

# The vanadium(V)-catalyzed oxidation of (1-hydroxyethylidene)bisphosphonic acid, $\text{CH}_3\text{C}(\text{OH})(\text{PO}_3\text{H}_2)_2$ , by hydrogen peroxide in aqueous solution

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## Abstract

The vanadium(V)-catalyzed oxidation of (1-hydroxyethylidene)bisphosphonic acid,  $\text{CH}_3\text{C}(\text{OH})(\text{PO}_3\text{H}_2)_2$ , by hydrogen peroxide in aqueous solution has been studied at temperatures between 50 and 80°C. In contrast to vanadium(V), six-valent Mo and W are without significant catalytic action, as is  $\text{SeO}_2$ , while  $\text{OsO}_4$  is only weakly catalytic. With excess substrate a limiting stoichiometry is reached in which ca. 4 mol  $\text{H}_2\text{O}_2$  are consumed per mol of substrate oxidized. With excess  $\text{H}_2\text{O}_2$ , the reaction competes with catalytic decomposition of the peroxide, and a substantial excess of peroxide is required to consume the substrate completely. The reaction is optimal near pH 1. At higher pH it becomes slower, while at lower pH the catalytic decomposition of  $\text{H}_2\text{O}_2$  comes to predominate. The principal reaction products are phosphoric and acetic acids and carbon dioxide, along with lesser quantities of CO and formic acid. The consumption of substrate in the presence of a large excess of  $\text{H}_2\text{O}_2$  follows first-order kinetics, but the apparent first-order rate constant shows a weak positive dependence on initial substrate concentration, which may be pH-related, and at high substrate concentration it shows a weak negative dependence on initial  $[\text{H}_2\text{O}_2]$ . The principal reactant appears to be the diperoxovanadium(V) anion,  $\text{OV}(\text{O}_2)_2^-$ , but the apparent rate shows a greater-than-first-order dependence on catalyst concentration, suggesting a secondary reaction path involving a dimeric peroxovanadium species. A free-radical mechanism has been proposed in which one-electron reduction of the vanadium accompanies oxidation of the substrate to an intermediate alkoxy radical species that can yield either acetic acid or  $\text{CO}_2$ . This mechanism is supported by the observation that vanadium(V) itself oxidizes the substrate at a measurable rate.

*Keywords:* Phosphonic acid; Hydrogen peroxide; Vanadium; Oxidation

## 1. Introduction

(1-Hydroxyethylidene)bisphosphonic acid,  $\text{CH}_3\text{C}(\text{OH})(\text{PO}_3\text{H}_2)_2$ , which we shall hereinafter designate as HEDPA, has been known

since the end of the last century [1]. It has been used in the past as a detergent builder [2] and more recently as an aqueous complexant for multi-charged metal cations [3]. Like other geminal diphosphonic acids, it forms strong complexes with these cations even in relatively acidic solutions in which such more traditional complexing agents as EDTA become relatively

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ineffective. For this reason it has been of interest in the development of procedures for the processing and separation of nuclear materials and wastes and for such applications as the determination of actinide elements in soil [4–6]. For example, HEDPA can be used to back-extract into aqueous solution uranyl salts that have been extracted into an organic solvent by means of a phosphine-oxide extractant or that have been absorbed onto phosphonic-acid-based ion-exchange columns.

The character of HEDPA as a tertiary alcohol gives it a substantial degree of resistance to chemical degradation. This is an advantage in its application as an extractant, but raises problems when it is subsequently desirable to eliminate its complexing action in order to liberate the complexed metallic species for further processing. A need therefore exists for a reasonable method of oxidatively degrading HEDPA after its use.

The use of  $d^0$  transition-metal species to catalyze the reaction of hydrogen peroxide with organic substrates has been the subject of numerous investigations and has been extensively reviewed [7–9]. Most of the studies, however, have focussed on oxygen addition to the multiple bonds of olefins and, to a lesser extent, of acetylenes, as well as to the nitrogen of amines and to the sulfur atom of thiocompounds. In addition, the oxidation of primary and secondary alcohols has been examined [10,11], as has the hydroxylation of aliphatic and aromatic hydrocarbons when vanadium(V) is the catalyst [12,13]. However, we have found no reports of the oxidation of a tertiary alcohol by hydrogen peroxide. In fact, the authors of the study of the oxidation of isopropanol note that under their reaction conditions *tert*-butanol is unaffected [11]. Furthermore, relatively little work has been carried out in aqueous solution, and it is not always reliable to attempt to extrapolate to aqueous systems the results of studies carried out in non-aqueous media. In recent years renewed interest in vanadium-catalyzed oxidations with hydrogen peroxide has arisen follow-

ing recognition of the role that such vanadium-containing enzymes as the haloperoxidases play in biochemical oxidations [14].

In this paper we examine the vanadium(V)-catalyzed oxidation of HEDPA by hydrogen peroxide in aqueous solution.

## 2. Experimental

### 2.1. Materials

HEDPA was obtained from Albright and Wilson Americas, Inc. as a 65 wt-% aqueous solution and was purified by crystallization from acetic acid. Vanadium(V) solutions were made by dissolving either sodium vanadate or ammonium vanadate in an excess of perchloric acid. Other materials were commercial products of reagent grade.

### 2.2. Analytical procedures

Hydrogen peroxide was determined by its molybdate-catalyzed reaction with excess iodide in acid solution, followed by titration of the liberated iodine with standard thiosulfate solution [15]. The phosphate present at the end of an HEDPA reaction was determined spectrophotometrically as the phosphomolybdovanadate complex [16]. Measurements were made at 400 nm with a Cary 14 spectrophotometer. Extinction coefficients were determined by analysis of a standard solution of  $\text{KH}_2\text{PO}_4$ . (This spectrophotometric procedure could only be used after complete reaction and decomposition of the hydrogen peroxide, since otherwise the peroxovanadium complexes would interfere with the spectrophotometric analysis.)

The relative amounts of HEDPA and phosphoric acid present during the course of a reaction were monitored by  $^{31}\text{P}$  NMR spectroscopy. Production of acetic and formic acids was determined by proton NMR spectroscopy, using 1-

dioxane as an internal standard. NMR measurements were carried out with a GE gn-based Model 293 Omega spectrometer (7.06 T) at Larmor frequencies of 300.52 and 121.65 MHz for protons and  $^{31}\text{P}$ , respectively. Proton spectra were recorded with 4 kHz spectral width, 5  $\mu\text{s}$  pulse width, 2 s acquisition time and 7 s repetition interval. Phosphorus-31 spectra were recorded with 10 kHz spectral width, 8  $\mu\text{s}$  (ca. 70°) pulse width, 1.6 s acquisition time, and 16.6 s repetition interval. Typical data sets were 8196 points for protons and 16,392 points for  $^{31}\text{P}$ .

Formation of  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  was determined by gas volumetry, using a standard volume and a Baratron pressure gauge. Gas composition was monitored mass spectrometrically with a Finnigan 400 quadrupole mass spectrometer. The  $\text{O}_2 + \text{CO}$  fraction was first separated from the  $\text{CO}_2$  cryogenically (vide infra), and the response of the mass spectrometer was calibrated against standard gas mixtures.

### 2.3. Measurements of stoichiometry and reaction products

For determination of the ratio of phosphate produced to hydrogen peroxide consumed, reactions were carried out in closed vials that were allowed to remain in a thermostatted water bath until all the hydrogen peroxide had reacted or decomposed. The phosphate was then determined spectrophotometrically. When necessary, correction was made for the small amount of inorganic phosphorus present in the HEDPA (ca. 0.25% of total P) and for the phosphate formed by direct reaction of HEDPA with vanadium(V) after the peroxide was consumed. For identification and determination of all of the reaction products, reactions were carried out in evacuated vessels on a vacuum line. After a period of heating in a water bath, the vessels were cooled with liquid nitrogen, and the  $\text{O}_2 + \text{CO}$  vapor fraction was expanded into a standard volume for pressure measurement and mass

spectrometric analysis. The reaction vessel was then warmed to dry ice temperature, and the  $\text{CO}_2$  fraction was analyzed similarly. Heating was resumed, and the procedure was repeated at intervals until no further gas was evolved. The remaining solution was analyzed spectrophotometrically for phosphate, by  $^1\text{H}$  NMR spectroscopy for acetate and formate, and by  $^{31}\text{P}$  NMR for unreacted HEDPA relative to phosphate. In some cases, the production of acetate and formate was monitored by NMR spectroscopy as the reaction proceeded.

### 2.4. Kinetic measurements

Most kinetic measurements were carried out in 5-mm o.d. NMR tubes in the probe of the NMR spectrometer, making use of the variable-temperature capability of the instrument. The solvent contained 15.6–17.6 mol-%  $\text{D}_2\text{O}$  to provide a deuterium lock for the spectrometer. The reaction mixtures were prepared at room temperature and brought as quickly as possible to the desired reaction temperature.  $^{31}\text{P}$  NMR measurements were made periodically to monitor the decrease in concentration of HEDPA and the buildup of phosphoric acid. The temperature readout of the spectrometer was calibrated to about  $\pm 0.2^\circ\text{C}$  against a copper–constantan thermocouple and Omega readout that had themselves been calibrated in ice and boiling-water baths.

The direct reaction of HEDPA with vanadium(V) was followed by monitoring as a function of time the absorbance of the vanadium(V) species at 460 nm, using a Cary 05 spectrophotometer with thermostatted cell holders.

A few experiments were carried out on the catalytic decomposition of hydrogen peroxide. Reaction mixtures were held in a thermostatted water bath and sampled periodically with a positive-displacement micropipet, followed by iodometric determination of the remaining hydrogen peroxide.

### 3. Results

#### 3.1. Convention regarding nominal pH

In most of our experiments involving HEDPA, the pH was controlled by the buffering action of the substrate itself. Where a nominal pH is specified, it was calculated from the solution composition and the 25°C values of 1.5 and 2.5, respectively, for  $pK_1$  and  $pK_2$  of HEDPA [17]. No corrections were made for the effects of temperature or  $D_2O$  content.

#### 3.2. Semi-quantitative observations and ancillary reaction studies

The uncatalyzed reaction between HEDPA and hydrogen peroxide was examined at 77°C, as was reaction in the presence of Mo(VI), W(VI),  $SeO_2$ , and  $OsO_4$  as potential catalysts at the 2 mM level. The uncatalyzed reaction was found to proceed at a barely detectable rate. At 77°C the reaction of 0.1 M HEDPA with 2 M  $H_2O_2$  in 0.01 M  $HClO_4$  consumed 1.3% of the HEDPA in 23 h, based on NMR determination of the phosphoric acid produced. This corresponds to an apparent first-order rate constant of about  $1.6 \times 10^{-7} s^{-1}$ . In the presence of 0.002 M Mo(VI), 1.65% of the HEDPA reacted in 23 h, while similar amounts of W(VI) and  $SeO_2$  resulted in reaction of only 0.5% and 0.6% of the HEDPA, respectively. Only  $OsO_4$  displayed significant catalytic activity, a 0.002 M solution bringing about reaction of 36.5% of the HEDPA in 23 h, corresponding to an apparent first-order rate constant of  $5.5 \times 10^{-6} s^{-1}$ . As will be seen from the results to be described later, the rate of the  $OsO_4$ -catalyzed reaction is still more than 100-fold less than the corresponding vanadium(V)-catalyzed rate.

A detailed investigation of the vanadium(V)-catalyzed decomposition of hydrogen peroxide has recently been reported [18]. However, since it was carried out under conditions that were

considerably different from those used in our studies, we undertook a few experiments that would permit us to relate the rate of the catalyzed decomposition to that of the catalyzed oxidation of HEDPA. In 0.1 M  $HClO_4$ , with  $H_2O_2$  concentrations between 0.26 and 0.52 M and vanadium(V) concentrations of  $9.3\text{--}9.5 \times 10^{-4}$  M, the decomposition of the  $H_2O_2$  appeared to follow approximately zero-order kinetics, with a rate constant of about  $6 \times 10^{-5}$  M/s at 79.5°C. The corresponding rate constant in 95 mol-%  $D_2O$  was found to be  $1.6 \times 10^{-4}$  M/s. In 1 M acid, the catalyzed decomposition of  $H_2O_2$  becomes much more rapid, and the kinetics become more complicated, with an initial rate of ca. 0.0036 M/s at 79.5°C, for an initial HEDPA concentration of 0.26 M and a vanadium(V) concentration of  $9 \times 10^{-4}$  M.

Vanadium(V) is a fairly potent oxidant in its own right, and it is not surprising that it itself is capable of oxidizing HEDPA. We have examined the reaction of 0.089 M HEDPA with 0.0036 M vanadium(V) in 0.01 M  $HClO_4$ . The reaction was found to have an apparent first-order rate constant of about  $7 \times 10^{-4} s^{-1}$  at 77°C. The rate was essentially unchanged in 89 mol-%  $D_2O$ . The vanadium(V) in these experiments appeared to be complexed to a substantial extent by the HEDPA, as evidenced by a marked shift of its absorption spectrum to longer wavelength.

In order to validate some of the fast following steps in our proposed mechanism for the vanadium(V)-catalyzed oxidation of HEDPA by  $H_2O_2$ , we undertook a few semiquantitative measurements of the analogous oxidation of phosphorous acid. In the absence of catalysts, phosphorous acid and hydrogen peroxide do not interact at a significant rate. The vanadium(V)-catalyzed reaction, however, is relatively rapid. In the presence of  $4 \times 10^{-4}$  M vanadium(V), the oxidation of 0.1 M  $H_3PO_3$  by 1.9 M  $H_2O_2$  in 0.1 M  $HClO_4$  containing 18 mol-%  $D_2O$  has a half-time of about 12 min at 77°C, corresponding to an apparent first-order rate constant of about  $0.001 s^{-1}$ .

### 3.3. Stoichiometry and reaction products of the HEDPA–H<sub>2</sub>O<sub>2</sub> reaction

The stoichiometry of the vanadium(V)-catalyzed oxidation of HEDPA by H<sub>2</sub>O<sub>2</sub> as a function of the initial concentration ratio  $[H_2O_2]_0/[HEDPA]_0$  is shown in Fig. 1. From the solid curve in the figure we see that when the HEDPA is in substantial excess, the stoichiometric ratio  $\Delta[H_2O_2]/\Delta[HEDPA]$  approaches a lower limit of about 4, but the ratio rises rapidly as the initial H<sub>2</sub>O<sub>2</sub> concentration increases. The dotted curve in the figure shows the amount of HEDPA remaining at the end of the reaction as a function of initial ratio of the reactants. It can be seen that even with a 10:1 initial ratio of H<sub>2</sub>O<sub>2</sub>:HEDPA, ca. 10% of the HEDPA remains unreacted. Within experimental uncertainty, the stoichiometry was found to be independent of temperature between 50 and 80°C.

Figs. 2 and 3 show the distribution of reaction products as a function of reactant ratio. From Fig. 2 we can see that with increasing H<sub>2</sub>O<sub>2</sub> the yield of formic acid decreases substantially and that of carbon monoxide increases

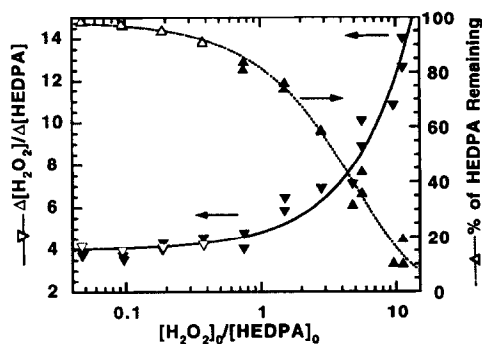


Fig. 1. Stoichiometry vs. initial ratio of reactants at 50–80°C.  $[V]_{tot} = 0.0009$  M,  $[HClO_4] = 0.007$ – $0.008$  M. Solid points:  $[HEDPA]_0 = 0.23$ – $0.29$  M, nominal pH = 1.1. Open points:  $[HEDPA]_0 = 0.94$ – $0.98$  M, nominal pH = 0.8. The smooth curves are arbitrary three-parameter exponential least-squares fits. The solid curve refers to the left-hand ordinate axis and illustrates the observed stoichiometric ratio of H<sub>2</sub>O<sub>2</sub> and HEDPA consumed. The dotted curve refers to the right-hand ordinate axis and illustrates the percentage of the initial HEDPA that remains at the end of the reaction.

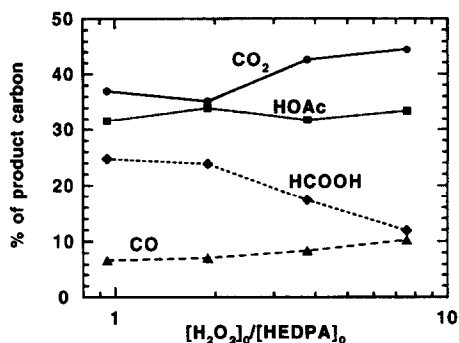


Fig. 2. Reaction products vs. initial ratio of reactants at 80°C.  $[HEDPA]_0 = 0.245$ – $0.285$  M,  $[V]_{tot} = 0.0010$ – $0.0012$  M,  $[HClO_4] = 0.01$  M, nominal pH = 1.1. The lines serve merely to connect the points.

slightly, but the yields of the major products, CO<sub>2</sub> and acetic acid, are largely unchanged. Product distributions determined during the course of the reaction were found to differ little from the gross product distribution. We have also established that the yield of acetic acid is virtually unaffected by changes in catalyst concentration between  $1.2 \times 10^{-4}$  and  $5 \times 10^{-3}$  M. Fig. 3 illustrates the fate of the oxidizing power of the H<sub>2</sub>O<sub>2</sub> when reaction is complete. (It is assumed that each mole of H<sub>3</sub>PO<sub>4</sub>, HCOOH, or CO produced accounts for the oxidizing power of one mole of H<sub>2</sub>O<sub>2</sub>, while each mole of CO<sub>2</sub> or O<sub>2</sub> produced accounts for the oxidizing power of two moles of H<sub>2</sub>O<sub>2</sub>.) It is evident from the figure that excess H<sub>2</sub>O<sub>2</sub> is largely converted into molecular oxygen.

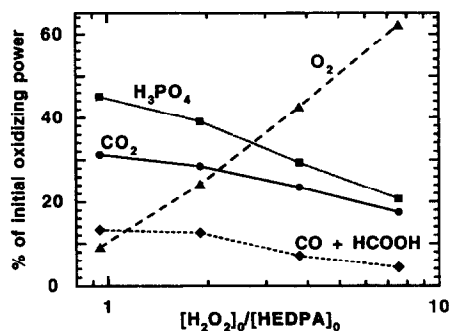


Fig. 3. Disposition of H<sub>2</sub>O<sub>2</sub> oxidizing power vs. initial ratio of reactants. Initial conditions the same as for Fig. 2. The lines serve merely to connect the points.

In separate experiments we determined that the vanadium(V)-catalyzed oxidation of formic acid produced mostly  $\text{CO}_2$ , while acetic acid was scarcely oxidized under similar conditions.

### 3.4. Kinetics of the HEDPA– $\text{H}_2\text{O}_2$ reaction

The vanadium(V)-catalyzed reaction of 0.06–0.12 M HEDPA with 19 times as much  $\text{H}_2\text{O}_2$  in 0.1 M  $\text{HClO}_4$  proceeded to within 95% of completion, and the decrease in HEDPA concentration followed simple first-order kinetics for at least four half-times. At the end of the reaction, the  $\text{H}_2\text{O}_2$  had been completely consumed, and the vanadium catalyst had been reduced to the tetravalent  $\text{VO}^{2+}$  cation. The  $^{31}\text{P}$  NMR spectrum gave clear indication of the end of the reaction and the formation of the paramagnetic vanadium(IV) species by a marked broadening of the phosphorus resonances, particularly that of the residual HEDPA. No phosphorus-containing species other than HEDPA and phosphoric acid were ever observed during the reaction. Figs. 4 and 5 show the reaction curves as functions of catalyst concentration and temperature, respectively. The data from Fig. 4 suggest a greater-than-first-order dependence of the apparent first-order rate constant,  $k$ , on total

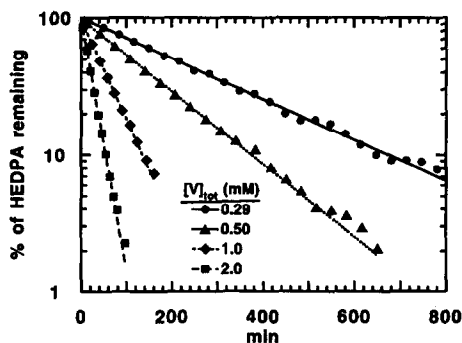


Fig. 4. Kinetic decay curves as a function of total vanadium(V) concentration for reaction of 0.117–0.119 M HEDPA with 2.24–2.28 M  $\text{H}_2\text{O}_2$  in 0.004–0.008 M  $\text{HClO}_4$ , 17.5 mol-%  $\text{D}_2\text{O}$  at  $77.0_6^\circ\text{C}$ . Nominal pH = 1.2<sub>5</sub>–1.3. Lines are exponential least-squares fits. Fitted first-order rate constants are respectively 0.56, 0.99, 2.75, and  $6.9 \times 10^{-4} \text{ s}^{-1}$ .

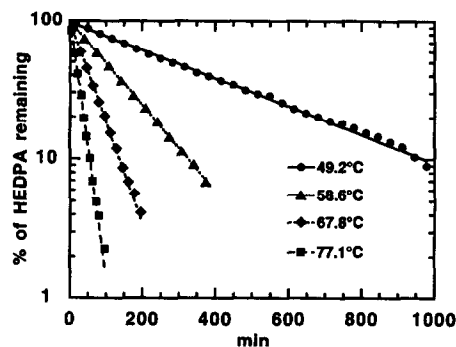


Fig. 5. Kinetic decay curves as a function of temperature for reaction of 0.117 M HEDPA with 2.24 M  $\text{H}_2\text{O}_2$  in 0.004 M  $\text{HClO}_4$ , 17.5 mol-%  $\text{D}_2\text{O}$ .  $[\text{V}]_{\text{tot}} = 0.00195 \text{ M}$ . Nominal pH = 1.3. Lines are exponential least-squares fits. Fitted first-order rate constants are respectively  $0.385$ ,  $1.17$ ,  $2.73$ , and  $6.9 \times 10^{-4} \text{ s}^{-1}$ .

vanadium concentration, and we have fitted the data to the relation

$$k = k_1[\text{V}]_{\text{tot}} + k_2[\text{V}]_{\text{tot}}^2 \quad (1)$$

where  $[\text{V}]_{\text{tot}}$  is the total stoichiometric concentration of vanadium species in solution. Fig. 6 is a plot of  $k/[\text{V}]_{\text{tot}}$  vs  $[\text{V}]_{\text{tot}}$ . The least-squares line corresponds to the intercept  $k_1 = 0.162 \pm 0.014 \text{ M}^{-1} \text{ s}^{-1}$  and the slope  $k_2 = 102 \pm 13 \text{ M}^{-2} \text{ s}^{-1}$ . A nearly equivalent fit can be obtained to a log–log plot of  $k$  vs.  $[\text{V}]_{\text{tot}}$ , which has a slope of  $1.35 \pm 0.04$ . Fig. 7 is an Arrhenius plot of the temperature dependence of the apparent first-order rate constant, from which we may derive the enthalpy of activation  $\Delta H^\ddagger = 22.3 \pm 0.6 \text{ kcal/mol}$ .

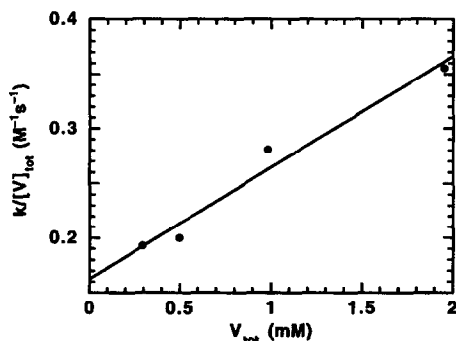


Fig. 6. Dependence of apparent first-order rate constant,  $k$ , on total vanadium concentration,  $[\text{V}]_{\text{tot}}$ , based on data from Fig. 4. Solid line is a least-squares fit with intercept  $0.162 \pm 0.014 \text{ M}^{-1} \text{ s}^{-1}$  and slope  $102 \pm 13 \text{ M}^{-2} \text{ s}^{-1}$ .

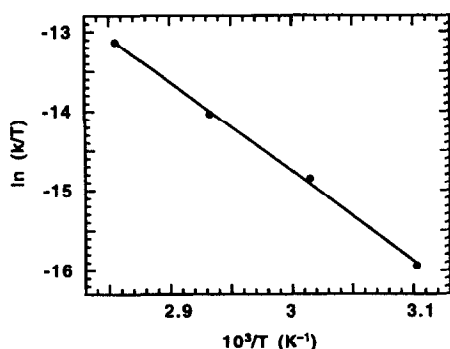


Fig. 7. Arrhenius plot based on apparent first-order rate constant,  $k$ , in units of  $s^{-1}$ , from Fig. 5. Solid line is a least-squares fit with slope  $1.12 \pm 0.03 \times 10^4$  K.

When the  $H_2O_2$  was in significantly less than 20-fold initial excess, a substantial portion of the HEDPA remained after the reaction was over, and first-order kinetic behavior was only observed over the first part of the reaction. This situation was particularly pronounced at higher acidity, when catalytic decomposition of the  $H_2O_2$  predominated over its reaction with the substrate. Under such conditions, "initial" rate constants were estimated from the first portion of the reaction curves (usually about the first

Table 1  
Dependence of apparent first-order rate constant,  $k$ , on pH, on concentration of  $D_2O$ , and on initial concentrations of HEDPA and  $H_2O_2$ <sup>a</sup>

Initial concentration (M)		Nominal	$10^4 k$
[HEDPA]	[ $H_2O_2$ ]	pH <sup>b</sup>	( $s^{-1}$ )
0.0583	0.55	1.4 <sub>5</sub>	2.67
0.0584	1.09	1.4 <sub>5</sub>	2.4
0.0584	2.24	1.4 <sub>5</sub>	2.5
0.117	1.13	1.2 <sub>5</sub>	3.3
0.117	2.26	1.2 <sub>5</sub>	2.75
0.117	2.20	1.2 <sub>5</sub>	5.3 <sup>c</sup>
0.235	1.13	1.1	3.85
0.235	2.24	1.1	3.4
0.235	2.26	<sup>d</sup>	3.67
0.222	2.13	2.0 <sup>e</sup>	1.45

<sup>a</sup>  $[V]_{tot} = 9.7\text{--}9.8 \times 10^{-4}$  M at 77.13°C.  $[D_2O] = 15.6\text{--}17.6$  mol-%.

<sup>b</sup> See text.

<sup>c</sup> In 77 mol-%  $D_2O$ .

<sup>d</sup> In 1 M  $HClO_4$ .

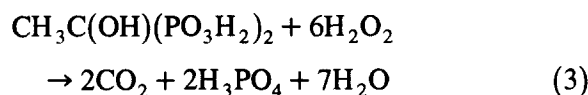
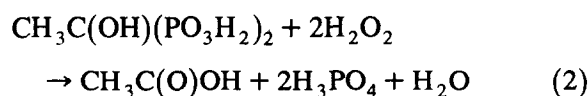
<sup>e</sup> 0.222 M NaOH added to neutralize one proton of each HEDPA molecule.

half-time). The results of a number of such experiments are summarized in Table 1. (For comparison, some experiments are included that had 20-fold excess  $H_2O_2$  and did follow good first-order kinetics throughout.) There appears to be a weak positive dependence of the apparent rate constant on HEDPA concentration, and at high HEDPA concentrations there is a weak negative dependence on the concentration of  $H_2O_2$ . There appears to be little change in the rate constant between pH 1 and 1 M acid, but a significant decrease at pH 2. The observed dependence on HEDPA concentration could therefore be the result of variations in pH. Table 1 also includes an experiment carried out in 77 mol-%  $D_2O$ , by which we may estimate the effect of the ca. 17 mol-%  $D_2O$  in the other kinetic experiments. The rate is seen to increase by a factor of 1.9 when going from 17.6 to 77 mol-%  $D_2O$ . If the isotope effect is linear with  $D_2O$  concentration, we may estimate a further 27% slowing in a solution in which only the natural deuterium abundance is present.

#### 4. Discussion

Our results do not suffice to define a unique mechanism for the vanadium(V)-catalyzed oxidation of HEDPA by  $H_2O_2$ . They do, however, allow us to draw some conclusions about the characteristics that such a mechanism must have.

We may write two limiting stoichiometric reactions:



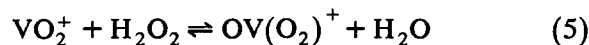
We have seen from Fig. 1 that at high initial ratios of substrate to  $H_2O_2$  our reaction approaches a limiting stoichiometry in which approximately four moles of  $H_2O_2$  are consumed for every mole of HEDPA that is oxidized. This

is intermediate between the stoichiometric ratios implied by reactions 2 and 3 and is consistent with the principal products being roughly comparable quantities of acetic acid and carbon dioxide, as is shown in Fig. 2. The fact that the yield of acetic acid does not decrease with increasing excess of  $\text{H}_2\text{O}_2$  indicates that acetic acid is not formed as an intermediate product during the oxidation of HEDPA to  $\text{CO}_2$ , but rather is produced by a reaction step that parallels the one producing carbon dioxide. In contrast, the yield of formic acid does decrease with increasing initial  $\text{H}_2\text{O}_2$ , implying that it is an intermediate that is further oxidized to  $\text{CO}_2$ . This is consistent with our observations that under these reaction conditions formic acid is oxidized to  $\text{CO}_2$ , while acetic acid is largely unaffected. We therefore require that the reaction proceed via two parallel paths, one of which simply hydrolyzes the HEDPA molecule and oxidizes the phosphorus to phosphate, leaving behind acetic acid, while the other breaks up the carbon skeleton with ultimate formation of carbon dioxide. The fact that the acetic acid yield is nearly independent of reaction conditions and catalyst concentration suggests, though it does not require, that the two paths are branches following a single rate-determining reaction step.

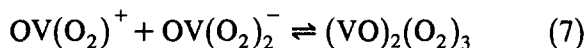
If we neglect the weak dependencies on initial HEDPA and  $\text{H}_2\text{O}_2$  concentrations, we may write the rate law for the oxidation of HEDPA by a large excess of  $\text{H}_2\text{O}_2$  as

$$\begin{aligned} -d[\text{HEDPA}]/dt &= k[\text{HEDPA}] \\ &= [\text{HEDPA}] \left( k_1[\text{V}]_{\text{tot}} + k_2[\text{V}]_{\text{tot}}^2 \right) \end{aligned} \quad (4)$$

In acid solution vanadium(V) is known to interact successively with  $\text{H}_2\text{O}_2$  to form a monoperoxo cation and a diperoxoanion [19,20]:



Evidence has also been obtained for a dimeric peroxyspecies,  $(\text{VO})_2(\text{O}_2)_3$ , or  $\text{H}_4(\text{VO}_2)_2(\text{O}_2)_3$ , formed via the equilibrium [21]



At ambient temperature, reaction 5 has an equilibrium constant of approximately  $4 \times 10^4$ , while reaction 6 has constants of 0.6 and 1.3 at ionic strengths 0.3 M and 1 M, respectively [19,20]. Two different groups have used  $^{51}\text{V}$  NMR to determine values of 9 and 30 for the equilibrium constant of reaction 7 [21,22]. Although we have no information regarding the values of any of these constants at elevated temperature, we may reasonably expect that dilute vanadium(V) solutions with high concentrations of  $\text{H}_2\text{O}_2$  at around pH 1 will contain the vanadium predominantly in the form of the diperoxoanion. The absence of any strong dependence of the first-order rate constant on either  $\text{H}_2\text{O}_2$  concentration or increasing acidity indicates that this anion is most likely the principal reactive oxidizing species, since the concentration of any of the other candidate species involved in reactions 5–7 would be strongly dependent on both acidity and  $\text{H}_2\text{O}_2$  concentration.

If the greater-than-first-order dependence of rate on catalyst concentration reflected by Eqs. 1 and 4 is not an artifact, it implies a secondary reaction path involving either a dimeric vanadium species or the interaction of two monomeric species. The values of  $k_1$  and  $k_2$  fitted to Eq. 1 indicate that when  $[\text{V}]_{\text{tot}} = 0.001$  M, approximately one-third of the reaction proceeds by a path involving a second-order dependence on the vanadium.

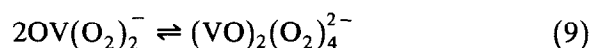
In a recent study of the vanadium(V)-catalyzed oxidation of bromide ion, Clague and Butler [22] found the rate to depend on the second power of the total vanadium concentration, and they suggested involvement of the dimeric species formed in reaction 7. It is tempting to invoke this same species to account for our results, but we must bear in mind that the  $\text{H}_2\text{O}_2$  concentrations in our experiments are



typically more than 1000 times those used by Clague and Butler. If, as seems reasonable, the principal vanadium species in most of our experiments is, in fact, the diperoxovanadium cation, then from equations 5–7 we may derive for the concentration of the dimeric species the relation

$$[(VO)_2(O_2)_3] = \frac{K_7[V]_{\text{tot}}^2[H^+]^2}{K_6[H_2O_2]} \quad (8)$$

From this relation we may conclude that the concentration of the dimeric species must increase quadratically with increasing acidity. Hence, if a reaction path involving the dimer is significant in 0.1 M acid, it should be dominant in 1 M acid and result in a very substantial increase in reaction rate, which we do not observe. The concentration of dimer should also increase linearly with decreasing  $[H_2O_2]$ . If we examine the data in Table 1 at 0.058 M HEDPA, we see that  $k$  is essentially independent of  $H_2O_2$  concentration, which is inconsistent with this dimer playing a significant role. It therefore seems more likely that if a dimeric vanadium(V) species is involved, it must be one the concentration of which does not depend on the concentrations of  $H^+$  and  $H_2O_2$ . A possible species that would meet this criterion, but for which we have no independent evidence in these acidic solutions, would be a dimer of the diperoxyanion:

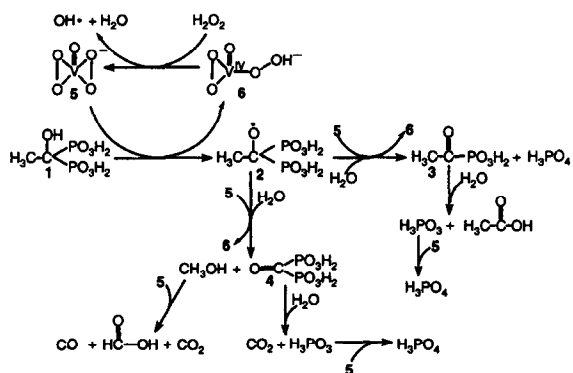


This species would be the conjugate acid of a 3– dimeric anion reported by Harrison and Howarth at higher pH [21], and, in fact, a tetramethylammonium salt of the 2– anion has actually been characterized [23].

In proposing a mechanism for the HEDPA– $H_2O_2$  reaction, we must take into account one other salient fact. This is the enormously enhanced catalytic action of vanadium(V) compared to other potential catalysts, in particular compared to hexavalent molybdenum and tungsten. Even if we take at face value the marginal

catalytic effect exhibited by Mo(VI) in our semi-quantitative experiments, we may set an upper limit of about  $2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  for the bimolecular rate constant for reaction of HEDPA at 77°C with a dominant Mo(VI) peroxyspecies. Hence our results indicate vanadium(V) to be more than  $10^4$ -fold more effective as a catalyst than either molybdenum(VI) or tungsten(VI). Direct quantitative comparisons of the catalytic efficacy of various metal ions for oxidations by hydrogen peroxide have not often been made, particularly in aqueous solution. However, a good idea of the relative catalytic activity of subgroup V and VI metals for oxygen-transfer reactions can be obtained from studies of the oxidation of the thiolato ligand,  $SCH_2CH_2NH_2^-$ , by peroxymetal complexes. For this reaction, hexavalent molybdenum and tungsten are typically three to four orders of magnitude more effective than vanadium(V) [24]. In fact, the vanadium complexes are only about 10-fold more reactive than  $H_2O_2$  itself. Six-valent molybdenum and tungsten are also generally more active than vanadium(V) as catalysts for the oxidation of bromide and iodide by  $H_2O_2$  [25], while in the oxidation of isopropanol by hydrogen peroxide, Mo and V have roughly comparable catalytic activity [11]. It is only for the hydroxylation of aliphatic and aromatic hydrocarbons by  $H_2O_2$  and for the disproportionation of  $H_2O_2$  itself that vanadium has been found to be a uniquely effective catalyst.

If we ask what distinguishes the chemistry of vanadium(V) from that of hexavalent molybdenum and tungsten, we must conclude that the most obvious distinction is the relative ease with which vanadium(V) can undergo one-electron reduction to vanadium(IV). It is reasonable, therefore, to look for a mechanism that involves a one-electron transfer step in which the vanadium center is reduced. Such a mechanism is particularly attractive in light of our observation that vanadium(V) itself is reduced by HEDPA at a significant rate in the absence of hydrogen peroxide. A mechanism of this sort would almost certainly also have to produce free-radical

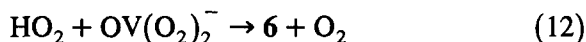
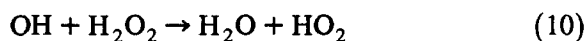


Scheme 1. Conjectural mechanistic scheme for the vanadium(V)-catalyzed oxidation of HEDPA by  $\text{H}_2\text{O}_2$  at nominal pH 1. Only the path that is first-order in vanadium is considered.

intermediate species, which would be consistent with the breakup of the carbon skeleton of the HEDPA. A similar rationale has been used in attempts to account for the vanadium(V)-catalyzed hydroxylation of aliphatic and aromatic hydrocarbons by hydrogen peroxide, though here, too, no unique or really complete mechanism has been formulated [12,13]. A free-radical mechanism involving changes in the oxidation state of the vanadium has also been proposed for the vanadium(V)-catalyzed disproportionation of hydrogen peroxide [18].

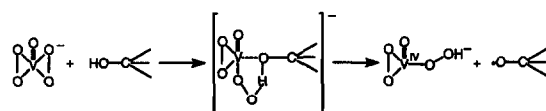
We may incorporate these ideas into the somewhat speculative mechanism shown in Scheme 1 for the portion of the reaction that is first-order in catalyst. (An analogous scheme involving a vanadium dimer could be written to account for the path that is second-order in catalyst.) In the rate-determining step the diperoxovanadium anion, 5, abstracts a hydrogen atom from the HEDPA molecule, 1, forming a transient vanadium(IV) peroxy species, 6, along with an alkoxy radical, 2, derived from the HEDPA. The latter can be oxidized further in one of two ways: to phosphoric acid and acetylphosphonic acid, 3, or to methanol and carbonylbisphosphonic acid, 4. Both of the species 3 and 4 may be expected to hydrolyze, the former to acetic and phosphorous acids [26], the latter to phosphorous acid and  $\text{CO}_2$  [27]. We have already shown that the phosphorous acid

will be rapidly oxidized to phosphoric acid by  $\text{H}_2\text{O}_2$  in the presence of vanadium(V), and we may also expect the vanadium(IV) species, 6, to undergo rapid oxidation by hydrogen peroxide, since  $\text{H}_2\text{O}_2$  is known to oxidize vanadium(IV) rapidly to peroxy complexes of vanadium(V) [28–30]. Because of the rapidity of this reaction, no peroxovanadium(IV) species has ever been isolated. Such species have, however, been postulated as intermediates in the reaction between vanadium(IV) and hydrogen peroxide [28]. It is very likely that OH radicals are produced as byproducts of this reaction, and these will most probably be scavenged by the reaction sequence:



As the concentration of  $\text{H}_2\text{O}_2$  decreases and that of HEDPA increases, the scavenging of OH by  $\text{H}_2\text{O}_2$  may become incomplete, and some of the OH may instead react with HEDPA. This could explain our observation that the apparent rate constant shows a weak positive dependence on the concentration of HEDPA and a weak negative dependence on  $\text{H}_2\text{O}_2$  concentration when [HEDPA] is high. (As we have already noted, however, pH variation may be responsible for the weak positive dependence of the rate on [HEDPA].)

Scheme 1 begs the question of the precise nature of the rate-determining electron-transfer step. We may imagine an attack of the vanadium on the alcoholic oxygen, as shown in Scheme 2. Such a mechanism has been suggested for the vanadium(V)-catalyzed oxidation of isopropanol by hydrogen peroxide [9]. We



Scheme 2. Possible mechanism for the rate-determining step in Scheme 1.

should note, however, that it is by no means necessary to postulate a scheme involving hydrogen-atom abstraction. We could construct an alternative mechanism in which the reagent **5** instead withdraws an electron from an HEDPA molecule to form a radical cation. We could even imagine two parallel reactions of **5** with HEDPA resulting in two different intermediates and reaction paths: electron transfer to form a radical cation and yield acetic acid, and hydrogen abstraction to form the alkoxyl radical and result in oxidation of the carbon skeleton of the HEDPA.

We also lack any definitive explanation of the slowing of the reaction at pH 2. At this pH the HEDPA is present primarily as the 1-ion, which may be less reactive than the undissociated molecule that predominates at higher acidity. On the whole, however, we must recognize that we have as yet only a very incomplete understanding of the mechanism of this reaction.

It is customary to compare the reactivity of peroxometal species with that of uncomplexed hydrogen peroxide. The uncatalyzed oxidation of HEDPA by hydrogen peroxide has a bimolecular rate constant no greater than  $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  at  $77^\circ\text{C}$ . This implies that in terms of its reaction with HEDPA, the diperoxovanadium anion has more than  $10^6$  times the reactivity of uncomplexed  $\text{H}_2\text{O}_2$ . Such a comparison, however, is most relevant when dealing with reactions that proceed by oxygen transfer from the peroxide moiety. If, as we propose, the oxidation of HEDPA involves reduction of the vanadium center, it would be more appropriate to compare the reactivity of the diperoxoanion with that of  $\text{VO}_2^+$ . We cannot make such a comparison rigorously because of the unknown extent of complexation of  $\text{VO}_2^+$  by HEDPA when  $\text{H}_2\text{O}_2$  is not present. However, if we consider only the bimolecular term in Eq. 4, we find the rate of reaction of HEDPA with excess  $\text{H}_2\text{O}_2$  at  $77^\circ\text{C}$  to be  $0.019 [\text{V}]_{\text{tot}} \text{ M/s}$ , which we may compare with a first-order rate constant of  $7 \times 10^{-4} \text{ s}^{-1}$  for the reaction of vanadium(V)

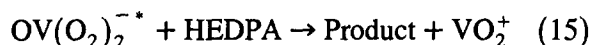
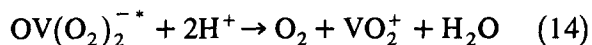
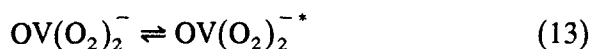
with 0.09 M HEDPA in the absence of  $\text{H}_2\text{O}_2$ . This represents a relatively modest difference in reactivity, and it lends support to the notion that both reactions proceed by way of mechanisms in which oxidation of the HEDPA is accompanied by reduction of the vanadium to the 4-valent state.

The oxidizing power of five-valent vanadium appears to put it within a 'window of opportunity' that permits a mechanism of this type for its catalytic activity. The standard electrode potential of the vanadium(V)–vanadium(IV) couple in acid solution is approximately 1 V. Were it significantly less, vanadium(V) would be unable to oxidize the substrate, as is the case with molybdenum(VI) and tungsten(VI). If, on the other hand, the potential were significantly greater, the vanadium(V) would be reduced by the hydrogen peroxide and would cease to function as a catalyst. This is often the case with chromium(VI).

In 0.1 M acid we observe the vanadium(V)-catalyzed decomposition of  $\text{H}_2\text{O}_2$  to be zero-order in  $\text{H}_2\text{O}_2$ , with an apparent rate constant of about  $6 \times 10^{-5} \text{ M/s}$  at  $79.5^\circ\text{C}$  in the presence of 0.001 M vanadium(V). This is consistent with the rate-determining step being decomposition of the diperoxovanadium(V) anion and implies a mechanism considerably different from that observed by Bonchio et al. in 1 M acid and at much lower  $\text{H}_2\text{O}_2$  concentrations [18]. If we accept our observed limiting stoichiometry of  $\Delta[\text{H}_2\text{O}_2]/\Delta[\text{HEDPA}] \cong 4$  and allow for differences in temperature and  $\text{D}_2\text{O}$  concentration, then the observed rates indicate that in pH 1 solutions containing 0.24 M HEDPA (Table 1), the  $\text{H}_2\text{O}_2$  is initially being consumed roughly five times as fast by reaction with HEDPA as by the catalyzed decomposition. In 1 M acid, on the other hand, the catalyzed decomposition clearly predominates. This, of course, assumes that the rate of the catalyzed decomposition reaction is unaffected by the presence of HEDPA. It is of interest to remark that the catalyzed decomposition of  $\text{H}_2\text{O}_2$  has a deuterium isotope effect very similar to that of the

catalyzed oxidation of HEDPA, whereas the direct reaction of vanadium(V) with HEDPA shows essentially no deuterium effect.

The similarity of the rate and D<sub>2</sub>O dependence of the vanadium(V)-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub> to those of the catalyzed oxidation of HEDPA obliges us at least to consider an alternative reaction sequence in which the two processes might be linked through a common intermediate, for example:



followed by reactions 5 and 6. However, for the sequence of reactions 13–14 to be compatible with our kinetic and stoichiometric observations, reaction 13 would have to be a rapid pre-equilibrium lying predominantly to the left. Such an equilibrium could conceivably account for our observed deuterium isotope effect. In any case, a definitive study of the mechanism of the vanadium(V)-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub> under conditions similar to those of our study should be extremely illuminating.

## 5. Conclusions

We have shown that under forcing conditions, vanadium(V) can effectively catalyze the oxidation by hydrogen peroxide of HEDPA, a diphosphonic acid containing a tertiary alcohol function. We have found no other catalyst to have comparable effectiveness, and it seems reasonable to ascribe the unique action of the vanadium to a free-radical mechanism that involves reduction and reoxidation of the vanadium center in a peroxovanadium complex. It appears that the principal reactive species is the diperoxovanadium anion, **5**, with possible involvement of an unidentified dimeric species derived from it.

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