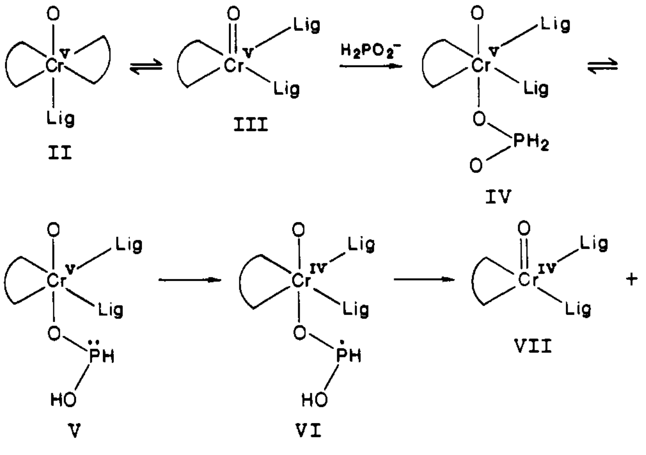
the chelate rings do not occur during the more rapid reductions of Cr(V) with 1e metal-center reductants.[4,8a] Ligand-exchange processes are favored here by the sluggishness of the Cr^{IV}–P^{I} reaction[23] and by the high concentration of $H_2PO_2^-$ used to allow the initial reaction to proceed at a convenient rate. Partition of the resulting Cr(III) products between hypophosphite-bound and carboxylate-bound species probably reflects the same equilibration process, for the ratio of the two types of ligation rises as the ratio $[H_2PO_2^-]/[Lig^-]$ in the reaction mixture is increased.

Jenkins and Yost[21d] have emphasized the importance of intramolecular proton transfer (P–H to O–H) in hypophosphite in determining its rates of oxidation by a variety of reagents. This transfer, however, proceeds with a half-life period greater than 2 days in the absence of Cr(V) in media similar to ours. Although there are other possibilities, the relatively high specific rates at which $H_2PO_2^-$ reacts with both Cr^V (k_1) and Cr^{IV} (k_3) in this study may then reasonably be attributed to preliminary coordination of the reductant to the strongly acidic Cr^V or Cr^{IV} center, thus mobilizing the P-bound protons.[24,25]

If, as we suspect, the Cr^V–P^I reaction proceeds through an oxygen-bridged intermediate, the bridge must arise from hypophosphite, rather than from the Cr(V) chelate, for there is no site on $H_2PO_2^-$ that can accommodate an incoming donor atom. An earlier study[4b] has shown that the Cr(V) chelate taken here undergoes additional ligation to form complex II (K_{assn} 51 M^{-1}) in the presence of an excess of the parent carboxylate anion; in the buffer systems used, only 5–12% of the added Cr(V) is present as the 5-coordinate species I. Loss of the axial carboxyl group from II would leave a place for ligation by $H_2PO_2^-$, but such a path should lead to values of k_1 that are dependent on $[Lig^-]^{-1}$, contrary to what is observed.

Our findings are consistent with sequence 8, in which breakage of one of the chelate rings in II (but not the departure of carboxylate) allows attachment of hypophosphite to form intermediate IV. The function of this intermediate is simply to hold the Cr^V and P^I centers in proximity; the bridging oxygen is not transferred.



$H_2PO_2^\bullet$ (8)

The tautomeric shift IV → V is then facilitated by the nearby Cr^V. This leaves an exposed electron pair on phosphorus and precedes the act of electron transfer (V → VI).

Although it is conceivable that the Cr(IV)–P(II) intermediate VI, formed via internal electron transfer, might undergo a second act of transfer, yielding Cr(III)-bound phosphorus(III), the nature of the predominant Cr(III) products requires that the principal fate of VI is heterolysis to the $H_2PO_2^\bullet$ radical (for which Cr^V and Cr^{IV} then compete in reactions 4 and 6) and a coordinatively unsaturated Cr^{IV} species, which, prior to further reduction, undergoes breakage of the chelate rings and the ligand redistribution reflected in the mix of Cr(III) products observed. The Cr(IV)–$H_2PO_2^-$ reaction (eq 3) which also appears to involve a bridged intermediate, may utilize a similar path, but one in which the participants are devoid of the chelate rings present in the Cr(V) reactant.

When autocatalysis in the Cr(V)–HSO_3^- system, leading to its "clocklike" character, was first described,[2,8b] it appeared that the proposed catalytic sequence might apply uniquely to the S(IV) reductant chosen. It is now evident, however, that a closely analogous mechanism operates not only in the Cr(V)–$H_2PO_2^-$ reaction at hand, but also in the reductions of Cr(V) with such diverse species as iodide, thiocyanate, and ascorbic acid.[26] Whether similar sequences can be established in the reductions of additional metal-center oxidants remains an open question.

Acknowledgment. The authors are grateful to Professor J. H. Espenson for valuable discussions.

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(23) For additional examples of slow reactions passing through Cr(IV) in which the ligand environment about that center is altered, see: (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *Ibid.* **1958**, *62*, 357. (c) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(24) The ratios $k_{Cr(IV)}/k_{Cr(V)}$ for reactions of these oxidation states with $H_2PO_2^-$ (k_3/k_1) and with $H_2PO_2^\bullet$ (k_4/k_2) are seen to lie below the estimated[25] lower limit ($k_{Cr(IV)}/k_{Cr(V)} > 20$) for outer-sphere reductions of these states by $Ti(OH)^{2+}$ in a similar medium. However, no obvious mechanistic inference may be drawn from this discrepancy since the predominant Cr(IV) species in this study are different from that in the Cr(V)–Ti(III) system.

(25) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

(26) Ghosh, S. K., unpublished experiments, 1986.

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Electron Transfer. 83. Reductions of Unsaturated Esters with Vitamin B_{12s} (Cob(I)alamin)[1]

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Received August 4, 1986

The diesters of maleic and fumaric acid are rapidly reduced to succinic esters by vitamin B_{12s} (cob(I)alamin) in aqueous media. The dimethyl ester of acetylenedicarboxylic acid is reduced in two stages: the first (very rapid) stage yields a fumaric ester, which is then converted more slowly to succinate. Reactions are first order each in redox partners and are fastest at highest acidities. Kinetic behavior is consistent with the partition of B_{12s} into an inactive nonprotonated, a moderately reactive monoprotonated, and a very reactive diprotonated form. It is proposed that the latter is a Co–H species, having hydride-like character, which is oxidized at a specific rate $>10^4$ M^{-1} s^{-1} (25 °C). The relative reactivities of acetylenic and olefinic esters (rate ratios 10^4–10^5) indicate that these reactions, like those of the parent diacids, are heterolytic (2e) rather than homolytic (1e) in nature. The reduction of acetylenedicarboxylate to fumarate is a net trans addition for which an olefinic–carbanion intermediate, which may maintain its geometric configuration, is suggested.

The action of strong reducing agents on vitamin B_{12} yields B_{12r} (cob(II)alamin), which may be further converted to vitamin B_{12s} (cob(I)alamin).[2] This cobalt(I) complex reduces a number of diverse organic species in solution,[3] leading to its expanding ap-

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Table I. Stoichiometries of the Reactions of Vitamin B_{12s} (Cob(I)alamin) with Unsaturated Carboxylic Esters[a]

ester	pH	10^5[ester], M	$10^5[B_{12s}]$, M	$10^5\Delta[B_{12s}]$, M	$\Delta[B_{12s}]/\Delta$[ester]
dimethyl maleate	2.3	1.03	7.40	2.45	2.38
	3.1	1.23	7.50	2.28	1.86
	3.3	0.62	7.30	1.21	1.94
	3.6	1.23	7.40	2.49	2.03
dimethyl fumarate	3.4	3.11	9.00	5.44	1.75
	3.5	2.48	8.75	5.18	2.08
	3.7	1.89	8.80	3.24	1.72
dimethyl acetylenedicarboxylate	3.1	1.09	6.23	2.11,[b] 2.28[c]	1.94,[b] 2.09[c]
	3.3	1.41	7.45	2.33,[b] 2.88[c]	1.66,[b] 2.04[c]
	3.4	1.78	9.05	3.62,[b] 4.14[c]	1.97,[b] 2.34[c]

[a] Reactions were monitored at 387 nm. [b] Rapid reaction immediately after mixing reagents. [c] Slower reaction after initial absorbance drop.

plication to synthetic sequences.[4] An earlier report[5] dealt with the reductions, using B_{12s}, of unsaturated dicarboxylic acids and presented evidence that these conversions are initiated by two-electron, rather than single-electron,[6] transactions. The present study, which treats the analogous diesters, points to a similar conclusion, but there are perceived differences in detail.

Experimental Section

Materials. Unsaturated esters (Aldrich), sodium borohydride and glycine (Fisher), and hydroxocobalamin hydrochloride (Sigma) were used as received. Lithium perchlorate, used as a supporting electrolyte in kinetic experiments, was prepared as described.[7] All reactions were carried out under oxygen-free conditions in distilled water that had been previously boiled and purged with N_2 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[8] and $NaBH_4$–$PdCl_4^{2-}$ in basic solution.[6a,c] For kinetic experiments using conventional mixing and for stoichiometric experiments, solutions were prepared in spectrophotometric cells;[8] for stop-flow experiments, solutions were prepared externally and then transferred under nitrogen.

Stoichiometric Studies. Stoichiometries of the three most rapid reactions, each with B_{12s} in excess, were determined in buffered media by generating Co(I) in acid solution, buffering the solution, adding a deficiency of the ester in methanol, waiting about 20 min, and then measuring the decrease in absorbance at 387 nm. The resulting changes were compared with those occurring when B_{12s} reacted with excess oxidant. Corrections were made for the loss in absorbance (about 10%) when the corresponding volume of pure methanol was added to B_{12s}. Results appear in Table I.

The behavior of acetylenedicarboxylic acid dimethyl ester in these studies was analogous to that previously observed for the parent acid.[5] Reaction here took place in two parts: a very rapid drop occurred immediately on mixing, followed by a slower decrease of comparable magnitude. As with the parent acid, both the starting material and its primary reduction product reacted with B_{12s}.

Kinetic Studies. Rates were estimated from measurements of decreases of absorbance at 387 nm, by using either a Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped flow spectrophotometer. Acidities were regulated by adding known quantities of glycine or phthalate buffers to the oxidant or reductant solutions before mixing,[9] and pH values of the resulting solutions were checked experimentally. Total ionic strengths were generally maintained near 0.2 M by addition of $LiClO_4$. Reactions were first order each in ester and Co(I) but were generally carried out with the ester in greater than tenfold excess. Experimental difficulties associated with stop-flow experiments using B_{12s} (transfer of very dilute solutions of a strong reductant, differentiation between the primary reaction and that of O_2, competitive regeneration of B_{12s} by added hydride, and distortion of the kinetic traces due to H_2 bubble formation) have been described.[3c,5,6c]

Table II. Representative Kinetic Data for the Reaction of Vitamin B_{12s} (Cob(I)alamin) with Dimethyl Maleate, 25 °C[a]

$10^5[H^+]$, M	$10^{-2}k_{obsd}$,[b] $M^{-1}\,s^{-1}$	$10^{-2}k_{calcd}$,[c] $M^{-1}\,s^{-1}$	$10^5[H^+]$, M	$10^{-2}k_{obsd}$,[b] $M^{-1}\,s^{-1}$	$10^{-2}k_{calcd}$,[c] $M^{-1}\,s^{-1}$
0.13	0.123	0.101	12.3	0.50	0.47
0.47	0.24	0.22	21.4	0.53	0.54
0.60	0.24	0.25	25.7	0.57	0.57
0.76	0.31	0.27	50	0.85	0.75
1.23	0.29	0.31	58	0.84	0.80
2.19	0.30	0.35	78	1.02	0.94
2.40	0.34	0.36	81	1.03	0.96
4.2	0.36	0.39	138	1.39	1.36
6.2	0.45	0.42	209	1.75	1.85
8.7	0.43	0.44			

[a] The supporting electrolyte used was $LiClO_4$ (μ = 0.20 M). Glycine and phthalate buffers were used. $[B_{12s}] = (6–8) \times 10^{-5}$ M; [maleic ester] = 3×10^{-4} to 3×10^{-3} M. [b] Second-order rate constants. [c] Calculated values obtained from (2) in text, by using parameters in Table III.

Conversions were followed for at least 5 half-lives. Specific rates from successive half-life values within a run generally agreed to within 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%.

Kinetic experiments gave no indication of cobalt-containing intermediates formed or destroyed on a time scale comparable to that for disappearance of B_{12s}. The electronic spectrum of the cobalt product formed corresponded, in all cases, to that of B_{12r} (cob(II)alamin).[8,10] Isosbestic points at 343, 416, and 543 nm were observed.

Experiments with B_{12s} in excess indicated that the primary product formed from reduction of acetylenedicarboxylic ester is dimethyl fumarate rather than dimethyl maleate. When the acetylenic ester (1.53×10^{-5} M) was mixed with B_{12s} (1.0×10^{-4} M) at pH 4.2, a rapid drop in the B_{12s} absorbance occurred, followed by a near-exponential decrease having a specific rate of 0.0053 s^{-1} but no additional (slower) kinetic component. When analogous experiments were carried out with the corresponding fumaric and maleic esters, there was no initial drop, but exponential decays having specific rates of 0.0056 (fumarate) and 0.0025 s^{-1} (maleate) were observed.[11]

Dimethyl glutarate did not react detectably with B_{12s} under our reaction conditions. In contrast, the reaction of acetylenedicarboxylic acid dimethyl ester was too rapid to monitor, even with stop flow. At pHs between 2 and 8, reactions with this ester at the 1.5×10^{-4} M level had half-life values less than 1 msec, corresponding to a bimolecular rate constant greater than 5×10^6 $M^{-1}\,s^{-1}$.

Results and Discussion

Esters of both maleic and fumaric acids are seen (Table I) to consume nearly 2 mol of cob(I)alamin/mol of oxidant. Since B_{12r} (cob(II)alamin) is formed, reactions may be written schematically

$$\underset{\text{cis or trans}}{\text{MeOOC—CH=CH—COOMe}} + 2\text{Co(I)} + 2\text{H}^+ \rightarrow \text{MeOOC—CH}_2\text{—CH}_2\text{—COOMe} + 2\text{Co(II)} \quad (1)$$

In no case was there any indication that further reduction of the ester function to an aldehyde or alcohol had taken place. The reaction of acetylenedicarboxylic ester is seen to proceed in two

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(1) Sponsorship of this work by the National Science Foundation (Grant No. 8313253) is gratefully acknowledged.

(2) Reviews: (a) Halpern, J. In *B_{12}*; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, p 501. (b) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105. (c) Pratt, J. M. *Inorganic Chemistry of Vitamin B_{12}*; Academic: London, 1972; p 96.

(3) (a) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 824. (b) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 4060. (c) Pillai, G. C.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3353.

(4) See, for example: (a) Dolphin, D. *Methods Enzymol.* **1971**, *18C*, 34. (b) Fischli, A. *Helv. Chim. Acta* **1982**, *65*, 1167, 2697.

(5) Pillai, G. C.; Gould, E. S. *Inorg. Chem.*, in press.

(6) Unequivocal examples of 1e reductions by B_{12s} are recognized. See, for example: (a) Kaufmann, E. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7051. (b) Balasubramanian, B. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 1791. For an ambiguous case, see: (c) Balasubramanian, P. N.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 1794.

(7) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

(8) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 2635.

(9) Master solutions of the esters were made in methanol to minimize complications resulting from ester hydrolysis. The small volumes of methanol added with the reacting esters were shown not to affect kinetic results.

(10) Bonnet, R. *Chem. Rev.* **1983**, *63*, 573.

(11) Attempts to confirm the formation of dimethyl fumarate, rather than the corresponding maleate, from reduction of the acetylenic ester by extracting the reaction mixtures with CH_2Cl_2 and subjecting the extracts to gas chromatography were unsuccessful in our hands, due in part to the very low level of substrate used, and in part to the similarity of retention times (on several different column materials) exhibited by the two isomeric esters. We thank Dr. S. Thakkar for help in this endeavor.

Table III. Kinetic Parameters for the Reactions of Vitamin B_{12s} (Cob(I)alamin) with Unsaturated Dicarboxylic Esters[a]

ester	k,[b] M^{-1} s^{-1}	$10^{-4}k'$,[c] M^{-2} s^{-1}	pK_R[d]
dimethyl maleate	40 ± 4	7.0 ± 1.0	5.4
diethyl maleate	32 ± 6	2.9 ± 0.6	5.5
dimethyl fumarate	183 ± 18	6.1 ± 1.0	5.4
diethyl fumarate	107 ± 10	3.1 ± 0.4	5.2
acetylenedicarboxylic acid dimethyl ester	$>5 \times 10^6$		
monoethyl fumarate	48 ± 2[e] 350 ± 10[f]	5.9 ± 0.4	5.9

[a] Reactions were carried out at 25 °C, $\mu = 0.2$ M ($LiClO_4$). [b] Specific rates pertaining to the nonprotonated (uncharged) esters, obtained by nonlinear least-squares treatment of kinetic data using (2) (see text). [c] Specific rates for the acid-catalyzed path, obtained by refinement of kinetic data using (2) and (3). [d] pK_A for B_{12s}. [e] Specific rate pertaining to the deprotonated (−1) form of monoethyl ester. [f] Specific rate pertaining to the neutral form of monoethyl ester.

steps: 2 equiv of B_{12s} are consumed very rapidly, yielding dimethyl fumarate, which, in turn, reacts with an additional 2 equiv of Co(I).

Representative kinetic data for the reduction of dimethyl maleate constitute Table II. For this and the other diesters, rates are seen to increase with acidity, but the dependencies are less marked than observed for the corresponding reactions of the parent acids.[5] Since theses oxidants are devoid of COOH groups, protonation equilibria must involve functions elsewhere in the system. Protonation of the benzimidazole side chain of B_{12s} near pH 5,[12] which has been shown to accelerate B_{12s} reductions of the analogous diacids[5] and those of oxyhalogen species as well,[6c] may be presumed to apply here. Additional increases at lower pHs point to a second acid-base equilibrium, which shows no sign of kinetic saturation in the range examined. If, in analogy to previous systems,[5,6c] it is assumed that the nonprotonated form of B_{12s} is negligibly reactive, operation of the two protonation equilibria leads to eq 2, where k_{obsd} is the second-order rate constant observed

$$k_{obsd} = \frac{[H^+]}{K_R + [H^+]}(k + k'[H^+]) \qquad (2)$$

at a given acidity, k and k' are rate constants pertaining to the two paths, and K_R is the acidity constant for the protonated form of B_{12s}.

The acidity pattern for the reduction of the monoethyl ester of fumaric acid is complicated by a third protonation equilibrium, the ionization of the free carboxyl group (pK_A 3.07).[13] This system may be described by eq 3, a slight modification of the

$$k_{obsd} = \frac{[H^+]}{K_R + [H^+]}\left(\frac{k_0K_A + k_1\,[H^+] + k'[H^+]^2}{K_A + [H^+]}\right) \qquad (3)$$

relationship applying to the reductions of the parent diacids.[5] Here, k_0 and k_1 are specific rates for the deprotonated (anionic) and protonated forms of this monoester, and k' again pertains to the high acidity path.

Nonlinear least-squares treatment[14] of the kinetic data for the four diesters (using eq 2) and the monoester (using eq 3) yields specific rates listed in Table III for the various contributing paths. Values of the rate constants for dimethyl maleate, calculated from (2), are compared with observed specific rates in Table II.

Undoubtedly the salient feature of this study is the very high rate for the acetylenic diester, which is reduced 10^4–10^5 times as rapidly as its alkenoic analogues under our conditions. A ratio of this magnitude, which is observed also for B_{12s} reductions of the corresponding dicarboxylic acids,[5] may be considered to be characteristic of a nucleophilic rather than a free-radical[15] addition and, in conjunction with the stereospecific course of the reaction (see below), indicates that the reduction is initiated by a 2e rather than a single-electron transaction.

At pHs greater than 3, where the acid-catalyzed (k') component is a minor one, the fumaric esters are found to be more reactive than the maleic, an apparent reversal of the order earlier observed for the analogous diacids.[5] The enhanced rate for maleic acid was attributed to internal hydrogen bonding between carboxyl groups, which was thought to restrict rotation about the C–C single bonds and thus to improve conjugation; this effect disappears on esterification. Note also that the anionic ($-COO^-$) form of fumarate monoester reacts about one-seventh as rapidly as the uncharged form. As in a variety of systems, including previously investigated[3c,5] reductions by B_{12s}, protonation of the oxidant facilitates reduction.

Acidity constants (pK_R values) for the conjugate acid of B_{12s} obtained from the five refinements are seen to be internally consistent and are in agreement with the pK reported by Rubinson and co-workers (5.6 in 0.5 M KCl).[12] The appearance of K_R in the denominators of (2) and (3) indicates that the effectiveness of B_{12s} as a reductant increases on protonation. This unusual facet of B_{12s} chemistry has been noted[6c] and attributed to a conformational change accompanying protonation of the benzimidazole function on the side chain, a process which may be thought to make the Co(I) center more accessible.

Inclusion of the acid-dependent k' term in both rate laws points to the existence of an additional reaction path proceeding through an activated complex featuring both redox partners and an additional proton. This path may, in principle, result from additional protonation of B_{12s} or protonation of the ester prior to the electron-transfer act. Bimolecular rate constants (pertaining to the protonated species) for such a path may be evaluated by multiplying k' (about 10^4 M^{-2} s^{-1} in each case) by the appropriate acidity constant. If the esters (for which pK_A may be estimated as −7)[16a] have undergone protonation, the protonated forms must be reacting at specific rates near 10^{11} M^{-1} s^{-1}, i.e. more rapidly than the diffusion-controlled limit in aqueous media.[16b] It is then reasonable to conclude that the k′ path stems instead from a second protonation of B_{12s}.

The nature of such a protonation (at very low pH) and, indeed, whether it occurs at all in aqueous media constitute unsettled questions. Earlier spectral studies by Das and co-workers[17] provided no support for such protonation. Lexa and Saveant,[18] in studying the variation of the B_{12s}/B_{12r} potential with pH, found a discontinuity near pH 1, which they attributed to an acid–base equilibrium involving B_{12s}, but more recent measurements by Rubinson, Mark, et al.[12] do not confirm this. Schrauzer and Holland[3b] have presented evidence that protonation of B_{12s} in acetic acid gives a cobalt species having a redox chemistry characteristic of a hydride source, with a spectrum unlike that of B_{12s} in water. Other aspects of B_{12s} chemistry have been considered similarly in terms of a cobalt-protonated reactant having, at the same time, the character of a Co(III) hydride.[19] The occurrence of a k' term

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(12) See, for example: Rubinson, K. A.; Parekh, H. V.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.* **1983**, *22*, 458.

(13) This pK value, for which we can find no previous report, pertains to 25 °C and was determined potentiometrically by partial acidimetric titration in 0.2 M $LiClO_4$.[3c]

(14) These treatments minimized the function $(k_{obsd} - k_{calcd})^2$, where the k's represent second-order specific rates; values of k_{calcd} were obtained from eq 2 and 3. Individual rate constants were weighted in inverse proportion to the square roots of their uncertainties. During these refinements, values of k, k', K_R, and (where appropriate) k_0 were allowed to vary, but K_A for monoethyl fumarate was kept fixed at the value here determined.[13]

(15) Compare, for example the following two references: (a) Julia, M. in *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Dekker: New York, 1969; p 336. (b) Acheson, R. M. *Adv. Heterocycl. Chem.* **1963**, *1*, 125. (c) This trend probably reflects the increased electronegativity of triply bonded carbon. See, for example: Rutledge, T. F. *Acetylenic Compounds*; Reinhold: New York, 1968; Chapter 1.

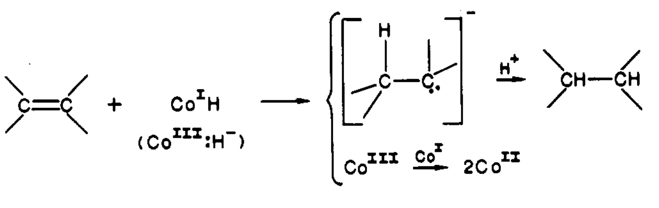
(16) See, for example: (a) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223 (Table XXIV). (b) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; p 96.

(17) Das, P. K.; Hill, H. A. O.; Pratt, J. M.; Williams, R. J. P. *Biochim. Biophys. Acta* **1967**, *141*, 644.

(18) Lexa, D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1976**, *98*, 2652.

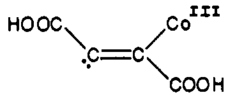
(19) See, for example: (a) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc. A* **1968**, 2886. (b) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1.

Scheme I



in the rate laws for five of our systems appears to be consistent with such a formulation. Since this path exhibits no kinetic saturation with respect to $[H^+]$ above pH 2, pK_A for the protonation should fall below 0, and the quantity of diprotonated B_{12s} is too small to be detected spectrophotometrically in the solutions at hand. The bimolecular specific rates for reactions of diprotonated B_{12s} with our esters would then exceed 10^4 M^{-1} s^{-1}.

The reduction of the acetylenic ester to fumarate results in a net trans addition, which may be taken to be closely related to the analogous transformation of the parent diacid.[5] The latter was depicted as a heterolytic sequence passing through (at least) one carbanion-like intermediate of type I, which is thought[20] to preserve its geometric configuration during reaction. A corresponding intermediate may be envisaged for reduction of the alkyne ester and, by implication, for the alkene esters as well, although with the latter the carbanion center would involve a σ-bonded carbon and need therefore not maintain its structural integrity.[21] A similar path (Scheme I) accommodates the $[H^+]$-proportional (k') path, but here the initial attack probably entails the "hydridic" hydrogen bound to cobalt. The Co(III) center freed in this step would not be expected to survive, for it has been shown[6a,22] to react very rapidly with Co(I) to yield Co(II), which is the observed corrin-bound cobalt product in all cases.



I

Acknowledgment. The authors are grateful to Professor R. N. Bose for help in computational procedures.

Registry No. cob(I)alamin, 13408-78-1; hydroxocobalamin hydrochloride, 59461-30-2; acetylenedicarboxylic acid dimethyl ester, 762-42-5; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; diethyl maleate, 141-05-9; diethyl fumarate, 623-91-6; monoethyl fumarate, 2459-05-4.

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(20) See, for example: (a) Nesmeyanov, A. N.; Borisov, A. E. *Tetrahedron*, **1957**, *1*, 157. (b) Dreiding, A. S.; Pratt, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 1902. (c) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2793.

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$[(phen)_2Mn^{IV}(\mu\text{-}O)_2Mn^{III}(phen)_2](PF_6)_3\cdot CH_3CN$ and $[(phen)_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}(phen)_2](ClO_4)_4\cdot CH_3CN$ (phen = 1,10-Phenanthroline): Crystal Structure Analyses at 100 K, Interpretation of Disorder, and Optical, Magnetic, and Electrochemical Results

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Received June 6, 1986

The crystal and molecular structures of the following two compounds have been determined: $[(phen)_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}(phen)_2](ClO_4)_4\cdot CH_3CN$ ($[\mathbf{1}](ClO_4)_4\cdot CH_3CN$, phen = 1,10-phenanthroline: monoclinic, $P2_1/c$, $a = 12.218$ (7) Å, $b = 29.431$ (9) Å, $c = 14.987$ (7) Å, $\beta = 112.22$ (5)°, $Z = 4$) and $[(phen)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(phen)_2](PF_6)_3\cdot CH_3CN$ ($[\mathbf{1}](PF_6)_3\cdot CH_3CN$: orthorhombic, $Pbcn$, $a = 9.891$ (3) Å, $b = 22.690$ (3) Å, $c = 22.858$ (8) Å, $Z = 4$). In the former complex cation $[\mathbf{1}]^{4+}$, the average distance of the Mn–N bonds perpendicular to the central MnO_2Mn ring (2.010 Å) is 0.066 Å shorter than the average distance of the Mn–N bonds in the plane of the ring, indicating a trans influence of O on N. In the latter complex cation $[\mathbf{1}]^{3+}$, an average structure, with two crystallographically equivalent Mn ions, is found. Detailed analysis of anisotropic atomic displacement parameters (temperature factors) indicates either static or dynamic disorder between a Mn(III)–Mn(IV) and a Mn(IV)–Mn(III) ion. An optical absorption is observed for $[\mathbf{1}]^{3+}$ at ~800 nm which is tentatively assigned as intervalence transition since its intensity is observed to increase with decreasing temperature. The exchange coupling constants for $[\mathbf{1}]^{3+}$ and $[\mathbf{1}]^{4+}$ ($J = -148$ (12) and -144 (3) cm^{-1}) are almost equal. The comproportionation constant obtained from cyclic voltammetry for the reaction Mn(IV)–Mn(IV) + Mn(III)–Mn(III) → 2(Mn(III)–Mn(IV)) is $\sim 10^{16}$.

Introduction

The mixed-valence complexes $[(phen)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(phen)_2]^{3+}$ ($[\mathbf{1}]^{3+}$, phen = 1,10-phenanthroline) and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ ($[\mathbf{2}]^{3+}$, bpy = 2,2′-bipyridine) are believed to be model compounds for Mn-containing species occurring in photosynthesis.[2] Solution chemistry,[3] infrared,[3] optical,[3] and EPR[4] spectra, magnetism,[4,5] and electrochemistry[3,6] have been studied for the perchlorate salts of $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{3+}$. According to the classification by Robin and Day[7] both ions are believed to be class II mixed-valence complexes. Indeed, the crystal structure of $[\mathbf{2}](ClO_4)_3\cdot 3H_2O$ shows two structurally inequivalent metal ions.[5] EXAFS studies,[2] calibrated with the known structure of $[\mathbf{2}]^{3+}$, show that the dimensions of the central Mn_2O_2 four-membered ring are very similar in $[\mathbf{1}]^{3+}$ and $[\mathbf{1}]^{4+}$.

In this work the crystal structures of the mixed-valence compound $[\mathbf{1}](PF_6)_3\cdot CH_3CN$ and of its oxidized form $[\mathbf{1}](ClO_4)_4\cdot C$-

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0020-1669/86/1325-4743$01.50/0