

The Kinetics of the Oxidation of Vanadyl Ion by Peroxodiphosphate in Aqueous Acid Solution

M. Andersen, J. O. Edwards, Sr. A. A. Green*, and Sr. M. D. Wiswell

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The reaction of peroxodiphosphate with vanadyl ion in dilute aqueous acid has been investigated. In the absence of other reducing agents, two vanadyl ions are oxidized by one peroxodiphosphate. The kinetics are first order each in oxidant and reductant. The rate is not markedly dependent on pH in the range from 1.1 to 3.5. The significant change in stoichiometry when organic buffers were employed indicates the presence of a reactive intermediate. The interaction of vanadyl ion with other species such as vanadium(V) and pyrophosphate to form complexes is seen from the variation of absorbance with concentration of additive. Because of these complications, the rate plots show curvature and there is a larger error than usual in the rate constants. Nevertheless, the results lead to reasonable conclusions concerning the reaction mechanism.

Introduction

The reaction of vanadyl ion with peroxodiphosphate was first reported by Chong.¹ He observed that the initial blue color of VO^{2+} changed upon addition of peroxodiphosphate to give the yellow color characteristic of pentavalent vanadium, but he did not study the system further. Yost studied the reaction of vanadyl ion with peroxodisulfate,² this reaction requires the presence of a silver ion catalyst to proceed at room temperature. Peroxodiphosphate reacts at a convenient rate with both vanadyl ion and silver ion.³ The present study was undertaken in the hope of more fully understanding the vanadyl oxidation by peroxodiphosphate and in order to continue our comparisons of the mechanisms for reactions of peroxodiphosphate and peroxodisulfate with reducing agents.

Although our data do allow some conclusions relative to the initial purposes of our study, the system is very complicated and the quantitative numbers obtained (such as rate constants) are dependent on the details of the experiment. Some interesting new phenomena are reported.

(* Public Health Service Fellow 1965-66; on leave from Immaculate Heart College, Los Angeles, California 90027.

(1) H. H. C. Chong, Ph. D. Thesis, Michigan State University (1958).

(2) D. M. Yost and W. H. Claussen, *J. Amer. Chem. Soc.*, **53**, 3349 (1931).

(3) M. Andersen, unpublished results, Brown University (1966).

Experimental Section

Reagents. All chemicals used were reagent grade, except the sodium salts of mono- and di-chloroacetic acid which were made by dissolving stoichiometric quantities of NaOH in the respective acid. Vanadyl sulfate was obtained as the dihydrate from the Fischer Scientific Company. Potassium peroxodiphosphate was prepared by the method of Chulski.⁴ Purification was accomplished by recrystallization of the product from a water-methanol solution and subsequent conversion to $\text{Li}_4\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$. Laboratory distilled water was used.

Analytical Methods. $\text{Li}_4\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ was standardized by adding excess ferrous ion solution to a weighed sample of the salt and then back titrating the unreacted ferrous ion with dichromate using diphenylamine sulfonate as the indicator. Solutions of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ were prepared by dissolving weighed material. VO^{2+} was analyzed by measuring the absorbance of the solution at 770 m μ ; the ϵ was taken to be 14.7 for a freshly-prepared solution. Vanadium(V) does not absorb appreciably at this wavelength. Determinations were also carried out by adding small aliquots of Ce^{IV} to a VO^{2+} solution; the absorbance at 770 m μ was plotted against the amount of added Ce^{IV} and the values extrapolated back to zero absorbance. Values for $[\text{VO}^{2+}]$ obtained by dissolving weighed samples and those by using Ce^{IV} always agreed.

Kinetics. For the kinetic runs, solutions to a total of 20 ml were made up from salt, buffer and reactants with the $\text{P}_2\text{O}_8^{4-}$ being added last. For example, a solution might have 2 or 3 ml of 0.082 M VO^{2+} stock solution, x ml of 2 M NaNO_3 , 6-x ml of the sodium salt of the buffer, 3.8 ml of the buffer acid, water in appropriate quantity and then the necessary quantity of 0.2 M $\text{P}_2\text{O}_8^{4-}$ to make up the total volume. In all rate experiments, the ionic strength was held constant at 0.6. The reaction mixture was transferred to a 50 mm Vycor cell and was followed by monitoring the absorbance at 770 m μ with a Beckman Model B spectrophotometer. All pH measurements were done on a Beckman Model G meter. Brackets are used to denote concentrations, and formulas such as VO^{2+} and $\text{P}_2\text{O}_8^{4-}$ are used to denote total concentration of the species irrespective of chemical state.

(4) T. Chulski, Ph. D. Thesis, Michigan State University (1953).

Results

Interaction of VO^{2+} with Solutes. It was found during the course of our studies that the apparent extinction coefficients ϵ' of VO^{2+} in aqueous solution is significantly dependent on the nature and concentration of other species in the reaction mixtures. Our data indicate that the anions OH^- , $P_2O_7^{4-}$, $P_2O_8^{4-}$ and PO_4^{3-} interact with the cation VO^{2+} to cause a measurable variation in the calculated ϵ' of the cation. It was also found that pentavalent vanadium (either when added as V_2O_5 in acidic solution or when formed during the course of the oxidation of the VO^{2+} by peroxodiphosphate) caused an increase in the value of ϵ' . The problem of stoichiometry evaluation was complicated by the formation of a precipitate (see below) when less than one-half mole of peroxodiphosphate per vanadyl ion was present. Consequently we sometimes added pyrophosphate ion to the solutions in order to complex the unreacted vanadyl ion and thereby to prevent its precipitation. Some results showing the interaction of vanadyl ion with vanadium(V) and with pyrophosphate are presented in Tables I and II respectively.

Table I. Changes in Absorbance of a VO^{2+} Solution upon Addition of V_2O_5 in 2 M $HClO_4$ ^a

$[V_2O_5], M$	O.D. ^b	ϵ'_{obs} ^b
0	0.421	15.4
1.33×10^{-3}	0.440	16.1
2.67×10^{-3}	0.466	17.0
4.00×10^{-3}	0.498	18.2
5.47×10^{-3}	0.532	19.4

^a At room temperature; $[VO^{2+}] = 5.47 \times 10^{-3} M$. ^b Optical density (O.D.) and apparent extinction coefficient (ϵ') at 770 m μ .

Table II. Absorption of a VO^{2+} Solution as a Function of the Pyrophosphate Concentration

$[P_2O_7^{4-}], M$	pH	O.D. ^b	ϵ'_{obs} ^b
0	2.27	0.302	14.7
1.0×10^{-2}	2.25	0.327	15.9
2.0×10^{-2}	2.02	0.332	16.2
3.0×10^{-2}	2.09	0.350	17.0
4.0×10^{-2}	2.21	0.361	17.6
5.0×10^{-2}	2.26	0.356	17.4
6.0×10^{-2}	2.28	0.375	18.3
7.0×10^{-2}	2.31	0.370	18.0
8.0×10^{-2}	2.36	0.372	18.1
9.2×10^{-2}	2.41	0.379	18.5

^a At room temperature; $[VO^{2+}] = 4.1 \times 10^{-3} M$. ^b Optical density (O.D.) and apparent extinction coefficient (ϵ') at 770 m μ .

Independent evidence for strong interaction of pyrophosphate and vanadyl ion in aqueous acid has been found by Reeder and Rieger.⁵ Their results, indicating several complexes, were obtained with electron spin resonance and pH titration curves. Near pH 2 in dilute solutions, the predominant complex appears

(5) R. Reeder and P. L. Rieger, unpublished results, Brown University (1969).

to have one pyrophosphate ion per vanadyl ion with a net minus two charge.

When varying amounts of a 0.01 M solution of V_2O_5 in 2 M $HClO_4$ were added to a VO^{2+} solution, the ϵ' value for VO^{2+} changes as may be seen in Table I. The values increase from 15.4 in the absence of pentavalent vanadium to 19.5 when the species (VO^{2+} and V_2O_5) are at equal concentration, even though there is no appreciable absorption of pentavalent vanadium at the wavelength employed. The nature of the interaction of the two vanadium species of different oxidation states is not clear; at least in part this is due to a lack of information concerning the exact nature of vanadium(V) in acid solution.⁶

The interaction of the anions with VO^{2+} (as shown by the spectrophotometric data) is believed to be related to the fact that anions act as ligands in complexes of VO^{2+} . In the absence of strongly-complexing anions, OH^- will interact with VO^{2+} . In the pH range from 1.0 to 3.5, the value of ϵ' at 770 m μ for VO^{2+} is constant; from 3.5 to 4.5, an increase was observed indicating hydrolysis to form VO_2H^+ has occurred. Above pH 4.5, a precipitate believed to be $VO(OH)_2$ is formed.⁷ Both $P_2O_7^{4-}$ (see Table II) and $P_2O_8^{4-}$ (the state of protonation of these two anions is discussed below) cause increases in the absorption when added to VO^{2+} solutions. These increases are of the same magnitude ($\approx 25\%$) as the absorption increase due to equimolar V_2O_5 only when the phosphorus anions are in tenfold excess; we conclude that the interaction of the pentavalent vanadium with VO^{2+} is very strong, or, alternatively, has a dramatic influence on the spectrum of VO^{2+} .

Stoichiometry. The stoichiometry of the redox reaction was determined in two ways. In a phosphate buffer, if less than stoichiometric quantities of $P_2O_8^{4-}$ were added, a dull-green flaky precipitate formed and the absorbance fell to zero. It seems probable that this precipitate contains vanadium in oxidation states +4 and +5 since a closely similar precipitate could only be obtained by adding a small amount of V_2O_5 to a solution of VO^{2+} in phosphate buffer. Since the precipitation caused a premature loss of the vanadyl color, we found it convenient to carry out some of the stoichiometry experiments in the presence of pyrophosphate. Although this complexing anion caused a variation in ϵ' , it was effective in keeping the tetravalent vanadium in solution (see above).

Some experiments for determination of stoichiometry are presented in Tables III and IV. The O.D. values which appear in the final columns of these tables were calculated on the basis of two assumptions; the value in parentheses is taken as the appropriate value of extinction coefficient for the particular set of experiments and the stoichiometry is taken to be 2 VO^{2+} per peroxodiphosphate. The values of O.D. (obs) and O.D. (calc) can be seen to be in reasonable

(6) (a) H. J. Emeleus and J. S. Anderson, «Modern Aspects of Inorganic Chemistry», D. Van Nostrand Co., New York (1960), pages 324-5; (b) J. A. Connor and E. A. V. Ebsworth in «Advances in Inorganic Chemistry and Radiochemistry», edited by H. J. Emeleus and H. G. Sharpe, Academic Press, N. Y., Vol. 6, 1964, pages 292-4.
(7) (a) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 9, 1177 (1955); (b) H. T. S. Britton and G. Welford, *J. Chem. Soc.*, 1940, 758.

Table III. Determination of the Stoichiometry in Phosphate Buffer in the Presence of Pyrophosphate^a

[P ₂ O ₈ ⁴⁻], M	[P ₂ O ₇ ⁴⁻], M	O.D. _{obs} ^b	O.D. _{calc}
0	7.2 × 10 ⁻²	1.16	(1.16) ^c
2.0 × 10 ⁻³	7.0 × 10 ⁻²	0.825	0.783
3.0 × 10 ⁻³	6.9 × 10 ⁻²	0.615	0.594
4.0 × 10 ⁻³	6.8 × 10 ⁻²	0.415	0.405
5.0 × 10 ⁻³	6.7 × 10 ⁻²	0.14	0.217

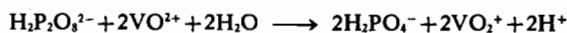
^a Each reaction mixture contained 3.8 ml H₃PO₄ and 6 ml NaH₂PO₄; [VO²⁺] = 1.23 × 10⁻² M. ^b At room temperature, at 770 mμ, and at pH = 2.3 ± 0.2. ^c Value used to calculate other O.D. (calc) values.

Table IV. Stoichiometry Determination in Unbuffered Solution^a

[P ₂ O ₈ ⁴⁻], M	pH	O.D. _{obs} ^a	O.D. _{calc}
0	2.38	0.97	(0.97) ^b
1 × 10 ⁻³	2.33	0.81	0.813
2 × 10 ⁻³	2.38	0.94	0.654
3 × 10 ⁻³	2.36	1.09	0.497
4 × 10 ⁻³	2.32	1.04	0.339
5 × 10 ⁻³	2.30	0.44	0.181
5.4 × 10 ⁻³	2.28	0.225	0.118
5.8 × 10 ⁻³	2.30	0.000	0.055

^a At room temperature and 770 mμ; [VO²⁺] = 1.23 × 10⁻² M. ^b Value used to calculate other O.D. (calc) values.

agreement for Table III. This stoichiometric experiment carried out in the presence of pyrophosphate gave a value of 2.06 moles of VO²⁺ reacted per peroxodiphosphate. Similar stoichiometric experiments in the absence of pyrophosphate (as in Table IV) were complicated by the vanadium(IV)-vanadium(V) interactions mentioned above, however it was found possible to obtain ratios of VO²⁺ oxidized to P₂O₈⁴⁻ added by detection of the point of vanadyl color disappearance. These determinations gave 1.97 ± 0.10 moles of VO²⁺ oxidized per mole of P₂O₈⁴⁻. Thus, as expected, the stoichiometry under a variety of conditions is:



wherein VO₂⁺ and H₂P₄O₈²⁻ are assumed to be the predominant forms of pentavalent vanadium⁶ and peroxodiphosphate⁸ respectively in these acidic solutions.

Kinetics. In a solution with tenfold excess P₂O₈⁴⁻ in phosphate buffer, the reaction was found to be first order in [VO²⁺]. The plots of log absorbance against time were almost linear, usually showing a slight downward curvature as shown in Figure 1. This curvature is presumed to arise from non-constancy of the extinction coefficient of VO²⁺ as the product vanadium(V) increases with time. Nevertheless, as may be seen in Figure 1, there was no significant variation in the pseudo first-order constants with change in the initial VO²⁺ concentration.

The dependence of rate on [P₂O₈⁴⁻] was determined using the initial rate method. A number of experiments are presented in Table V. For seven of these

experiments NaH₂PO₄ was used as buffer anion, and an average value for the order in [P₂O₈⁴⁻] of 1.04 (± .15) was obtained. Whenever there was NO₃⁻ or ClO₄⁻ present but no buffer anion, the dependence on [P₂O₈⁴⁻] was less than first order; an average value of 0.79 for three sets of experiments with NaNO₃ present and a value of 0.74 in one set with NaClO₄ were found as may be seen in the bottom four rows of Table V. These values of less than one for the order in P₂O₈⁴⁻ are independent evidence for complexation of VO²⁺ by the peroxoanion when no phosphate buffer (which can competitively bind to VO²⁺) is present. If the peroxodiphosphate were in sufficient excess to completely complex the VO²⁺, a rate which is zero order in P₂O₈⁴⁻ would be observed; if the amount of P₂O₈⁴⁻ was small (essentially no complexing), a rate which is first order in P₂O₈⁴⁻ would be observed. In intermediate ranges of peroxodiphosphate concentration, a dependence between zero order and first order is expected and this seems to be the situation under our conditions. Since the deviation from first order in the absence of phosphate buffer can be readily explained by complex formation between the reactant species, we can conclude that the order in peroxodiphosphate concentration can be considered as first.

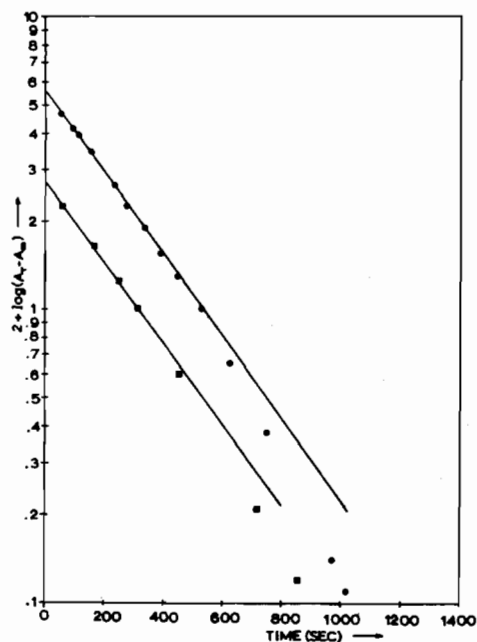


Figure 1. Pseudo first order plots for experiments at two initial [VO²⁺]. The initial slopes are the same demonstrating the first order dependence on [VO²⁺]; at high percentage reaction there is an apparent increase in rate (see text). [P₂O₈⁴⁻]₀ = 8.2 × 10⁻² M. For circles, [VO²⁺]₀ = 6.15 × 10⁻³ M; for squares [VO²⁺]₀ = 3.08 × 10⁻³ M. Data for phosphate buffer at pH 2.3.

The rates were studied over a range of pH values from 1.0 to 4.8. In the range from 1.0 to 3.5 in phosphate buffer, there was no variation in rate outside of the experimental error. Above pH 3.5, the rate is higher and the experiments suffer from non-constant ε values and from precipitation.

(8) (a) M. M. Crutchfield and J. O. Edwards, *J. Amer. Chem. Soc.*, 82, 3533 (1959); (b) M. M. Crutchfield, Ph. D. Thesis, Brown University (1960).

Table V. Dependence of rate on peroxodiphosphate concentration using initial rate method^{a, b, c}

Expt. No.	Salt ^d	[H ₃ PO ₄]	[VO ²⁺] × 10 ²	pH ₁	[P ₂ O ₈ ⁴⁻] ₁ × 10 ²	($\frac{dx}{dt}$) ₁ ^e	pH ₂	[P ₂ O ₈ ⁴⁻] ₂ × 10 ²	($\frac{dx}{dt}$) ₂ ^e	η ^f
1	NaH ₂ PO ₄	0.362	1.17	2.06	1.17	3.19	2.12	2.34	7.16	1.16
2	NaH ₂ PO ₄	0.362	1.17	2.12	2.34	6.01	2.08	4.68	13.47	1.16
3	NaH ₂ PO ₄	0.380	1.23	2.09	1.50	4.12	2.35	3.00	8.07	0.96
4	NaH ₂ PO ₄	0.380	1.23	2.23	3.60	7.98	2.42	7.20	15.82	0.99
5	NaH ₂ PO ₄	0.500	1.23	1.87	4.00	8.47	1.98	6.00	13.02	0.89
6	NaH ₂ PO ₄	2.280	1.23	1.09	3.60	7.80	1.13	7.20	16.00	1.04
7	NaH ₂ PO ₄	0.380	1.23	2.32	3.60	9.47	2.49	7.20	20.00	1.08
8	NaNO ₃	0.362	1.17	1.37	2.34	7.34	1.55	4.68	12.63	0.79
9	NaNO ₃	0.380	1.23	1.52	3.60	12.43	1.69	7.20	21.9	0.82
10	NaNO ₃	0.600	1.23	1.09	2.46	7.40	1.10	4.92	13.80	0.75
11	NaClO ₄	0.380	1.23	1.42	3.50	11.7	1.62	7.08	19.35	0.74

^a All concentrations in moles per liter. ^b Each pair was at matched temperatures; but temperature varied a little from 22° from one experiment to another. ^c Subscript 1 represents the first run and subscript 2 represents the second run. ^d When NaH₂PO₄ was employed the system was buffered because its conjugate acid H₃PO₄ was added. When NaNO₃ or NaClO₄ was employed, there is a slight buffering effect because a little of the H₃PO₄ reacts immediately with the Li₄P₂O₈. ^e Slope of the pseudo first order plot in [VO²⁺] times 10⁴. Time in seconds. ^f η is the calculated order in [P₂O₈⁴⁻].

A large number of kinetic runs were carried out in hopes of obtaining valid rate constants. The data in chloroacetate and dichloroacetate buffers exhibited marked curvature in the direction of slower rates; as the reaction proceeds, the half-life increases (see below). A downward curvature beginning at about 40% reaction was apparent in sulfate buffer. In the phosphate buffers, only a slight curvature (in a few cases, none) was observed. In nitrate and perchlorate media with small amounts of H₃PO₄ present, the rates were slightly less than first order in peroxodiphosphate and were somewhat larger than those in phosphate buffer. Not surprisingly, the rate of reaction in the presence of pyrophosphate ion was very much slower.

In view of the many complications in this redox system, exact rate constants could not be obtained. Suffice it to report here the value of 5×10^{-2} liter mole⁻¹ sec⁻¹ for 25°, ionic strength 0.6, phosphate buffer and pH range from 1.1 to 3.5. This value is believed to be reproducible to $\pm 1 \times 10^{-2}$.

Organic Buffers. In monochloroacetate buffer the reaction proceeded to completion as indicated by the complete disappearance of the blue color, however a blue color found to be identical to that of VO²⁺ returned upon standing overnight. There was also a deviation in the first order plot for determination of the order in [VO²⁺]; plots which suggested a slowing down in rate as the reaction proceeded were obtained. This type of rate behavior was also seen in dichloroacetate buffer, however the blue color did not reappear on standing. By way of contrast, the blue color typical of VO²⁺ was not produced by adding 0.01 M V₂O₅ (in HClO₄) to the monochloroacetate buffer at room temperature and allowing the reaction mixture to stand for a similar period of time.

A series of experiments to determine the stoichiometry in monochloroacetate buffer gave results indicating that 1.2 ± 0.2 moles of P₂O₈⁴⁻ were used up for every mole of VO²⁺. This indicates that much of the oxidizing capacity of P₂O₈⁴⁻ is going towards the oxidation of something other than VO²⁺. Presumably the other reducing agent is the buffer; the rate results mentioned above fortify this conclusion.

Discussion

The reaction of peroxodiphosphate with vanadyl ion in acid solution shows a large number of complications. We feel, therefore, that our observations are interesting in that they demonstrate these complications as well as clarify the mechanism of the oxidation reaction. Complexation of VO²⁺ by the anions and by vanadium(V) seems proven. Also the species involved in this redox reaction undergo acid-base reactions in aqueous solution, and their constitutions are important to a discussion of the reaction mechanism. Tetravalent vanadium is present over most of this pH range as VO²⁺ with water of solvation,⁷ whereas pentavalent vanadium is presumably VO₂⁺ again with water of solvation.⁶ Peroxodiphosphate would exist throughout this range as H₂P₂O₈²⁻,⁸ whereas pyrophosphate would be mostly as H₂P₂O₇²⁻ with some H₃P₂O₇⁻ at lower pH.⁸ It was on this basis that the stoichiometry above was written.

The reported values of kinetic orders and stoichiometries have larger errors than in usual studies of this kind. This is because of the marked interaction of VO²⁺ with V^V and with other molecules, especially P₂O₈⁴⁻ and OH⁻. The interaction of VO²⁺ and V^V can account for the fact that the first order plots exhibit a small curvature. The ratio of V^{IV} to V^V changes during the course of a reaction and so then does the ε₇₇₀ of the remaining VO²⁺, even though V^V does not absorb in this region. This complex also interfered in the stoichiometry determinations, especially in unbuffered solution, however the final values agree with the predicted value of two moles of VO²⁺ per mole P₂O₈⁴⁻.

The rate law can now be expressed as:

$$\frac{-d[\text{VO}^{2+}]}{dt} = k[\text{VO}^{2+}][\text{H}_2\text{P}_2\text{O}_8^{2-}]$$

where the value of k is somewhat dependent on the conditions in view of the obvious complexities of the system. Since the stoichiometry is two VO²⁺ molecules per 1 molecule of P₂O₈⁴⁻, order and stoichiometric numbers for vanadyl ion are not identical

and there must be an intermediate after the transition state.⁹

A possible mechanism is a two-step reaction having a first, slow step where a free radical is formed,



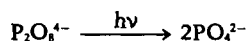
which is followed by a fast step in which the radical attacks another VO^{2+} ion.



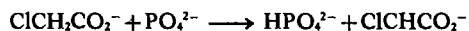
We assume here that the reactive radical formed in the rate-determining step is the phosphate ion-radical PO_4^{2-} , however VO_2^{2+} or some related vanadium species could also fit the data. Independent evidence for PO_4^{2-} has been found in this laboratory.¹⁰ Ultraviolet light in the range where $\text{P}_2\text{O}_8^{4-}$ absorbs initiates the photolytic oxidation of water



and the mechanism seems to involve the primary step



The deviations in kinetics and stoichiometry observed in organic buffers provide convincing evidence for such a free radical. The stoichiometry of $\approx 1:1$ in monochloroacetate is explicable if the free radical formed in the rate step can attack the buffer in competition with the attack on VO^{2+} in the second step of the postulated mechanism. A step of the type



followed by reduction of $\text{P}_2\text{O}_8^{4-}$ or VO_2^+ by the organic radical ClCHCO_2^- is postulated. Presumably labile organic species formed in these radical reactions then slowly reduce the pentavalent vanadium to bring about return of the blue color of VO^{2+} on standing overnight. It is known¹¹ that pentavalent vanadium can oxidize certain types of organic molecule. Further work on the vanadium-induced oxidation of organic compounds by peroxodiphosphate would be worthwhile.

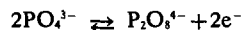
(9) See, for example, J. O. Edwards, E. F. Greene and J. Ross, *J. Chem. Educ.*, **45**, 381 (1968).

(10) W. M. Risen and R. Lussier, unpublished results.

(11) W. A. Waters and J. S. Littler, Chapter III in « Oxidation in Organic Chemistry », K. B. Wiberg, editor, Academic Press, New York (1965).

As mentioned above $\text{H}_2\text{P}_2\text{O}_8^{2-}$ and VO^{2+} are the predominant reactant species in the pH range of this study. Thus, since the reaction is first order in each species and the rate is essentially independent of pH, the constitution of the transition state is $\text{VP}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ with x being unknown. In view of the ability of peroxodiphosphate to form complexes,⁸ it seems appropriate to postulate a transition state in which the peroxyoanion acts as chelate ligand and is bound to the vanadyl ion. Support for this postulation is found in the fact that $\text{S}_2\text{O}_8^{2-}$, which is isoelectronic with $\text{H}_2\text{P}_2\text{O}_8^{2-}$ but does not appear to form complexes, reacts only very slowly with vanadyl ion. Again, as was found for the iodide ion,¹² tris(phenanthroline)iron(II),¹³ and bis(terpyridyl)iron(II) cation,¹⁴ peroxodiphosphate and peroxodisulfate oxidize by quite different mechanisms. Peroxodisulfate often oxidizes by an outer-sphere mechanism, whereas peroxodiphosphate reactions proceed by way of an inner-sphere complex as is proposed here.

The facts, that peroxodiphosphate will oxidize manganese ion¹⁴ and vanadyl ion at a measureable rate whereas peroxodisulfate does not appear to oxidize these cations, are therefore most probably indicative of a kinetic rather than a thermodynamic difference. It seems reasonable that the oxidation potential for the couple



is not greatly different from the potential for the corresponding peroxodisulfate couple which is -2.01 v.¹⁵

Finally we wish to reiterate that the extinction coefficient of VO^{2+} in aqueous solution is markedly dependent on the other species present in the solution. Therefore it is important that the extinction coefficients be evaluated for each system under investigation.

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(13) Sr. A. A. Green, J. O. Edwards and P. Jones, *Inorg. Chem.*, **5**, 1858 (1966).

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(15) W. M. Latimer, « Oxidation Potentials », Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 2nd Edition (1952); pag. 78.