

## Electron Transfer. 87. Autocatalysis in the Reductions of Vanadium(IV) and Molybdenum(VI) with Vitamin B<sub>12s</sub> (Cob(I)alamin)<sup>1</sup>

G. Chithambarathanu Pillai, Rathindra N. Bose,<sup>2</sup> and E. S. Gould\*

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Vitamin B<sub>12s</sub> (cob(I)alamin) reduces vanadium(IV) and molybdenum(VI) in aqueous solution. With excess reductant in phthalate buffers, these reactions yield V(II) and Mo(III). However, kinetic behavior with the oxidant in excess points to net one-electron changes, yielding V(III) and Mo(V), together with cob(II)alamin (B<sub>12r</sub>). Consumption of B<sub>12s</sub> is markedly autocatalytic in both systems. It is proposed that reductions of the principal products, V(III) and Mo(V), by B<sub>12s</sub> (reactions 4 and 12 in the text) are much more rapid than those of the oxidants taken (reactions 3 and 11), and that the resulting "2e products", V(II) and Mo(IV), undergo rapid comproportionations (reactions 5 and 13) with the oxidants in excess. Differential equations based upon the proposed mechanisms closely reproduce the observed kinetic profiles but do not allow a choice between two kinetically equivalent sequences (eq 8-11 and eq 12-14) for the Mo(VI) reaction. The specific rate for reduction of V(III) ( $5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , 25 °C,  $\mu = 0.20 \text{ M}$ ) estimated from the autocatalytic sequence is in agreement with that measured independently. Retardation of the V(IV)-B<sub>12s</sub> reaction (eq 3) by excess phthalate indicates the distribution of V(IV) between two ligation levels differing by one phthalate unit, with the more fully anated form ( $K_{\text{asn}} 4.7 \times 10^2 \text{ M}^{-1}$ ) one-eighth as reactive as the less anated. In the Mo(VI)-B<sub>12s</sub> system, Mo(VI) is partitioned between three protonation levels, with reactivity toward both B<sub>12s</sub> and Mo(IV) dominated by a small diprotonated fraction. Coordination of Mo(VI) with phthalate increases, rather than decreases, its reactivity toward B<sub>12s</sub>. It is suggested that the necessity for stretching the V=O bond in V(IV) complexes elevates the Franck-Condon barrier to 1e reduction, thus retarding the V(IV)-B<sub>12s</sub> reaction in relation to the V(III)-B<sub>12s</sub> reaction, which has the less favorable potential.

Previous studies dealing with reduction by vitamin B<sub>12s</sub> (cob(I)alamin, the cobalt(I) analogue of B<sub>12</sub>)<sup>3</sup> emphasized the ease with which it reacts with a variety of organic and inorganic species. Moreover, the ability of B<sub>12s</sub> to undergo both 1e and 2e oxidations contributes to the chemical versatility of this reagent. Reductions by B<sub>12s</sub> of coordinated Co(III) to Co(II)<sup>4</sup> are necessarily single-electron transactions, but the reductions of alkenes to alkanes,<sup>5</sup> epoxides to alcohols,<sup>6</sup> and carboxylic anhydrides to aldehydes<sup>7</sup> are almost certainly initiated by transfers of two electrons. Variably persuasive evidence has been presented that the reductions of nitrate to ammonia,<sup>8</sup> substituted hydroxylamines to amines,<sup>9</sup> and unsaturated dicarboxylic acids to saturated acids<sup>10</sup> are triggered by acceptance of two electrons from B<sub>12s</sub>, whereas mechanistic ambiguity persists for the rapid reductions of oxyhalogens to halides<sup>11</sup> and organic disulfides to thiols.<sup>12</sup>

It has recently been pointed out, in connection with redox systems in which both partners may participate either in one- or two-electron changes, that appropriate interplay of specific rates for the various contributing 1e steps may lead to marked autocatalysis.<sup>13</sup> Several examples of such systems have been described,<sup>13,14</sup> each involving the reduction of carboxyl-bound chromium(V) with an anionic reductant. We here report related autocatalysis of the reductions, with B<sub>12s</sub>, of vanadium(IV) and

molybdenum(VI), both of which can readily undergo reduction by at least two successive single-electron transfers.<sup>15</sup>

### Experimental Section

**Materials.** Vanadyl sulfate ("VOSO<sub>4</sub>·xH<sub>2</sub>O") and phthalic acid (Aldrich), sodium molybdate (Matheson Coleman and Bell), and hydroxocobalamin hydrochloride (Sigma) were used as received. Lithium perchlorate, for use in kinetic experiments, was prepared as described.<sup>16</sup> Solutions of VO(ClO<sub>4</sub>)<sub>2</sub> were prepared from VOSO<sub>4</sub> as described,<sup>17</sup> analyzed for vanadium(IV)<sup>17,18</sup> and reduced to V(II) with zinc amalgam.<sup>18</sup> Solutions of V(III) were prepared from VO<sup>2+</sup> and V(II).<sup>19</sup> All reactions were carried out under oxygen-free N<sub>2</sub> in distilled water that had been previously boiled and sparged with N<sub>2</sub> for at least 4 h.

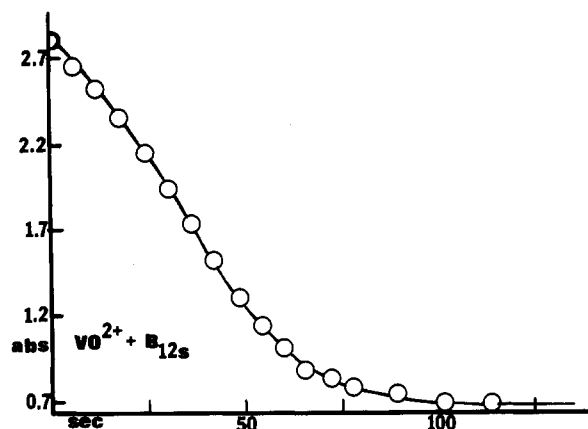
Cob(I)alamin was generated in solution from the cobalt(III) complex hydroxocobalamin hydrochloride by using zinc amalgam for reduction in acid solution.<sup>8</sup> Kinetic runs could not, as in previous studies,<sup>8,10</sup> be carried out with zinc amalgam in the reaction vessel since some reduction of V(IV) and Mo(VI) by the amalgam took place during the run. Instead, B<sub>12s</sub> was generated in dilute HClO<sub>4</sub> and then transferred carefully by syringe to the buffered supporting medium just before the oxidant was added.

**Kinetic Studies.** Reactions were monitored by following absorbance decreases at 387 nm on a Beckman Model 5260 recording spectrophotometer.<sup>20a</sup> Total ionic strength was maintained near 0.2 M by addition of LiClO<sub>4</sub>, and pH values were regulated by addition of known concentrations of phthalate buffers.<sup>20b</sup> Temperatures were kept at 25.0 ± 0.2 °C in all experiments. All kinetic runs were carried out with the oxidant in excess.

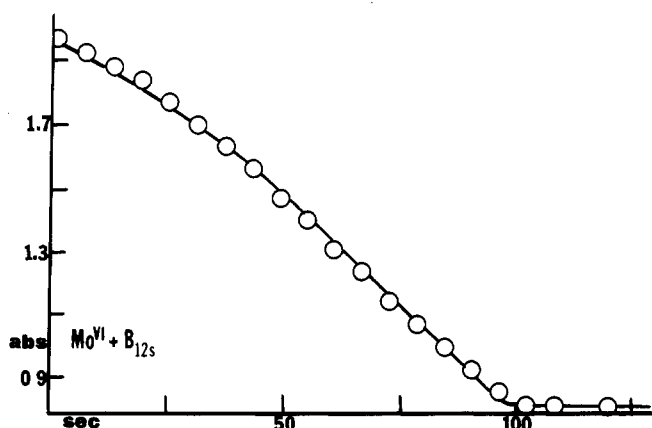
In none of the oxidations by V(IV) or Mo(VI) were simple exponential kinetic curves obtained. Instead, slopes increased steadily as the reactions

- (1) Joint sponsorship of this work by the National Science Foundation (Grant No. 8619472) and by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health (Grant No. BRSG SO7 RR-07208-8), is gratefully acknowledged.
- (2) Present address: Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762.
- (3) Reviews: (a) Dolphin, D. *Methods Enzymol.* **1971**, *18C*, 34. (b) Halpern, J. In *B<sub>12</sub>*; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, p 501. (c) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105. (d) Pratt, J. M. *Inorganic Chemistry of Vitamin B<sub>12</sub>*; Academic: London, 1972; p 96.
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- (12) Pillai, G. C.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3353.
- (13) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349.
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- (15) What appears to be autocatalysis of this type has been described for the reduction of ClO<sub>4</sub><sup>-</sup> by Mo(III); see: Hills, E. F.; Sharp, C.; Sykes, A. G. *Inorg. Chem.* **1986**, *25*, 2566. However, in this study, contributing reaction steps were not characterized nor were individual specific rates evaluated.
- (16) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.
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- (19) Rotzinger, F. P. *Inorg. Chem.* **1986**, *25*, 4571.
- (20) (a) The autocatalytic nature of these reactions precluded obtaining useful data by employing a stop-flow spectrophotometer (which uses equal or comparable volumes of the two reagents) since consumption of B<sub>12s</sub> by adventitious traces of O<sub>2</sub> on mixing obscured the early (slow) portion of the reaction. This difficulty was minimized in conventional mixing experiments by adding a very small known volume of a concentrated solution of the oxidant to a B<sub>12s</sub> solution of determined concentration. (b) Reactions carried out in solutions buffered with *N*-(2-acetamido)-2-aminoethanesulfonic acid ("ACES", pK<sub>a</sub> 6.9) and its conjugate base were much slower and gave poorly reproducible curves.



**Figure 1.** Kinetic profile at 387 nm for the reaction of vitamin B<sub>12s</sub> (cob(I)alamin) ( $9.2 \times 10^{-5}$  M) with  $\text{VO}(\text{ClO}_4)_2$  ( $2.5 \times 10^{-4}$  M) at 25 °C. The supporting medium was 0.02 M each in sodium phthalate and sodium biphthalate, the pH was 4.5, and  $\mu = 0.20$  M ( $\text{LiClO}_4$ ). The circles represent absorbances calculated from (6) in the text, taking  $k_1$  and  $k_2$  as 31 and  $644 \text{ M}^{-1} \text{ s}^{-1}$ . The solid line is the experimental curve. Extinction coefficients used ( $\text{M}^{-1} \text{ cm}^{-1}$ ): B<sub>12s</sub>,  $29 \times 10^3$ ; B<sub>12r</sub>,  $6.5 \times 10^3$ . Optical path length: 1.00 cm.



**Figure 2.** Profile at 387 nm for the reaction of B<sub>12s</sub> ( $6.6 \times 10^5$  M) with sodium molybdate ( $1.02 \times 10^{-4}$  M) at 25 °C. The supporting medium was 0.065 M in sodium phthalate and 0.005 M in sodium biphthalate, the pH was 5.6, and  $\mu = 0.20$  M ( $\text{LiClO}_4$ ). The circles represent absorbances calculated from sequence (11)–(13) in the text, taking  $k_1'$ ,  $k_2'$ , and  $k_3'$  as 38, 196, and  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ . The solid line is the experimental curve. Extinction coefficients used are those listed for Figure 1.

got under way and then remained nearly constant until late in the reaction, finally decreasing in the final stages (Figures 1 and 2). Fits of such kinetic profiles to autocatalytic sequences (see Results and Discussion) were achieved initially by using the program INTEGRAL to generate curves to be compared with those observed.<sup>13,21,22</sup> Specific rates resulting in reasonable agreement between calculated and observed absorbances were further refined by an iterative nonlinear least-squares procedure.<sup>23,24</sup>

(21) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,<sup>22</sup> were accomplished by a FORTRAN-77 program on an IBM 3081D computer system. The FORTRAN-IV version of the program, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH), was modified to incorporate the appropriate differential equations and stoichiometric relationships. Copies of the modified program may be obtained from R.N.B.

(22) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. In *Techniques of Chemistry*, 3rd Ed.; Lewis, E. S. Ed.; Wiley: New York, 1974; Vol. VI, Part I, p 764.

(23) This program, which was developed by R. Moore and T. W. Newton of Los Alamos National Laboratory, was obtained from Professor Gilbert Gordon. The FORTRAN-IV version was changed, with the help of Dr. J. W. Reed, to FORTRAN-77 in order to adapt to the IBM 3100 system. The program, which minimizes the function  $(\text{Abs}_{\text{calcd}} - \text{Abs}_{\text{obsd}})^2$ , uses the Gaussian method described by McWilliams and co-workers.<sup>24</sup> Trial values of the rate constants were those obtained from the INTEGRAL procedure. Individual experimental points were unweighted.

**Table I.** Kinetic Parameters for the Autocatalytic Reduction of Vanadium(IV) by Vitamin B<sub>12s</sub> (Cob(I)alamin)<sup>a</sup>

$10^4[\text{V}^{\text{IV}}]$ , M	$10^5[\text{B}_{12s}]$ , M	$[\text{HPth}^-]$ , <sup>b</sup> M	$[\text{Pth}^{2-}]$ , <sup>c</sup> M	pH	$k_1$ , <sup>d</sup> $\text{M}^{-1} \text{ s}^{-1}$	$10^{-2}k_2$ , <sup>d</sup> $\text{M}^{-1} \text{ s}^{-1}$
0.53	2.00	0.02	0.02	4.83	26	6.1
0.53	3.23	0.02	0.02	4.81	29	5.1
1.06	4.72	0.02	0.02	4.66	27	5.9
2.51	10.15	0.02	0.02	4.62	31	6.1
1.37	5.92	0.005	0.02	5.11	29	5.3
1.33	8.72	0.08	0.02	4.20	32	5.0
1.34	6.05	0.001	0.001	4.30	87	5.2
1.34	4.46	0.002	0.002	4.46	75	4.8
1.36	5.79	0.005	0.005	4.45	50	5.4
1.38	4.61	0.015	0.015	4.60	34	5.5
1.36	8.90	0.030	0.030	4.71	23	6.0
1.37	6.07	0.050	0.050	4.84	20	4.6

<sup>a</sup>Reactions were carried out at 25 °C;  $\mu = 0.20$  M ( $\text{LiClO}_4$ ).  
<sup>b</sup>HPth<sup>-</sup> = hydrogen phthalate anion. <sup>c</sup>Pth<sup>2-</sup> = phthalate anion.  
<sup>d</sup>Specific rates obtained from nonlinear least-squares refinement in which absorbances were compared with those obtained by integration of the differential equation (6). (See text and ref 13 and 23.)

Reactions of V(III) with B<sub>12s</sub> exhibited simple exponential decay curves and were first order in each reagent; these were carried out with V(III) in greater than fivefold excess. Specific rates from successive half-life values within a run generally agreed to 5%, and average values did not differ significantly from those obtained from slopes of logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs checked to better than 8%.

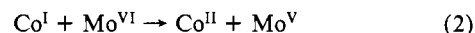
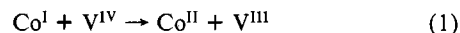
**Additional Observations.** In all cases, the electronic spectrum of the cobalt product formed with oxidants in excess corresponded to that of B<sub>12s</sub> (cob(II)alamin).<sup>8,25</sup>

Stoichiometric experiments, carried out with B<sub>12s</sub> in excess as described,<sup>8,10</sup> indicated that  $3.18 \pm 0.21$  mol of B<sub>12s</sub> were consumed per mole of Mo(VI) and  $1.84 \pm 0.08$  mol of B<sub>12s</sub> per mole of V(IV). The very high molar absorbances of the B<sub>12</sub> species, as compared with those of the vanadium- and molybdenum-center ions, precluded spectrophotometric determinations of stoichiometry with oxidant in excess.

Attempts to characterize a Mo(V) reaction species by using ESR and to estimate its concentration were unsuccessful.<sup>26</sup>

## Results and Discussion

Measured stoichiometries indicate that Mo(VI) is reduced by excess B<sub>12s</sub> to Mo(III), and V(IV) to V(II). Since, however, kinetic runs were carried out with B<sub>12s</sub> in deficiency, the reduction product in each case is taken to lie just one unit below the reactant. Mechanistic pictures (see below) in accord with net conversions (1) and (2) encounter no major inconsistencies.



Kinetic curves for oxidation of B<sub>12s</sub> in phthalate buffers (either by excess V<sup>IV</sup> or excess Mo<sup>VI</sup>) depict a relatively slow initial change, some acceleration early in the reaction, and nearly constant velocity during the intermediate stages, which is followed finally by the expected rate decrease as nearly all of the B<sub>12s</sub> is consumed (Figures 1 and 2). These features are characteristic of an autocatalytic sequence in which the drop in rate due to depletion of reactants is (except in the final stages of conversion) compensated by the growth of a catalytic species.

It is proposed that the catalytic species is, in both cases, the principal reduction product, which is reduced by B<sub>12s</sub> at a greater specific rate than that for the oxidant taken, generating a third metal oxidation state (two units below the original), which is then

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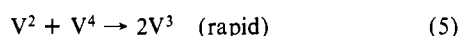
(26) Attempted detection of X-band ESR spectra of reduced molybdenum solutions utilized a Varian V-4500 spectrometer. For a summary of the difficulties surrounding measurements of ESR spectra of simple Mo(V) species in solution, see: Steifel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 67.

**Table II.** Kinetic Data for the Reduction of Vanadium(III) by Vitamin B<sub>12s</sub> (Cob(I)alamin)<sup>a</sup>

10 <sup>4</sup> [V <sup>III</sup> ], M	10 <sup>5</sup> [B <sub>12s</sub> ], M	10 <sup>-2</sup> k, M <sup>-1</sup> s <sup>-1</sup>
1.29	2.63	5.8
1.29	2.76	6.2
1.30	3.29	6.1
1.30	1.42	6.6
2.59	3.13	6.4
2.58	5.16	6.4
2.57	4.54	6.4
2.59	4.41	6.4
		av 6.3 ± 0.2

<sup>a</sup> Reactions were carried out at 25 °C; μ = 0.20 M (LiClO<sub>4</sub>). Solution were buffered at pH 4.60–4.70 by addition of equal concentrations of phthalate and biphthalate.

consumed by excess oxidant. For oxidation by V<sup>IV</sup>, we suggest the sequence (3)–(5), a path that is consistent also with experi-



ments using externally generated vanadium(III). If step (5) is assumed to be rapid enough to allow its combination with (4), this sequence generates the differential equation (6). To apply

$$\frac{-d[\text{V}^4]}{dt} = \frac{-d[\text{Co}^1]}{dt} = k_1[\text{V}^4][\text{Co}^1] + k_2[\text{V}^3][\text{Co}^1] \quad (6)$$

the Runge–Kutta integration technique<sup>22</sup> to this system,<sup>27</sup> a 5-s time interval between kinetic points was taken, and values of k<sub>1</sub> and k<sub>2</sub> were allowed to vary. Integration then yielded the concentrations of V<sup>4</sup>, V<sup>3</sup>, Co<sup>1</sup>, and Co<sup>2</sup> at 5-s intervals. Incorporation of molar absorbances of the two B<sub>12</sub> species (Co<sup>1</sup> and Co<sup>2</sup>) yielded calculated values for the optical density of the mixture at each point.<sup>28</sup> Values of k<sub>1</sub> and k<sub>2</sub> giving a reasonable fit to the observed profiles were used as trial values for a final interative nonlinear least-squares refinement.<sup>23</sup>

Table I lists values of k<sub>1</sub> and k<sub>2</sub> resulting from refinements applied to the V(IV)–B<sub>12s</sub> reaction. Calculated absorbances (circles) obtained for a typical run are compared with the corresponding experimental curve in Figure 1. Rate constants are seen to be nearly independent of reagent concentrations<sup>29</sup> and of pH within the indicated ranges. However, k<sub>1</sub> (pertaining to the Co(I)–V(IV) reaction) is inhibited by phthalate, approaching 19 M<sup>-1</sup> s<sup>-1</sup> at high phthalate concentrations and 90 M<sup>-1</sup> s<sup>-1</sup> at low concentrations, thus indicating the partition of V(IV) between two ligation levels (differing by a single phthalate) of which the more fully ligated is the less reactive. Such a distribution between paths is described by (7), where k and k' refer to the more reactive

$$(k_1)_{\text{obsd}} = \frac{k + k'K[\text{Pth}^{2-}]}{1 + K[\text{Pth}^{2-}]} \quad (7)$$

(27) Since the sequence (3)–(5) implies that V(II) attains only a small steady-state concentration, Δ[V<sup>3</sup>] ≈ -Δ[V<sup>4</sup>]. With this constraint, (6) can be integrated in closed form, but work with the resulting integrated expression is more cumbersome than the approach chosen. Moreover, our procedure is readily adaptable to alternate trial mechanisms.

(28) Values of ε<sub>Co(I)</sub> (2.9 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) and ε<sub>Co(II)</sub> (6.5 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) at 387 nm were taken from the initial and final absorbances of the reaction mixture. Molar absorbances of VO<sup>2+</sup> and V(III) are negligible in relation to these.

(29) In experiments using higher concentrations of V(IV) (0.0004–0.0012 M), necessarily involving higher values of [V(III)] during the progress of the reaction, apparent values of k<sub>2</sub> increase significantly, suggesting the participation of a dimeric form of V(III) that is somewhat more reactive toward B<sub>12s</sub> than is the monomer. The data at hand are too few and of insufficient precision to allow calculation of a specific rate pertaining to the dimer or the association constant governing the monomer–dimer equilibrium. An analogous trend was not observed for values of k<sub>1</sub>.

**Table III.** Kinetic Parameters for the Autocatalytic Reduction of Molybdenum(VI) by Vitamin B<sub>12s</sub> (Cob(I)alamin)<sup>a</sup>

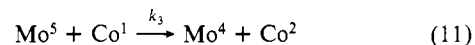
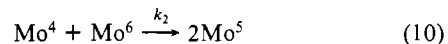
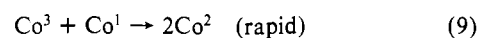
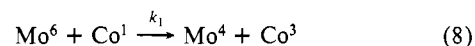
10 <sup>4</sup> [Mo <sup>VI</sup> ], M	10 <sup>5</sup> [B <sub>12s</sub> ], M	[Pth <sup>2-</sup> ] <sup>b</sup> , M	pH	k <sub>1</sub> (or k <sub>1'</sub> ) <sup>c,e</sup> , M <sup>-1</sup> s <sup>-1</sup>	10 <sup>-2</sup> k <sub>2</sub> (or 10 <sup>-2</sup> k <sub>2'</sub> ) <sup>d,e</sup>
1.03	5.07	0.065	5.64	35	1.9
1.03	9.08	0.065	5.62	39	2.4
1.42	6.05	0.065	5.62	32	2.3
2.13	9.08	0.065	5.62	31	2.5
3.95	8.90	0.065	5.61	35	2.5
1.04	9.08	0.033	5.62	12	1.8
1.03	7.16	0.016	5.61	6.3	2.8
1.04	7.77	0.065	5.86	12	1.1
1.00	6.63	0.065	5.47	79	2.9
1.00	8.50	0.065	5.32	147	5.3
0.99	8.86	0.065	5.27	187	5.9

<sup>a</sup> Reactions were carried out at 25 °C; μ = 0.20 M (LiClO<sub>4</sub>). Solutions were buffered with measured concentrations of phthalate and biphthalate. <sup>b</sup> Pth<sup>2-</sup> = phthalate anion. <sup>c</sup> Specific rates for initiation reactions 8 and 12 in text. <sup>d</sup> Specific rates for Mo<sup>4</sup>–Mo<sup>6</sup> reaction (eq 10 and 14 in text). <sup>e</sup> Values obtained from nonlinear least-squares refinements in which absorbances were compared with those resulting from differential equations based on reaction sequence (8)–(11) (or sequence (12)–(14)). (See text and ref 13, 23, and 33).

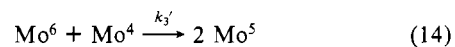
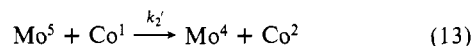
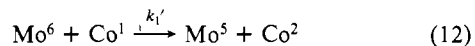
and less reactive forms of V(IV), and K is the association constant for anation by phthalate (Pth<sup>2-</sup>). Nonlinear least-squares refinement of values of (k<sub>1</sub>)<sub>obsd</sub> yields k = 127 ± 7, k' = 17 ± 1 M<sup>-1</sup> s<sup>-1</sup>, and K = (4.7 ± 0.8) × 10<sup>2</sup> M<sup>-1</sup> (25 °C, μ = 0.20 M).

The value of k<sub>2</sub>, applying to the V<sup>3</sup>–Co<sup>1</sup> reaction, (4), is confirmed by examination of straightforward exponential kinetic profiles of this reaction in the absence of V(IV) (Table II). The specific rate estimated in this manner is (6.3 ± 0.2) × 10<sup>2</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>30,31</sup>

Kinetic curves for the Mo(VI)–B<sub>12s</sub> reactions exhibit the same general features as those for reaction with V(IV), but the region in which the rate is nearly constant persists until much later in reaction (Figure 2). Two reaction sequences, (8)–(11) and (12)–(14), appear to be compatible with the kinetic profiles for this system. In both, the rapid step is the reaction between B<sub>12s</sub> (Co<sup>1</sup>) and Mo<sup>6</sup>, and in both, Mo<sup>5</sup> is generated from Mo<sup>6</sup> and Mo<sup>4</sup>. The initiation steps are different; the first sequence begins with a slow 2e transaction between Mo(VI) and Co<sup>1</sup>



whereas the alternate sequence is initiated by a single-electron transfer between the same two reaction partners

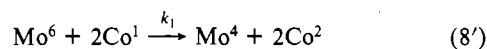


Since the Co<sup>3</sup>–Co<sup>1</sup> reaction has been found to proceed at a specific

(30) Our suggestion that comproportionation reaction 5 between V(II) and V(IV) is rapid occasions some comment in view of the report by Newton and Baker<sup>31</sup> that the specific rate for the corresponding reaction at 0 °C and pH 0–1 lies near 0.1 M<sup>-1</sup> s<sup>-1</sup>. Aside from the temperature difference, our reactions are carried out 4–5 pH units higher and in a phthalate medium, in which one or both vanadium reactants are complexed. The low extinction coefficients of the vanadium species militate against direct kinetic examination of this reaction in our media, because the concentrations needed to obtain measurable absorbance changes result in precipitation. In a few instances where precipitation is delayed, we estimate a lower limit 6 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> (pH 5.4) for this reaction.

(31) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1964**, *3*, 569.

rate near  $10^7 \text{ M}^{-1} \text{ s}^{-1}$  under our conditions,<sup>32</sup> steps 8 and 9 may be combined, yielding (8'), and making the two sequences very



nearly kinetically equivalent except during the very early stages of reaction.<sup>33</sup>

Integration procedures, applied to the resultant differential equations, and subsequent refinement (both carried out in a manner analogous to that described for V<sup>IV</sup>-B<sub>12s</sub>) yield specific rates listed in Table III for the slower steps in both sequences but give no reliable information about the Mo<sup>5</sup>-Co<sup>1</sup> reaction ( $k_3$  or  $k_2'$ ) except that it is much more rapid than the other steps.<sup>34</sup> Figure 2 compares calculated absorbances for a representative run with the observed kinetic curve.

Although our experiments encompass a relatively narrow range of acidities<sup>35</sup> and buffer concentrations, it is clear that specific rates of both evaluable kinetic components are dependent on the medium. That for the initial B<sub>12s</sub>-Mo(VI) reaction ( $k_1$  or  $k_1'$ ) is very nearly proportional to  $[\text{H}^+]^2$ , whereas that for the Mo<sup>6</sup>-Mo<sup>4</sup> reaction ( $k_2$  or  $k_3'$ ) conforms to binomial expression 15, where

$$(k_2)_{\text{obsd}} = a[\text{H}^+] + b[\text{H}^+]^2 \quad (15)$$

$a = (6.9 \pm 0.5) \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$  and  $b = (8 \pm 1) \times 10^{12} \text{ M}^{-3} \text{ s}^{-1}$ . Both dependencies almost certainly reflect the partition of Mo(VI) into three protonation levels, with reactivity increasing with the degree of protonation (as is often the case with reduction of oxyacid species). The reaction with B<sub>12s</sub> appears to be dominated by a

(32) Ryan, D. A.; Espenson, J. H.; Meyerstein, D.; Mulac, W. A. *Inorg. Chem.* **1987**, *17*, 3726.

(33) This near equivalence reflects the circumstance that the specific rate for the Mo<sup>5</sup>-Co<sup>1</sup> reaction ( $k_3$  or  $k_2'$ ) is very much greater than that for the Mo<sup>6</sup>-Co<sup>1</sup> reaction ( $k_1$  or  $k_1'$ ). An analogous ambiguity does not complicate the V<sup>4</sup>-Co<sup>1</sup> reaction because the corresponding individual constants, pertaining to reactions 3 and 4, are more nearly equal, each being, however, much less than that for the V<sup>2</sup>-V<sup>4</sup> reaction (eq 5).

(34) The quality of fit between calculated and observed absorbances is virtually independent of the specific rate assigned to the Mo<sup>5</sup>-Co<sup>1</sup> reaction, provided this value exceeds  $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . For ease in computation, this specific rate was fixed at  $10^5 \text{ M}^{-1} \text{ s}^{-1}$  during refinement, and the remaining rate constants were allowed to "float".

(35) The upper limit of our pH range is fixed by the pK<sub>A</sub> of the biphthalate anion, whereas reactions at pH values below 5.2 are too rapid to monitor by our procedures.

relatively small fraction bearing two protons more than the principal Mo(VI) component.

In addition, the Mo<sup>6</sup>-Co<sup>1</sup> reaction, but not the Mo<sup>6</sup>-Mo<sup>4</sup> reaction, is approximately first order in phthalate (within the range examined), suggesting that partition of Mo(VI) between ligation levels is occurring, with the more fully ligated species being the more readily reduced (in contrast to what has been inferred for the V(IV) system).

Although a more specific interpretation of the observed kinetic behavior must await detailed study of the coordination equilibria involving vanadium and molybdenum centers in phthalate media, one may nevertheless ask why, in the suggested reaction sequences, the oxidation state taken is reduced much more slowly than that lying one unit below, although the latter has the less favorable potential. In the V(IV) system, for which we may assume both reductions by B<sub>12s</sub> (reactions 3 and 4) to be outer sphere, V<sup>4</sup> is an oxo-bound species whereas the two lower states are not. The 4+/3+ electron self-exchange will then require marked structural adjustment (severe stretching of the V<sup>IV</sup>=O bond) to achieve a configuration that is intermediate between the two ground states, and this should be reflected in a Franck-Condon barrier which substantially exceeds that for the 3+/2+ exchange, thus retarding electron transfer to V<sup>4</sup>.

Extension of this reasoning to the Mo(VI) reaction is more tenuous, for here we are less certain as to the ligation states and degrees of aggregation (monomer, dimer, or oligomer) of the various species involved. Moreover, our kinetic analysis has led to a mechanistic ambiguity. If the initial Mo<sup>6</sup>-Co<sup>1</sup> step is a 1e transaction (sequence 12-14) and if we are dealing again with monomers, an argument similar to that applied to the V(II,III,IV) system is not unreasonable. If, on the other hand, two electrons are transferred to Mo<sup>6</sup> (sequence 8-11), we must infer initiation to occur through an inner-sphere process, for outer-sphere 2e transfers have not been documented. A sluggish first step might then reflect a poorly associated Mo(VI)-O-Co(I) precursor complex, a slow oxygen atom transfer within the complex, or a combination of both.

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**Registry No.** Vitamin B<sub>12s</sub>, 18534-66-2; vanadium(IV), 22541-76-0; molybdenum(VI), 16065-87-5.