Inorganica Chimica Acta, 19 (1976) 181–187

A Kinetic Study of Pyrophosphate and Peroxodiphosphate Complexation of Oxovanadium(IV) Ion*

M. R. HOFFMANN, R. A. STERN, P. H. RIEGER** and J. O. EDWARDS
Department of Chemistry, Brown University, Providence, Rhode Island 02912, U.S.A.
Received February 24, 1976

The formation constant of the vanadyl pyrophosphate complex, $VO(H_2P_2O_7)$, determined spectrophotometrically in acidic 1.0 M $NaClO_4$ solution, is $\log K = 4.4 \pm 0.1$ at 25 °C. The kinetics of the complexation of vanadyl ion by pyrophosphate and peroxodiphosphate were studied at pH 2.0 using stopped-flow spectrophotometry. The reactions are first-order in ligand and in vanadyl ion with rate constants $k_2 = 2.3 \times 10^4$ and 7.5×10^3 M^{-1} sec^{-1} at 12 °C for $H_2P_2O_7^{2-}$ and $H_2P_2O_8^{2-}$, respectively. The complexation reactions were followed by slower secondary processes which are attributed to polymerization. The results for the complexation reactions are consistent with an interchange mechanism for the formation of a monodentate complex, followed by rapid closure of the chelate ring. Peroxodisulfate, studied under similar conditions, showed no evidence of inner-sphere complexation.

Introduction

The pentaaquo oxovanadium(IV) ion (hereafter vanadyl ion) is oxidized to vanadium(V) by peroxodiphosphate in aqueous acid solution,

$$H_2P_2O_8^{2-} + VO(H_2O)_5^{2+} \rightarrow 2H_2PO_4^- + 2VO_2(H_2O)_4^+ + 2H^+ \quad (1)$$

The reaction proceeds through a series of color changes from the initial blue to a final dark yellow. An investigation[1] of this oxidation in the presence of phosphate and pyrophosphate buffers indicated that phosphate, pyrophosphate, and peroxodiphosphate anions interact with the vanadyl ion to cause measurable increases in the apparent molar extinction coefficient at 770 nm. When no phosphate buffers were present, the kinetic order of the reaction in peroxodiphosphate was significantly less than one and the rates were higher. In view of the ability of peroxodiphosphate to form complexes with alkali and alkaline earth metals,[2] these results were interpreted as evidence for complexation of vanadyl ion by peroxodiphosphate before oxidation.

Vanadyl ion has been shown to form a 1:1 trinuclear complex with pyrophosphate,[3,4] formulated as $(VOP_2O_7)_3^{6-}$; this species exhibits a 22-line e.s.r. spectrum which is easily detectable above pH 2.5. At lower pH values, complex formation with pyrophosphate is expected, but no species distinguishable from the vanadyl ion was detected in the e.s.r. studies.[4]

The vanadyl ion forms a variety of stable complexes in acid solution with ligands having electronegative donor atoms such as fluorine, oxygen, and chelate nitrogen.[5,6] The most stable complexes are formed with multidentate ligands in which at least one ligand atom is oxygen. Pyrophosphate and linear polyphosphates are expected to form strong complexes with vanadyl ion because of the ability to donate electrons of the unshared oxygen atoms, forming chelate complexes. Since the exchange rate for the equatorial water molecules is rapid (k_{ex} = 640[7], 500[8] sec^{-1} at 25 °C), substitution of either pyrophosphate or peroxodiphosphate into the coordination sphere of the vanadyl ion is expected to be fast.

Knowledge of the elementary equilibrium properties and substitution dynamics of simple vanadium(IV) systems can be of value in understanding the interactions of vanadium species with biological phosphates. Such knowledge should also help to explain the fact that peroxodiphosphate[1] reacts more rapidly with vanadyl ion than does the isoelectronic peroxodisulfate,[9] in contrast with most other oxidations where peroxodisulfate reacts more rapidly.[10–12]

Experimental

Lithium peroxodiphosphate was prepared from FMC potassium peroxodiphosphate by the addition of an excess of lithium perchlorate in a minimum amount of deionized water. After filtering off the potassium perchlorate precipitate, the product was obtained by the addition of methanol.

---

* Taken in part from the Ph.D. Thesis of M. R. H., Brown University, 1973.

** To whom correspondence should be addressed.

An acidic stock solution of vanadyl perchlorate was prepared using Fisher vanadyl sulfate and barium perchlorate as described by Jones and Larsen.[13] The solution was analysed for vanadium(IV) by permanganate titration and for free acid using the ion exchange technique described by Reeder and Rieger.[14] The concentrations of subsequent solutions, prepared from the stock solution, were checked by measuring the absorbance at 770 nm.

Baker and Adamson sodium pyrophosphate decahydrate and sodium peroxodisulfate and G. F. Smith sodium perchlorate (used to adjust the solution ionic strength) were reagent grade and were used without purification.

All solutions were prepared under nitrogen to prevent air oxidation of vanadium(IV). Vanadium(V) species have large extinction coefficients in the ultraviolet region; even trace amounts can produce noticeable deviations. For analytical spectra, solutions were prepared volumetrically using doubly-distilled water which was reboiled and allowed to cool under nitrogen. Solution preparation was carried out in a nitrogen-filled glove bag. Water used for preparing solutions for kinetic runs was degassed by a series of freeze–pump–thaw cycles on a vacuum line. Pyrophosphate and peroxodiphosphate solutions were freshly prepared before each series of measurements.

A Cary 15 spectrophotometer was used for survey and analytical spectra. The 1-cm absorbance cells were thermostatted using a Haake NBS constant temperature circulator and water-jacketted cell holders. The temperature was monitored within the cell compartment with a mercury thermometer mounted through the cell compartment cover. The spectrophotometer was flushed with prepurified nitrogen before use.

pH measurements were made with a Leeds and Northrup pH meter with miniature electrodes.

Kinetic determinations were made with a Durrum–Gibson D-110 stopped-flow spectrophotometer equipped with a Hewlett–Packard 1207A storage oscilloscope. Temperature was maintained within 0.02°C using the Haake NBS system with a heat exchanger for operation below ambient temperature. After filling the drive syringes, 20 minutes was allowed for thermal equilibration before the first kinetic determination. The stop block of the stopped-flow apparatus was positioned so that the maximum volume of each reactant was dispensed, about 0.36 ml, so as to minimize the effects of temperature gradients in the valve block.[15] Substitution kinetics were followed at 240 nm.

All kinetic runs were under pseudo-first-order conditions with an excess of ligand. Data from each kinetic run was obtained in the form of a Polaroid photograph of the oscilloscope trace. The photographs were analysed using a Hewlett–Packard 9107A magnetic digitizing board, having a resolution of 0.01 inches, which was linked to a Hewlett–Packard 9100B programmable calculator with an extended memory bank. The digitized data were scaled and subjected to least-squares analysis, assuming first-order kinetics. Output data from the procedure were values of $\ln(A_\infty - A)$ and time for each point selected as well as the slope and intercept from the least-squares fit. To reduce the effect of random errors, at least three traces were photographed and analysed for each set of reaction conditions. Thus rate constants reported below are the average of at least three determinations.

Results

Formation Constant of the Vanadyl Pyrophosphate Complex

Spectra of the vanadyl pyrophosphate system were recorded for solutions at pH 1.8 and ionic strength 1.0*M*, containing a constant vanadyl concentration of 0.62 m*M* and pyrophosphate concentrations ranging from 0.30 to 12 m*M*. Plots of the apparent molar extinction coefficients *vs.* the pyrophosphate concentration for wavelengths of 220, 230, 240, and 260 nm are shown in Figure 1.

The spectrophotometric data were subjected to matrix rank analysis. In this procedure, the experimental absorbances of nine solutions at eight different wavelengths were used to construct the 8 × 8 matrix,

$$B_{\lambda\lambda'} = \sum_i A_{\lambda i} A_{\lambda' i} \tag{2}$$

where $A_{\lambda i}$ is the absorbance of the *i*th solution wave wavelength λ. Hugus and El-Awady[16] have shown that the number of independent absorbing species is equal to the rank of the matrix B which may be determined by finding the number of non-zero (*i.e.*, statistically significant) eigenvalues. The results of the matrix rank treatment are given in Table I. The χ^2 test, which is critically dependent on the error estimates for the experimental points, suggests a rank of either two or three, but only the first two eigenvalues are significantly different from zero. Thus the absorbance data can be explained in terms of two absorbing species, presumably the vanadyl ion and a vanadyl pyrophosphate complex.

Stability constants were first determined by a graphical method. Assuming that the vanadyl pyrophosphate complexation can be represented by a simple equilibrium,

$$VO^{2+} + H_nP_2O_7^{n-4} \rightleftarrows VO(H_nP_2O_7)^{n-2}, \tag{3}$$

absorbance data collected for constant total vanadyl concentrations and constant path length should obey the following relation:[17]

$$(A - A_0)/[H_nP_2O_7^{n-4}]_f = K(A_1 - A) \tag{4}$$

where K is the stability constant, A is the observed absorbance, A_0 is the absorbance of vanadyl ion when

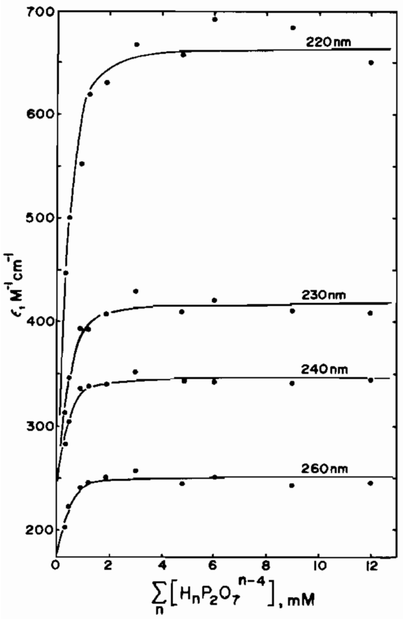


Figure 1. Apparent molar extinction coefficients of 0.62 m*M* vanadyl ion in 1.0*M* $NaClO_4$, pH 1.8, as functions of total pyrophosphate concentration at wavelengths of 220, 230, 240, and 260 nm.

TABLE I. Matrix Rank Treatment of Vanadyl–Pyrophosphate Absorbance Data[a].

Rank	Eigenvalue[b]	Misfits[c]	χ^2 (exptl)	$\chi^2_{n,.5}$[d]
1	1296.6 ± 2.7	26	1094	62
2	3.5 ± 1.6	0	77	53
3	0.08 ± 1.6	0	32	44
4	0.03 ± 1.1	0	15	35
5	0.02 ± 1.5	0	5	26
6	0.01 ± 0.9	0	2	17
7	0.00 ± 0.7	0	1	8
8	0.00 ± 0.3	0	–	–

[a] Nine solutions at eight wavelengths, pH 1.8, 25 °C, 1.0*M* ionic strength. [b] $\times 10^4$. [c] Number of points which deviate from the fit by more than twice the estimated standard deviation. [d] Expectation value.

no pyrophosphate is present, and A_1 is the absorbance of the system if all the vanadyl ions were in the form of the complex; the pyrophosphate concentration term represents the free anion. A plot of $(A-A_0)/[H_nP_2O_7^{n-4}]_f$ *vs.* A with reasonable estimates of the concentrations of free pyrophosphates gives an estimate of K which may be used to refine the concentrations. The procedure was iterated until a constant value of K was obtained. Data collected at 220 nm, 25 °C, gave a final value of $K = 1.5 \times 10^4$ (1*M* standard states).

The stability constant was also determined by a nonlinear least-squares fit[18] of absorbance data collected at seven wavelengths and ten pyrophosphate concentrations to obtain a single valuc of $K = (1.25 \pm 0.28) \times 10^4$ at 25 °C. In the least-squares fit, the extinction coefficients of free vanadyl ion and of the vanadyl pyrophosphate complex, ε_0 and ε_1, were treated as fitted parameters and are given in Table II. The solid curves, shown in Figure 1, were computed using the least-squares parameters. Thus 15 parameters were determined from 70 data points.

The equilibrium constant obtained from either of the two methods may be written

$$K = (\sum_n[VO(H_nP_2O_7)^{n-2}])/([VO^{2+}]\sum_n[H_nP_2O_7^{n-4}]). \qquad (5)$$

If we assume that only the pyrophosphate dianion forms a complex with the vanadyl ion, then the apparent equilibrium constant must be corrected by the factor

$$1+[H^+]/K_{a2}+[H^+]^2/K_{a1}K_{a2}. \qquad (6)$$

Given the ionization constants of pyrophosphoric acid, K_{a1} and K_{a2}, Table III, this factor at pH 1.8 is 2.13, leading to a corrected equilibrium constant of $K = (2.7 \pm 0.6) \times 10^4$ for the equilibrium

$$VO^{2+} + H_2P_2O_7^{2-} \rightleftarrows VO(H_2P_2O_7). \qquad (7)$$

Kinetics of the Reaction of Vanadyl Ion with Pyrophosphate

The vanadyl–pyrophosphate reaction was followed by stopped-flow spectrophotometry at 240 nm. The reaction proved to be too fast to follow conveniently at 25 °C, so that data were collected in the tempera-

TABLE II. Least-squares Fitted Extinction Coefficients[a].

	Wavelength, nm						
	270	260	250	240	230	220	210
ε_0:	127 ± 4	180 ± 6	232 ± 11	247 ± 11	250 ± 15	285 ± 33	463 ± 40
ε_1:	176 ± 1	252 ± 3	304 ± 3	348 ± 3	419 ± 4	667 ± 9	1099 ± 11

[a] M^{-1} cm^{-1}.

TABLE III. Acid Dissociation Constants of Pyrophosphoric Acid and Peroxodiphosphoric Acid[a].

	$H_4P_2O_7$	$H_4P_2O_8$
pK_1	0.82[b]	−1.3[c]
pK_2	1.81[b]	−0.48[c]
pK_3	6.13[b]	4.79[d]
pK_4	8.93[b]	7.32[d]

[a] At 25°C, 1.0*M* ionic strength. [b] S.M. Lambert and J. I. Watters, *J. Am. Chem. Soc., 79,* 4262 (1957). [c] Reference 11. [d] Reference 2.

ture range 7–12°C. Kinetics were determined under pseudo-first-order conditions; the results are summarized in Table IV. The kinetic order of each reactant was determined by the differential method of van't Hoff;[19] the rate law was found to be first-order in pyrophosphate and in vanadyl concentrations:

$$d[VOH_2P_2O_7]/dt = k_2[VO^{2+}]\sum_n[H_nP_2O_7^{n-4}]. \tag{8}$$

From the observed pseudo-first-order rate constants, values of the second-order rate constants, $k_2 = k_{obs}/\sum_n[H_nP_2O_7^{n-4}]$, were calculated and are also given in Table IV. The average value of k_2 at 12°C, pH 2, is $(1.3 \pm 0.4) \times 10^4 M^{-1}$ sec^{-1}. Assuming that only the pyrophosphate dianion is reactive and that the pK_a's given in Table III are approximately correct at 12°C, the rate constants may be corrected, using eq. (6), to give an average value, $k_2' = (2.3 \pm 0.5) \times 10^4 M^{-1}$sec^{-1}, corresponding to the rate law

$$d[VOH_2P_2O_7]/dt = k_2'[VO^{2+}][H_2P_2O_7^{2-}]. \tag{9}$$

The above assumption is consistent with the smaller value of k_2 found at pH 1.0 which presumably reflects the lower concentration of the pyrophosphate dianion in the more acidic solution.

A secondary process, involving a small further increase in absorbance but proceeding at a slower rate, was observed in the vanadyl–pyrophosphate reaction. The relaxation times of the two processes were sufficiently different that there was no difficulty in separating them.

Kinetics of the Reaction of Vanadyl Ion with Peroxodiphosphate

The reaction of vanadyl ion with peroxodiphosphate was followed at 12°C by stopped-flow spectrophotometry at 240 nm in solutions adjusted to pH 2.0 and 1.0*M* ionic strength. Under pseudo-first-order conditions, stopped-flow curves were obtained which showed two well separated relaxation times. Analysis of the kinetic data showed that both the primary and secondary processes were cleanly first-order; the values of k_{obs} obtained are given in Table V. Analysis of the primary (fast) process by the van't Hoff method shows that the reaction is first-order each in vanadyl ion and in the peroxodiphosphate dianion, which is by far the dominant species at pH 2 (see Table III). Thus the rate law may be written:

$$d[VOH_2P_2O_8]/dt = k_2[VO^{2+}][H_2P_2O_8^{2-}]. \tag{10}$$

The second-order rate constants, $k_2 = k_{obs}/[H_2P_2O_8^{2-}]$, are given in Table V; the average value is $k_2 = (7.5 \pm 0.1) \times 10^3 M^{-1}$ sec^{-1}.

Unlike the secondary process observed in pyrophosphate kinetic runs, which was barely detectable, that observed in the vanadyl–peroxodiphosphate reaction involves a substantial absorbance change, about twice the change found for the primary process. Plots of $\ln(A_\infty - A)$ *vs.* t for the secondary process are linear and, as seen in Table V, give observed rate constants which are independent of the peroxodiphosphate concentration, but nearly proportional to the initial vanadyl concentration.

Vanadyl–Peroxodisulfate

When a sodium peroxodisulfate solution was mixed with vanadyl perchlorate in the stopped-flow apparatus under the same conditions used for the phosphate ligands, no change in absorbance was detected. Ap-

TABLE IV. Kinetic Data for the Reaction of Vanadyl Ion with Pyrophosphate.

Temp. C	pH	$[VO^{2+}]^a$	$[H_nP_2O_7^{n-4}]^a$	$k_{obs}{}^b$	$10^{-4}k_2{}^c$
12.0°	1.0	0.62	6.2	47 ± 1[d]	0.75 ± 0.02[d]
11.8°	1.9	0.62	3.0	54 ± 5	1.8 ± 0.2
11.8°	1.92	0.62	6.0	89 ± 4	1.48 ± 0.06
12.0°	1.95	0.72	3.0	44 ± 3	1.5 ± 0.1
12.0°	2.0	0.62	12.0	146 ± 11	1.3 ± 0.1
12.0°	2.0	1.24	12.0	110 ± 10	0.90 ± 0.08
12.0°	2.0	1.86	12.0	194 ± 16	1.6 ± 0.1
7.0°	2.35	0.31	6.2	72 ± 1	1.16 ± 0.02
7.0°	2.35	0.62	6.2	74 ± 10	1.2 ± 0.2
7.0°	2.35	0.91	6.2	85 ± 1	1.37 ± 0.02

[a] m*M*. [b] sec^{-1}. [c] M^{-1} sec^{-1}. [d] Standard deviation.

TABLE V. Kinetic Data for the Reaction of Vanadyl Ion with Peroxodiphosphate[a].

$[VO^{2+}]$[b]	$[H_2P_2O_8^{2-}]$[b]	k_{obs}[c] Primary	k_{obs}[c] Secondary	$10^{-3}k_2$[d]
0.62	1.2	–	0.86 ± 0.01[e]	–
0.62	3.0	22.3 ± 0.6[e]	–	7.4 ± 0.2[e]
0.62	3.1	23.0 ± 0.8	0.86 ± 0.01	7.4 ± 0.3
0.62	6.2	46.4 ± 2.2	0.88 ± 0.01	7.5 ± 0.4
1.2	6.2	47.7 ± 1.3	1.92 ± 0.24	7.7 ± 0.2

[a] At pH 2.0, 12 °C, 1.0*M* ionic strength. [b] m*M*. [c] sec^{-1}. [d] M^{-1} sec^{-1}. [e] Standard deviation.

parently peroxodisulfate does not form a strong complex with vanadyl ion.

Discussion

The formation constant of the vanadyl dihydrogen pyrophosphate complex, $\log K = 4.4 \pm 0.1$, was measured at pH 1.8 and corrected for undissociated $H_4P_2O_7$ and $H_3P_2O_7^-$ under the assumption that the only complex present at pH 2 is $VO(H_2P_2O_7)$, which contains a six-membered pyrophosphate chelate ring.

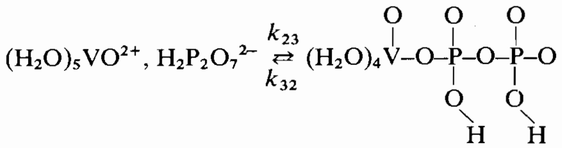
The formation constant of $VO(H_2P_2O_7)$ is, as might be expected, significantly larger than that of the 1 : 1 vanadyl dihydrogen phosphate complex, $\log K_1 = 3.2$.[18] On the other hand, if pyrophosphate in $VO(H_2P_2O_7)$ is bidentate and orthophosphate in $VO(H_2PO_4)^+$ and $VO(H_2PO_4)_2$ is monodentate, one would expect from entropy considerations (the "chelate effect") the formation constant for $VO(H_2P_2O_7)$ to be greater than β_2 for $VO(H_2PO_4)_2$ by at least an order of magnitude,* but β_2 is about 10^5.[18] Assuming that the formation constants are nearly correct, the most likely explanation for this apparent anomaly is that orthophosphate acts at least in part as a bidentate ligand in the vanadyl complex. Salmon[21] has presented arguments for bidentate phosphate in complexes with a number of metal ions including vanadyl, and compelling evidence exists for bidentate phosphate in Co(III) complexes.[22]

By analogy with vanadyl dihydrogen pyrophosphate, we assume that the $H_2P_2O_8^{2-}$ complex is a moderately strong bidentate chelate, although the kinetic results suggest that a considerable degree of polymerization occurs which may involve peroxodiphosphate as a bridging ligand (*vide infra*). By analogy with other systems,** we would expect the formation constant for $VO(H_2P_2O_8)$ to be smaller than the corresponding pyrophosphate constant by one to two orders of magnitude. On the other hand, the ligand concentration in the kinetic runs was 3–6 m*M*; since a substantial amount of complex apparently was formed, the formation constant must be greater than or on the order of 10^3.

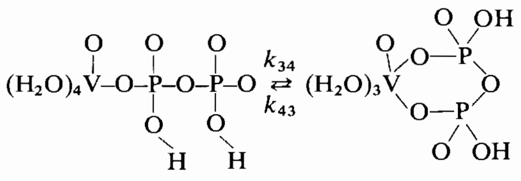
The rate law found for the reaction of either $H_2P_2O_7^{2-}$ or $H_2P_2O_8^{2-}$ with VO^{2+} is first-order in vanadyl and first-order in the diphosphate ligand. The second-order rate constants found at 12 °C, pH 2.0 and 1.0*M* ionic strength, are $k_2 = 2.3 \times 10^4$ and 7.5×10^3 M^{-1} sec^{-1} for pyrophosphate and peroxodiphosphate, respectively.

The reaction of vanadyl ion with $H_2P_2O_7^{2-}$ or $H_2P_2O_8^{2-}$ probably occurs via a three-step mechanism: (1) diffusion-controlled formation of an ion pair; (2) exchange of an inner-sphere water molecule with the outer-sphere diphosphate ion to form a monodentate complex; and (3) exchange of a second inner-sphere water molecule with a second oxygen ligand of the diphosphate to form a six- or seven-membered ring. Thus, with pyrophosphate, for example, the mechanism can be written:

$$(H_2O)_5VO^{2+} + H_2P_2O_7^{2-} \overset{K_0}{\rightleftarrows} (H_2O)_5VO^{2+},\ H_2P_2O_7^{2-} \qquad (11a)$$



$$(H_2O)_5VO^{2+},\ H_2P_2O_7^{2-} \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} (H_2O)_4V\text{–}O\text{–}P(O)(OH)\text{–}O\text{–}P(O)(OH)\text{–}O + H_2O \qquad (11b)$$



$+ H_2O$ (11c)

---

[*] The formation constants of vanadyl oxalate and malonate complexes have recently been found to be 10^7 and 10^6, respectively.[20] Vanadyl acetate formation constants have not been measured, but β_2 is probably less than 10^4.[14]

[**] The formation constants of the Mg^{2+}, HL^{3-} complexes are $10^{3.06}$ and $10^{1.76}$ for pyrophosphate[23] and peroxodiphosphate,[2] respectively.

If the second step is rate-determining, the expected rate law is identical to the observed rate laws, eqs (9) and (10), with $k_2 = K_0k_{23}$.

The detailed mechanism of an anation reaction at a transition metal center is frequently describable either as a dissociative interchange, I_d, or as an associative interchange, I_a.[24] Ligand replacements at Co(III) centers usually occur via an I_d process[24] whereas, at least in some cases, Cr(III), Rh(III), and Ir(III) undergo anations via an interchange mechanism with a greater associative character.[25] The transition state of an I_d process involves dissociation of an inner-sphere water molecule followed by collapse of the outer-sphere ligand into the coordination vacancy. The rate constant k_{23} in an I_d mechanism thus has the rate of water dissociation as an upper bound. For an I_a mechanism, k_{23} may exceed the water exchange rate constant if the incoming ligand is a stronger nucleophile than water.

The water exchange rate, extrapolated to 12 °C, is $k_{ex} = 190$ sec^{-1}.[7,8] If we assume an I_d mechanism and take $k_{23} < k_{ex}$, we obtain lower bounds for the ion pair formation constants: $K_0 > 120$ and 40 for the $H_2P_2O_7^{2-}$ and $H_2P_2O_8^{2-}$ ion pairs, respectively. Ion pair formation constants of this magnitude should have led to deviations from first-order dependence of the observed rate on diphosphate ligand concentrations; unfortunately, the data in Table IV show too much scatter and those in Table V cover too small a concentration range to convincingly confirm or reject this prediction. The formation constant of the VO^{2+}, SO_4^{2-} ion pair is $K_0 = 125$, when corrected to zero ionic strength, but only 32 at $\mu = 0.05\,M$.[26] The formation constant would doubtless be smaller still in the $1.0\,M$ $NaClO_4$ medium used in the present work. Thus an ion pair formation constant greater than 120 seems inexplicably large. This and the apparent selectivity demonstrated by the two rate constants ($H_2P_2O_7^{2-}$ reacts more than three times as fast as $H_2P_2O_8^{2-}$) suggest that step (11b) is not adequately described as a simple I_d process.

Although the reactions seem inconsistent with an I_d mechanism, we have no evidence in support of an I_a process. It is possible that, because of the non-equivalent water coordination sites on the vanadyl ion, anation reactions can never be described as simple processes. Faced with a somewhat similar problem in their discussion of the kinetics of formation of the vanadyl–glycine complex, Tomiyasu, Dreyer, and Gordon[27] suggested initial rapid formation of an axial complex. Tomiyasu *et al.*, have invoked a similar mechanism for ligand exchange with the vanadyl malonate complex;[28] Fitzgerald and Chasteen[29] have made a similar suggestion to explain the very rapid rate of reaction of vanadyl ion with bovine carbonic anhydrase.

If the encounter step (11a) is followed by rapid formation of an axial complex, the ligand interchange step (11b) would involve ligand transfer from the axial site to an equatorial site. In the case of a bidentate ligand, the equatorial ligation step might involve ring closure to form a short-lived axial–equatorial chelate. If we assume that such a process is essentially I_d, the rate would depend on the rate of water exchange and on the entropy lost on ring closure. In this model, peroxodiphosphate would be expected to be slower than pyrophosphate, as was observed.

A slow absorbance change following the primary process was observed in the stopped-flow studies of the reaction of vanadyl ion with both pyrophosphate and peroxodiphosphate. These secondary processes might be polymerizations or possibly slow closure of the chelate ring (or slow conversion of the axial–equatorial chelate to equatorial–equatorial). Chelate ring closure has been shown to be slow, compared with the second step of the formation of the corresponding *bis* monodentate complex, in systems where there is unusual steric strain or an unfavourable entropy loss.[30] However, the very rapid reaction of $VO(H_2PO_4)^+$ with $H_2PO_4^-$ to form the *bis* complex (2×10^6 M^{-1} sec^{-1} at 25 °C[31]) suggests that the presence of an anionic ligand in the vanadyl coordination sphere dramatically increases the rate of subsequent anation steps. Labilization of equatorial water ligands, relative to the vanadyl ion, has been observed in a number of other vanadyl complexes.[32] Thus water expulsion in the third step of the complexation mechanism (11c) is expected to be much faster than the rate of formation of the monodentate diphosphate complexes. Furthermore, if the second relaxation process corresponded with chelate ring closure, the absorbance change would have been expected to be comparable with that occurring in the first step.[18] The observed absorbance change for $H_2P_2O_7^{2-}$ was very small, indeed only barely detectable.

The more prominent secondary process in the peroxodiphosphate reaction permitted determination of the rate constants given in Table V. The apparent dependence of the rate on the initial vanadyl concentration is further evidence against ring closure as an explanation for the secondary process. If we assume a slow dimerization,

$$2\,M \underset{k_r}{\overset{k_f}{\rightleftarrows}} D, \tag{12}$$

the absorbance is expected to show the following time dependence:

$$\frac{d\ln(A_\infty - A)}{dt} = 4k_f[M]_\infty + k_r + 2k_f[M]_0\left(\frac{A_\infty - A}{A'_\infty - A_0}\right) \tag{13}$$

where A is the observed absorbance, A_0 and A_∞ are the initial and final absorbances, $A_\infty{}'$ is the (hypothetical) absorbance when the reaction goes to completion, and $[M]_0$ and $[M]_\infty$ are the initial and final monomer concentrations. Since the experimental rate plots are quite linear, the dimerization must stop well short of completion in order that the constant term may dominate in the above equation. On the other hand, the dependence of k_{obs} on the initial vanadyl concentration suggests that

$$\frac{k_f[M]_\infty}{k_r} = \frac{[D]_\infty}{[M]_\infty} \gtrsim 1 \qquad (14)$$

which is consistent with the observed large absorbance change for the secondary process. In the absence of further information about this equilibrium, the rate constants k_f and k_r cannot be evaluated, nor can we rule out higher degrees of polymerization. Equilibrium information is difficult to obtain since oxidation proceeds at a significant rate (though considerably more slowly than the processes studied in this experiment).

Since vanadyl pyrophosphate is known to polymerize (to form a trimer[3,4]) at only slightly higher pH, it seems likely that the secondary process corresponds to polymer formation in the pyrophosphate case as well.

Evidence obtained in this study for the direct complexation of vanadyl ion by peroxodiphosphate and the failure to detect a similar interaction with peroxodisulfate under identical conditions support our proposition[1,10,11] that the primary difference between peroxodiphosphate and peroxodisulfate oxidations of +2 metal ions is the tendency of peroxodiphosphate to form inner-sphere complexes before electron transfer, whereas peroxodisulfate oxidations normally occur through an outer-sphere electron transfer process.

Acknowledgements

Stimulating discussions with M. W. Kendig and N. D. Chasteen are gratefully acknowledged. This work was supported in part by FMC Corporation and the Air Force Office of Scientific Research.

References

1 M. Anderson, J.O. Edwards, Sr. A.A. Green and Sr. M. D. Wiswell, *Inorg. Chim. Acta, 3,* 665 (1969).

2 M.M. Crutchfield and J.O. Edwards, *J. Am. Chem. Soc., 82,* 3533 (1960).

3 A. Hasegawa, Y. Yamada and M. Miura, *Bull. Chem. Soc. Japan, 42,* 846 (1969); A. Hasegawa, *J. Chem. Phys., 55,* 3101 (1971).

4 C.C. Parker, R.R. Reeder, L.B. Richards and P.H. Rieger, *J. Am. Chem. Soc., 92,* 5230 (1970).

5 J. Selbin, *Chem. Rev., 65,* 153 (1965); *Coord. Chem. Rev., 1,* 293 (1966).

6 R.J.H. Clark, "The Chemistry of Titanium and Vanadium", Elsevier, London, 1968.

7 J. Reuben and D. Fiat, *Inorg. Chem., 6,* 579 (1967).

8 K. Wüthrich and R.E. Connick, *ibid., 6,* 583 (1967).

9 D.M. Yost and W.H. Claussen, *J. Am. Chem. Soc., 53,* 3349 (1931); S.-A. Frennesson and S. Fronaeus, *Acta Chem. Scand., 26,* 3917 (1972).

10 Sr. A.A. Green, J.O. Edwards and P. Jones, *Inorg. Chem., 5,* 1858 (1966); E. Chaffee, I.I. Creaser and J.O. Edwards, *Inorg. Nucl. Chem. Lett., 7,* 1 (1971); J.O. Edwards, *Coord. Chem. Rev., 8,* 87 (1972).

11 I.I. Creaser, unpublished work; I.I. Creaser and J.O. Edwards, *Topics in Phosphorus Chemistry, 7,* 379 (1972).

12 E. Chaffee, *Ph.D. Thesis,* Brown University, Providence, R.I., 1971.

13 K.M. Jones and E. Larsen, *Acta Chem. Scand., 19,* 1205 (1965).

14 R.R. Reeder and P.H. Rieger, *Inorg. Chem., 10,* 1258 (1971).

15 P.K. Chattopadhyay and J.F. Coetzee, *Anal. Chem., 44,* 2117 (1972).

16 ZZ. Hugus, Jr. and A.A. El-Awady, *J. Phys. Chem., 75,* 2954 (1971).

17 T.W. Newton and G.M. Arcand, *J. Am. Chem. Soc., 75,* 2449 (1953).

18 W.C. Copenhafer, M.W. Kendig, T.P. Russell and P.H. Rieger, *Inorg. Chim. Acta, 17,* 167 (1976).

19 K.J. Laidler, "Chemical Kinetics", 2nd ed, McGraw-Hill, New York, N.Y., 1965, p. 15.

20 H. Hoffmann and W. Ulbricht, *Ber. Bunsenges. Phys. Chem., 76,* 1052 (1972).

21 J.A.R. Genge and J.E. Salmon, *J. Chem. Soc.,* 1459 (1959); J.E. Salmon and D. Whyman, *ibid., A,* 980 (1966).

22 S.F. Lincoln and D.R. Stranks, *Aust. J. Chem., 21,* 37, 57 (1968).

23 S.M. Lambert and J.I. Watters, *J. Am. Chem. Soc., 79,* 5605 (1957).

24 C.H. Langford and H.B. Gray, "Ligand Substitution Processes", Benjamin, New York, N.Y., 1966.

25 F. Monacelli, *Inorg. Chim. Acta, 2,* 263 (1968); E. Borghi, F. Monacelli and T. Prosperi, *Inorg. Nucl. Chem. Lett., 6,* 667 (1970); D.R. Stranks and T.W. Swaddle, *J. Am. Chem. Soc., 93,* 2783 (1971); T.W. Swaddle and D.R. Stranks, *ibid., 94,* 8357 (1972); J.O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta, 11,* 47 (1974).

26 G. Köhler and H. Wendt, *Ber. Bunsenges. Phys. Chem., 70,* 674 (1966).

27 H. Tomiyasu, K. Dreyer and G. Gordon, *Inorg. Chem., 11,* 2409 (1972).

28 H. Tomiyasu, S. Ito and S. Tagami, *Bull. Chem. Soc. Japan, 47,* 2843 (1974).

29 J.J. Fitzgerald and N.D. Chasteen, *Biochem., 13,* 4338 (1974).

30 K. Kustin and J. Swinehart, *Prog. Inorg. Chem., 13,* 106 (1971).

31 M.W. Kendig and P.H. Rieger, *Inorg. Chim. Acta, 17,* 175 (1976).

32 K. Wüthrich and R.E. Connick, *Inorg. Chem., 7,* 1377 (1968); A.H. Zeltmann and L.O. Morgan, *ibid., 10,* 2739 (1971).