{OV}(\text{O}_2)_2^-]$ and thus reduce the reaction rate with other conditions kept the same. A set of experiments was carried out, and the results confirmed this prediction (Figure 4), at least in a qualitative sense. Further quantification was not possible, however, because of the complications arising from the effects of $[\text{H}^+]$ and changing ionic strength on the vanadium– H_2O_2 system and on phosphine oxidation.

Oxidation of Methyl Aryl Sulfides. The reaction between organic sulfides and hydrogen peroxide proceeds very slowly, even with the acid-dependent reaction pathways.¹² In the presence of vanadium(V), however, the oxidation of methyl phenyl sulfide proceeded smoothly, affording the sulfoxide within a few hours. Under conditions similar to those used for phosphine oxidations, with excess hydrogen peroxide, the absorbance–time traces followed pseudo-first-order kinetics. The values of k_{obs} were fitted against $[\text{H}_2\text{O}_2]$ and

(11) Scientist, version 2.01; MicroMath software: Salt Lake City, UT, 1995.

(12) Dankleff, M. A. P.; Curci, R.; Edwards, J. O.; Pyun, H.-Y. *J. Am. Chem. Soc.* **1968**, *90*, 3209–3218.

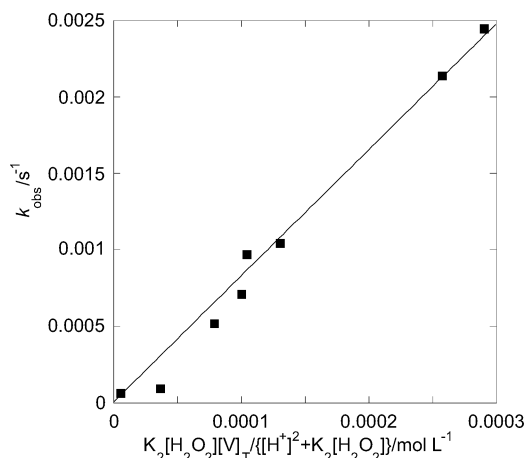


Figure 5. The plot of k_{obs} against $K_2[\text{H}_2\text{O}_2][\text{V}]_{\text{T}}/([\text{H}^+]^2 + K_2[\text{H}_2\text{O}_2])$ for PhSMe. This gives a straight line because $k_u = k_3 = 0$. Here, $K_2 = 1.0 \text{ mol L}^{-1}$, $[\text{H}^+] = 0.1 \text{ mol L}^{-1}$. The slope of the line gives $k_4 = 8.24 \pm 0.25 \text{ L mol}^{-1} \text{ s}^{-1}$.

Table 3. Values of k_4 for the Oxidation of $p\text{-X-C}_6\text{H}_4\text{SCH}_3$ by Hydrogen Peroxide Catalyzed by Vanadium(V) in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at 25°C

X	$k_4/\text{L mol}^{-1} \text{ s}^{-1}$	σ
CH ₃	13.0 ± 1.1	-0.17
H	8.24 ± 0.25	0
NO ₂	2.03 ± 0.08	0.78

$[\text{V}]_{\text{T}}$ according to eq 9 with the Scientist program to obtain k_3 and k_4 values with $k_u = 0$ and $0.10 \text{ mol L}^{-1} \text{ H}^+$. Again, no meaningful k_3 value could be obtained. Fittings were repeated with k_3 fixed at 0 to obtain the optimal values of k_4 for $\text{OV}(\text{O}_2)_2^-$ for three methyl aryl sulfides. The results are summarized in Table 3. Figure 5 shows a plot of k_{obs} against $K_2[\text{H}_2\text{O}_2][\text{V}]_{\text{T}}/([\text{H}^+]^2 + K_2[\text{H}_2\text{O}_2])$ for PhSMe, the slope of which affords k_4 .

Discussion

Coordination to transition metals often, but not always, activates hydrogen peroxide toward the oxidation of various substrates. Indeed, the oxidation of phosphines and sulfides by hydrogen peroxide is appreciably accelerated in the presence of dioxovanadium ion, VO_2^+ , in acidic 1:1 $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solutions. That VO_2^+ itself shows no reactivity toward these substrates indicates that the interaction between VO_2^+ and hydrogen peroxide plays an important role in the catalysis.

We find it surprising that the oxo-diperoxovanadium complex $\text{OV}(\text{O}_2)_2^-$ is much more reactive toward phosphines and sulfides than the oxo-monoperoxovanadium complex, $\text{OV}(\text{O}_2)^+$; that is, that $k_4 \gg k_3$ (see eqs 6 and 7). It might have been expected that $\text{OV}(\text{O}_2)^+$ would be highly reactive toward nucleophilic attack not only because it is a cationic species in which the positive metal center would withdraw more electron density from peroxo ligands and make them more electrophilic, but also because VO_2^+ would be the direct product, enabling an efficient closed cycle between reactions in eqs 1 and 6. In contrast, the diperoxo species is anionic, which naturally makes it less electrophilic.

Generally, both mono- and di-peroxo transition metal complexes exercise comparable reactivities toward the same

substrates, as was found in the $\text{MTO}-\text{H}_2\text{O}_2$ system, wherein a factor of 3 in either direction ($k_3 > k_4$ or $k_3 < k_4$) covers almost all of the variations for a wide variety of substrates.⁵ On the other hand, it should be noted that extreme situations in either direction, $k_3 \gg k_4$ ¹³ or $k_3 \ll k_4$,¹⁴ do exist for MTO-catalyzed oxidations.

As for vanadium, the majority of the oxidation system in the literature contains oxomonoperoxo groups. When diperoxo complexes are available, it often is found that they are more reactive. In acidic aqueous solutions, the oxidizing strength of $\text{OV}(\text{O}_2)_2^-$ was found to be higher than that of $\text{OV}(\text{O}_2)^+$ based on the rate of decomposition of $\text{OV}(\text{O}_2)_2^- \cdot \text{O}_2\text{H}$ relative to $\text{OV}(\text{O}_2)^+ \cdot \text{O}_2\text{H}$.¹⁵ This is also reflected in the oxidation of iodide ions, where the diperoxo complex was shown to be more reactive.⁸ As with rhenium, extremes exist. For the oxidation of the (thiolato)cobalt(III) complex $(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2^{2+}$ to the sulfenato complex, the oxo-diperoxo(picolinato)vanadium(V) complex, $\text{VO}(\text{O}_2)_2(\text{pic})^{2-}$, was $\sim 10^4$ times more reactive than the oxoperoxo(dipicolinato)vanadium(V) complex $\text{VO}(\text{O}_2)(\text{dipic})^-$.¹⁶ Likewise, for the same substrate, the second-order rate constant for $\text{OV}(\text{O}_2)_2^-$ oxidation was determined to be $\sim 11 \text{ L mol}^{-1} \text{ s}^{-1}$, whereas the corresponding rate constant for $\text{OV}(\text{O}_2)^+$ was too small for evaluation. The same reactivity pattern was also observed in a Mo system.¹⁷ In an alternative scenario, the dioxotriperoxodivanadium(V) complex $(\text{VO})_2(\text{O}_2)_3$,¹⁸ formed from the dimerization of $\text{OV}(\text{O}_2)^+$ and $\text{OV}(\text{O}_2)_2^-$, was identified as the active species for the oxidation of bromide ions.⁶

It was suggested that the oxo-diperoxo configuration of transition metal complexes may be especially effective at activation of peroxides on the basis of studies with oxovanadium(V) complexes in aqueous solutions.¹⁶ However, the reason behind this is not easily understood. One possible explanation for this reactivity difference comes from the comparison of bond lengths in available crystal structures. Careful inspection reveals that the O—O bond length in the oxo-diperoxo complexes is on average 0.03–0.04 Å longer than that in the oxo-peroxo forms for a given metal center (V, Mo).¹⁶ This observation agrees with the IR data on the peroxide O—O stretching frequencies. In mono-peroxo vanadium complexes, the O—O stretch occurs at ca. 920–960 cm^{-1} ,¹⁹ whereas oxo-diperoxo vanadium complexes exhibit the O—O stretch at ca. 850–890 cm^{-1} .²⁰ The weakening of the O—O bond in diperoxo complexes may result from the less effective overlap of the metal d orbitals with the peroxo π^* orbitals. In a more general study,

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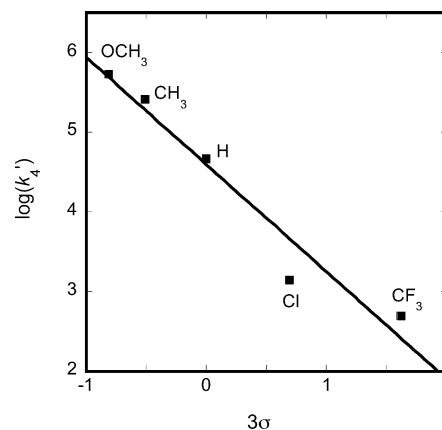
Table 4. Oxidation of Phosphines ($p\text{-X-C}_6\text{H}_4\text{)}_3\text{P}$ Catalyzed by Vanadium(V)

X	3σ	$\text{p}K_{\text{a}}^a$	k_4^b	$k_4'^b$
OMe	-0.81	4.57	137 ± 6	$(5.3 \pm 0.2) \times 10^5$
Me	-0.51	3.84	374 ± 19	$(2.6 \pm 0.1) \times 10^5$
H	0	2.73	845 ± 25	$(4.6 \pm 0.1) \times 10^4$
Cl	0.69	1.03	672 ± 33	$(1.39 \pm 0.07) \times 10^3$
CF ₃	1.62	(-1.14)	490 ± 20	$(4.9 \pm 0.2) \times 10^2$

^a $\text{p}K_{\text{a}}$ values for Ar_3PH^+ were taken from the literature,²³ except for X = CF₃, which was obtained by extrapolation by a Hammett correlation of this series of phosphines. ^b $\text{L mol}^{-1} \text{s}^{-1}$.

Reynolds and Butler identified the same pattern when correlating the reactivity of transition metal peroxo complexes with their spectroscopic properties such as IR, UV-vis, and ¹⁷O NMR spectroscopy.²¹ Also, the M-O_{peroxo} bond in the oxo-diperoxo complexes is asymmetric, with one being longer than the other. Both observations point to an increased reactivity in oxo-diperoxo species. In the present study, the different degrees of coordination of H₂O may also play a role. The diperoxo species most likely adopts a pentagonal bipyramidal geometry with two coordinated water molecules, whereas the monoperoxo species likely has four coordinated waters.

The values of k_4 for triarylphosphines, at first glance, are puzzling as well. For one thing, PPh₃ has the largest k_4 while ($p\text{-MeO-C}_6\text{H}_4\text{)}_3\text{P}$ is the slowest, resulting in a curved Hammett plot. In principle, this might be explained by a change of reaction mechanism, but it would be extremely hard to see why it is so here. An alternative had then to be sought. Protonation of $\text{OV}(\text{O}_2)_2^-$ seems less likely, because the stoichiometry of eq 2 has been established by careful spectral and equilibrium studies.^{7,22} On the other hand, aryl- and alkyl-substituted phosphines are fairly strong bases, partially protonated in acidic solutions. The $\text{p}K_{\text{a}}$ values (Table 4) of the corresponding phosphonium ions (Ar_3PH^+) are known in aqueous solution²³ and can be correlated to the $\text{p}K_{\text{a}}$ values in nonaqueous solvents.²⁴ Under our experimental conditions, phosphines are expected to be protonated to a considerable extent. This reduces the effective concentration of the free phosphines in solution. Control experiments

**Figure 6.** The Hammett correlation between the rate constants for reactions of ($p\text{-X-C}_6\text{H}_4\text{)}_3\text{P}$ with $\text{OV}(\text{O}_2)_2^-$. The linear fit gives the reaction constant ρ of -1.35 ± 0.18 .

showed that the quaternary methyltriphenylphosphonium ion does not react with hydrogen peroxide, with or without the presence of vanadium(V), as expected. It then appears reasonable to apply a correction factor, $(K_{\text{a}} + [\text{H}^+])/K_{\text{a}}$, for the experimental k_4 values. The result appears as k_4' in the last column in Table 4. A plot of $\log(k_4')$ versus 3σ was constructed (Figure 6), which results in a straight line that affords the reaction constant $\rho = -1.35$. The negative value of ρ implicates nucleophilic attack of phosphine on the electrophilic peroxo oxygen. The ρ value is considerably more negative than that originally reported for the oxidation of triarylphosphines in the MTO-H₂O₂ system ($\rho = -0.21$).⁹

Protonation of phosphines was not recognized in the earlier work, which now needs to be corrected. With allowance for protonation, a reaction constant $\rho = -1.56$ was obtained for MTO. Thus, the two values of ρ are totally comparable (-1.35 for V versus -1.56 for Re).

The second series of compounds, methyl aryl sulfides, provides an easier test of this mechanism, because organic sulfides are poor Bronsted bases and as such remain unprotonated. The second-order rate constants for sulfide oxidation are comparable to values reported for other vanadium(V)-containing species. For example, the second-order rate constant for the oxidation of PhSMe in acetonitrile by the $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]\text{-H}_2\text{O}_2$ system (where $\text{H}_2\text{heida} = N\text{-}(2\text{-hydroxyethyl})\text{iminodiacetic acid}$) is $8.1 \text{ L mol}^{-1} \text{ s}^{-1}$.²⁵ Note that, in these systems, a monoperoxo species was the catalytically active reagent.

The rate constants for ArSMe follow a Hammett correlation, with $\rho = -0.83$. This value is not too dissimilar from that of MTO-catalyzed aryl methyl sulfide oxidation, $\rho = -0.98$.²⁶

Although protonation of organic sulfides does not pose a problem, the oxidation by peroxo vanadium complexes is not without its own complication. For instance, the sulfoxide products could be further oxidized to sulfones, which would certainly complicate the kinetic analysis. In particular, vanadium(V) complexes have been shown to be unique among peroxometal complexes in this respect. For example,

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in the competitive oxidation of *p*-ClC₆H₄SCH₃ and C₆H₅S(O)CH₃ by VO(O₂)(pic)(H₂O)₂, comparable amounts of sulfoxide *p*-ClC₆H₄S(O)CH₃ (60%) and sulfone C₆H₅S(O)₂CH₃ (40%) were obtained, whereas Mo and W peroxo complexes showed clear reactivity preferences for sulfide over sulfoxide.²⁷ Thus, the oxidation of C₆H₅S(O)CH₃ was monitored with ¹H NMR spectroscopy. It was found that sulfoxide could be oxidized to sulfone in the present vanadium(V)–H₂O₂ system, but the estimated rate constant k_4^{SO} is on the order of $\sim 10^{-2}$ L mol⁻¹ s⁻¹. Under the conditions used for sulfide oxidation, sulfoxides are not oxidized to any observable extent over the same time. This lends support to the notion that the main active species in the present system is the oxo-diperoxo complex rather than the oxo-monoperoxo and that the reaction occurs by attack of the nucleophilic substrates on the metal peroxo group.

As compared to the reactions catalyzed by the MTO system, it can be seen that the vanadium–H₂O₂ system is less effective in oxidizing phosphine and sulfide substrates. For example, the values of k_4 for PhSMe oxidation are 8.1 and 962 L mol⁻¹ s⁻¹ for VO₂⁺ and MTO, respectively.²⁶ It is also clear that the reactivity of OV(O₂)₂⁻ correlates well with the nucleophilicity of the substrate. This provides further support for the proposed nucleophilic attack mechanism.

The last question arises concerning the identity of the immediate product of OV(O₂)₂⁻ after oxygen atom transfer to substrates. In the MTO–H₂O₂ system, the diperoxo species MeReO(O₂)₂ loses one peroxide oxygen and goes back to monoperoxo species MeReO₂(O₂) directly after oxygen atom transfer. The same process here would generate a dioxo-peroxo vanadium species, OVO(O₂)⁻, which is experimentally unknown (eq 7). However, calculations have indicated that a similar species ligated with imidazole, OVO(O₂)(Im)⁻, appears to have a lifetime on the order of several picoseconds.²⁸ It reacts quickly with H₂O₂ to regenerate OV(O₂)₂⁻.

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