Internal electron transfer (IET) within II and V yields the radical $ArO_2H^{\bullet}$, for which Cr(V) and Cr(IV) compete in 1e oxidations to the quinone "$Ar(=O)_2$". The latter competition (as measured by the ratio k_2/k_4) is related to the extent of autocatalysis. Two molecules of the diol have been incorporated into intermediate V, for the diol unit that appears in the ligand sphere of the (substitution-inert) Cr(III) product, VI, cannot be that which undergoes oxidation to the $ArO_2H^{\bullet}$ radical. Since the $Ar(OH)_2$–Cr(IV) step (k_5) in this reaction exhibits no kinetic dependency on [diol], we infer that conversion to V is rapid and essentially complete under our reaction conditions. An analogous scheme may be applied to the oxidation of hydroquinone, but chelation is precluded with this 1,4-diol. In an alternate path, $ArO_2H^{\bullet}$ formed in the initial internal electron transfer remains bound to Cr(IV) while undergoing a second 1e oxidation to yield Cr(III) and quinone. Although conceptually simple, this cannot be a major contributor, for release of free $ArO_2H^{\bullet}$ appears to be essential for the observed catalysis.

In the consideration of the reactions of Cr(V) with the several "ambifunctional" reductants (Table V) that utilize sequences related to (3)–(6), it has been noted[3b] that the most dramatic autocatalysis and the appearance of clocklike behavior are associated with the greatest reversals in selectivities toward Cr(V) and Cr(IV) when these reductants are compared with the radicals that they generate, i.e., when the differences between the ratios k_1/k_3 and k_2/k_4 are most marked. Moreover, there is considerably less variation in the latter ratio than in the former, and in previous instances, the severity of autocatalysis was determined principally by the selectivity of the primary reductant. This is not the case with reduction by hydroquinone, for which k_1/k_3 is found to lie very close to the corresponding ratio for iodide, a strongly autocatalytic reductant. Were it not for the poor selectivity of the semiquinone radical, we should observe a clock reaction in this reaction as well.[39]

Acknowledgment. We are grateful to Arla White for technical assistance.

Registry No. I, 84622-43-5; hydroquinone, 123-31-9; 2,3-dihydroxybenzoic acid, 303-38-8; catechol, 120-80-9; resorcinol, 108-46-3; 4-nitrocatechol, 3316-09-4; 6,7-dihydroxy-2-naphthalenesulfonic acid, 92-27-3; 3,4-dihydroxybenzoic acid, 99-50-3; 2,3-dihydroxyacetophenone, 13494-10-5; 2,6-dihydroxynaphthalene, 581-43-1; 1,4-dihydroxy-2-naphthoic acid, 31519-22-9.

(39) It is reasonable to ask what structural characteristics of the reagents summarized in Table V govern their reactivities and those of their radicals. We see no straightforward relationship between these reactivities and the formal potentials of the reductants, their geometric or electronic structures (and those of the radicals), and the identity of the nucleophilic sites from which electrons are removed. We thus remain puzzled on this important point.

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Electron Transfer. 92. Reductions of Vitamin B_{12a} (Hydroxocobalamin) with Formate and Related Formyl Species[1]

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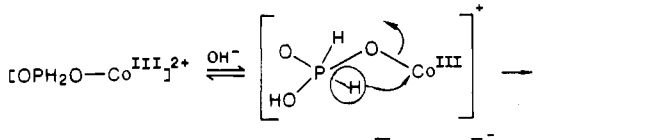
Vitamin B_{12a} (hydroxocobalamin) is reduced to B_{12r} (cob(II)alamin) with formate in aqueous media. One unit of formate consumes nearly two molecules of B_{12a}. At formate concentrations below 0.1 M, reactions are first order in both reagents. Rates vary with pH, approach a maximum in the range pH 5–7, and conform to eq 4 in the text, indicating that the active species are the formate anion and the protonated form of B_{12a}. At formate concentrations exceeding 0.1 M, the formate dependence exhibits kinetic saturation, pointing to the formation of a B_{12a}–formate complex having $K_{assn} = 4.6\ M^{-1}$. The reaction is inhibited moderately by acetate and thiocyanate but severely by imidazole. The observed deuterium isotope effect, $k_{HCOO^-}/k_{DCOO^-} = 1.8$, is very close to that reported for the Cannizzaro reaction of benzaldehyde and is thus consistent with a path entailing migration of hydride from a formyl carbon to cobalt. The proposed mechanism for this reaction (sequence (6) – (9)) then features an internal hydride shift ($k = 0.016\ s^{-1}$) within a B_{12a}–formate complex to yield a protonated Co^{I} (B_{12s}-like) intermediate, which very rapidly undergoes a comproportionation reaction with unreacted B_{12a}. The reduction proceeds inconveniently slowly, or not at all, with a number of formyl-substituted carboxylic acids in which the aldehydo group is not properly positioned for hydride migration to carboxyl-bound Co^{III} or, in the case of glyoxylic acid, is nearly completely converted by hydration to its less reactive *gem*-diol form.

A recent report[2] described the reduction of cobalt(III) by bound hypophosphite and presented evidence that this transformation, which does not occur with phosphite or with free hypophosphite, proceeds via base-induced internal hydride transfer from P(I) to Co(III), (1), yielding a Co(I) species, which then rapidly reduces unreacted Co(III) to Co(II) (2). In considering the extension of this type of reaction to other systems, we noted that formate, potentiometrically a weaker reductant than hypophosphite,[3,4] functions as a hydride donor toward a number of metal centers.[5] The formato complex $HCO_2Co(NH_3)_5^{2+}$ was nevertheless found to survive conditions much more severe than those bringing about



$$H{:}Co^{I} + [Co^{III}{-}OPH_2O]^{2+} \rightarrow 2Co^{II} + H_3PO_2 \quad (2)$$

(1) Sponsorship of this work by the National Science Foundation (Grant No. 8619472) is gratefully acknowledged.
(2) Linn, D. E., Jr.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3442.
(3) The formal potential for the 2e oxidation of hypophosphorous acid is listed[4a] as −0.50 V at pH 0 (25 °C), and that for $H_2PO_2^-$, as −1.57 V at pH 14. The potential appropriate for P(I) in the medium at hand (pH near 5) is then approximately −0.90 V. The potential for 2e oxidation of formate to CO_2 lies near −0.4 V at pH 7.[4b]
(4) (a) Latimer, W. H. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 111. (b) See, for example: Fruton, J. S.; Simmonds, S. *General Biochemistry*, 2nd ed.; Wiley: New York, 1958; p 299.
(5) See, for example: (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075. (b) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028. (c) King, A. D., Jr.; King, R. B.; Sailers, E. L., III. *J. Am. Chem. Soc.* **1981**, *103*, 1867. (d) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (e) Bar, R.; Sasson, Y. *Tetrahedron Lett.* **1981** *22*, 1709. (f) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59. (g) Krautler, B.; Caderas, C. *Helv. Chim. Acta* **1984**, *67*, 1891. (h) Linn, D. E., Jr. Ph.D. Thesis, University of Georgia, 1983; Chapters 3, 7.

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Table I. Stoichiometry of the Reaction of B_{12a} (Hydroxocobalamin) with Formate[a]

pH	[formate], $M \times 10^3$	$\Delta[B_{12r}]$, $M \times 10^3$	$\Delta[B_{12r}]/\Delta$[formate]	reacn time, h
7.02	0.885	1.69	1.91	7
7.02	0.708	1.24	1.75	10
7.02	0.443	0.79	1.78	12
3.30	0.885	1.67	1.88	70

[a] Reactions were carried out under N_2 at 25 °C. Except for the final entry (which was unbuffered), pH values were maintained by addition of phosphate buffer. $[B_{12a}]_0 = 1.77 \times 10^{-3}$ M throughout; $\lambda = 600$ nm.

reaction of the corresponding hypophosphite complex.[2] However, when cobalt(III) is incorporated into corrin-bound (B_{12}) systems (thus increasing the accessibility of the Co^I state),[6] reductions by formate proceed with ease.[7]

The present study deals with the kinetics of the reaction of vitamin B_{12a} (hydroxocobalamin) with formate in buffered aqueous media and compares this reaction with those of related compounds bearing the H–C=O (formyl) function. Note that this system constitutes an interface between metabolic reducing species (two-electron-transfer agents) such as formate and the single-electron reduction of vitamin B_{12a} (hydroxocobalamin) to B_{12r} (cob(II)alamin). The latter has been shown to be a cofactor in the biosynthesis of 5′-deoxy-5′-adenosylcobalamin,[6c] a coenzyme that is thought to catalyze skeletal rearrangements in biosystems.[8]

Experimental Section

Materials. Hydroxocobalamin (B_{12a}) hydrochloride (Sigma Chemical) was used as received. Aqueous sodium formate and sodium formate-d_1 ($Na^+DCO_2^-$, from neutralization of 30% aqueous DCOOH supplied by Cambridge Isotopes) were deaerated under N_2 and were standardized by titration with permanganate.[9] Buffer solutions were prepared by partial neutralization of the appropriate aqueous acids with NaOH. Lithium perchlorate, employed as a supporting electrolyte in kinetic runs, was prepared as described by Dockal[10] and twice recrystallized before use. Organic reagents (Aldrich products) were used as received. All reactions were carried out under prepurified N_2.

Stoichiometric Studies. The stoichiometry of the B_{12a}–formate reaction was determined by addition of known deficiencies of buffered formate to solutions of B_{12} under N_2, waiting until reaction was very nearly complete, and then comparing the resulting spectral changes at 600 and 473 nm to those observed when B_{12a} was treated with excess formate. Results are summarized in Table I. Aerial oxidation of the resulting B_{12r} (cob(II)alamin) solutions with stirring gave the initial B_{12a} spectrum[11] in less than 2 h at room temperature.

Kinetic Studies. Conversions of B_{12a} to B_{12r} by formate yielded isosbestic points at 360, 490, 579, and 634 nm (pH 2.55). The disappearance of B_{12a} was followed at 525.5 nm with formate in large excess. Acidities were regulated by known concentrations of acetate, phthalate, borate, or phosphate buffers. Total ionic strength was maintained at 1.0 M by addition of twice-recrystallized $LiClO_4$. All reactions were first order in B_{12a}. Rates were also proportional to [formate] at low concentrations of this reductant but appeared to approach a limiting value at high concentrations. All conversions were followed for at least 5 half-life periods. Pseudo-first-order specific rates were obtained from an unweighted least-squares treatment of logarithmic plots of absorbance difference against reaction times. Specific rates from replicate runs diverged by less than 10%. Temperatures were kept at 25.0 ± 0.2 °C.

Attempted reductions of B_{12a} with several formyl (aldehydo) derivatives resulted in conversions that were much slower than those with formate under analogous conditions. In a few instances (Table V), approximate specific rates could be estimated from initial slopes, but more often only upper limits were obtained. Hydroquinone showed no reactivity at pH 4.9. In contrast, ascorbic acid (0.002–0.005 M) reacted quickly with B_{12a} at pH 2, but the resulting profiles exhibited distinct biphasic character; examination of this system at several wavelengths yielded no evidence for a reaction intermediate.

Table II. Kinetic Acidity Dependence for the Reduction of B_{12a} (Hydroxocobalamin) with Formate[a]

$[HCOO^-]_t$[b]	buffer	[buffer], M	pH	$10^3 k_{obsd}$,[c] s^{-1}	$10^3 k_{calcd}$,[d] s^{-1}
0.0101	phth	0.30	4.72	0.60	
0.0203	phth	0.30	4.72	1.1	
0.0405	phth	0.30	4.72	2.2	
0.0405	phth	0.10	4.72	2.4	
0.0405	phth	0.20	4.72	2.3	
0.0405	phth	0.40	4.72	2.0	
0.0810	phth	0.30	4.72	4.0	4.1
0.0810	phth	0.30	5.26	4.3	4.3
0.0810	phth	0.30	5.89	4.2	4.3
0.0810	acet	0.30	4.90	4.1	4.2
0.0810	acet	0.30	4.50	3.8	3.9
0.0810	tosylate	0.30	2.55	0.37	0.41
0.0810	phos	0.30	6.61	4.5	4.2
0.0810	borate	0.30	8.12	2.5	2.3
0.0810	borate	0.30	9.61	0.15	0.16
0.0810	formate	0.08	3.80	3.2	2.8

[a] Reactions were run at 25 °C under N_2; $\mu = 1.0$ M ($LiClO_4$). $[B_{12a}]$ was 2.7×10^{-4} M throughout. [b] Total added formate. [c] Pseudo-first-order specific rates = $-d \ln [B_{12a}]/dt$. [d] Pseudo-first-order specific rates, rate/$[B_{12a}]$, pertaining to 0.0810 M formate, calculated from eq 4, with pK_A taken as 3.53,[9] pK_{Co} as 8.2, and k as 0.0535 s^{-1}. The last two parameters were obtained from nonlinear least-squares refinement of unweighted data (see text).

Table III. Kinetic Saturation and Deuterium Isotope Effect for the Reduction of B_{12a} (Hydroxocobalamin) with Formate[a]

[red], M[b]	$10^3 k_{obsd}$, s^{-1} [c]	$10^3 k_{calcd}$, s^{-1} [d]	[red], M[b]	$10^3 k_{obsd}$, s^{-1} [c]	$10^3 k_{calcd}$, s^{-1} [d]
		Reactions with HCOOH			
0.051	2.0	2.2	0.33	8.5	8.3
0.081	3.2	2.8	0.50	9.9	10.0
0.100	4.1	3.8	1.00	12	12
0.200	6.6	6.2			
		Reactions with DCOOH			
0.100	2.0	1.9	0.50	5.3	5.3
0.20	2.9	3.2	0.75	6.2	6.3
0.33	4.7	4.3	1.00	7.0	6.9

[a] Reactions were run at 25 °C at pH 3.80 under N_2; $\mu = 1.0$ M ($LiClO_4$). $[B_{12a}] = 2.7 \times 10^{-4}$ M throughout. [b] Total concentration of formate. [c] Pseudo-first-order specific rates = $-d \ln [B_{12a}]/dt$. [d] Pseudo-first-order specific rates, calculated from eq 5, with K_{assn} taken as 3.0 M^{-1} (for both HCOOH and DCOOH), k_{lim} for HCOOH as 0.0160 s^{-1}, and k_{lim} for DCOOH as 0.0087 s^{-1} (see text).

Results and Discussion

The approach to 2:1 stoichiometry for the B_{12a}–formate reaction, in conjunction with the observed formation of B_{12r} (cob(II)alamin), allows us to represent the principal transformation as (3), in agreement with the formulation by Bayston.[12]

$$2Co^{III}(corrin) + HCO_2^- \rightarrow 2Co^{II}(corrin) + CO_2 + H^+ \quad (3)$$

Kinetic data pertaining to this conversion are presented in Tables II and III. Experiments in Table II were carried out at low formate concentrations where rates are very nearly proportional to $[HCOO^-]$. These runs emphasize the dependence of rate on acidity within the pH range 2.6–9.6. The experiments summarized in Table III, for which pH was held at 3.80, demonstrate kinetic saturation exhibited by this reaction at high formate concentrations and also include runs with deuterium-labeled formate.

(6) For reviews, see: (a) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105. (b) Halpern, J. In B_{12}; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 1, p 501. (c) Huennekens, F. M.; Vitol, K. S.; Fujii, K.; Jacobsen, D. W. *Ibid.*, pp 158–164.
(7) (a) Bayston, J. H.; King, N. K.; Looney, F. D.; Winfield, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 2775. (b) Bayston, J. H.; Looney, F. D.; Pilbrow, J. R.; Winfield, M. E. *Biochemistry* **1970**, *9*, 2164.
(8) Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1984**, *106*, 8319.
(9) Welcher, F. J., Ed. *Standard Methods of Chemical Analysis*, 6th ed.; Van Nostrand: Princeton, NJ, 1963; Vol. 12, Part A, p 588.
(10) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.
(11) See, for example: Nexo, E.; Oleson, H. *Biochim. Biophys. Acta* **1976**, *446*, 143.
(12) Bayston, J. H.; Winfield, M. E. *J. Catal.* **1967**, *9*, 217.

Table IV. Inhibition, by Added Nucleophiles, of the Reduction of B_{12a} (Hydroxocobalamin) with Formate[a]

buffer	inhibitor (concn, M)	pH	$10^3 k_{obsd}$, s^{-1} [b]
OAc^-	OAc^- (0.15)	4.5	3.8
OAc^-	OAc^- (1.0)	4.6	1.8
HPO_4^{2-}	none	6.6	4.5
HPO_4^{2-}	SCN^- (0.002)	6.5	2.0
HPO_4^{2-}	imidazole (0.002)	6.5	0.087

[a] Reactions were run at 25 °C under N_2; μ = 1.0 M ($LiClO_4$). $[B_{12a}]$ was 2.7×10^{-4} M; total added formate was 0.081 M throughout. [b] Pseudo-first-order specific rates = $-d \ln [B_{12a}]/dt$.

A plot of specific rates vs pH (Figure 1) yields a bell-like profile with a (rather broad) maximum in the range pH 5–7, confirming the existence of (at least) three protonation levels for the redox couple. Of these, an "intermediate level", in which just one of the two partners is converted to its conjugate acid, represents the reactive assembly, whereas activity becomes almost negligible for combinations in which both species are protonated or both non-protonated. For a reaction involving the formate anion and the protonated form of B_{12a} (at formate concentrations well below the range of kinetic saturation), expression 4 applies. Here,

$$\text{rate} = k[\text{formate}]_t[B_{12}]_t\left(1 + \frac{[H^+]}{K_A} + \frac{K_{Co}}{[H^+]} + \frac{K_{Co}}{K_A}\right)^{-1} \quad (4)$$

$[\text{formate}]_t$ and $[B_{12}]_t$ indicate the total added concentrations of the redox partners, whereas K_A and K_{Co} are the acidity constants for formic acid and B_{12a}.

Nonlinear least-squares refinement of kinetic acidity data (pertaining to runs with $[\text{formate}]_t$ = 0.0810 M) in terms of eq 4 yields a K_{Co} value of $(6.15 \pm 0.44) \times 10^{-9}$ M and a pseudo-first-order specific rate $k = 0.053 \pm 0.002$ s^{-1} (corresponding to a second-order rate constant 0.65 M^{-1} s^{-1}).[13] The derived acidity constant for B_{12a} ($pK_{Co} = 8.2 \pm 0.1$) is in reasonable agreement with an earlier value, 7.8,[14] recorded in 0.5 M KCl.

Specific rates measured at higher formate concentrations (Table III) are in accord with eq 5 for reactions of both formate and

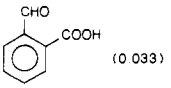
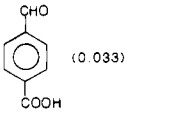
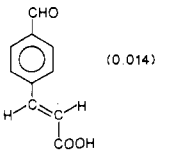
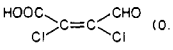
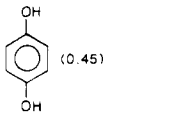
$$k_{obsd} = \frac{k_{lim}}{(1/K_{assn}[\text{formate}]) + 1} \quad (5)$$

deuterioformate. This expression points to the formation of a 1:1 B_{12}–formate complex having an apparent association constant K_{assn} and indicates a limiting specific rate, k_{lim}. Refinement of the formate data leads to $k_{lim} = (1.6 \pm 0.1) \times 10^{-2}$ s^{-1} (pH 3.80) and $K_{assn} = 3.0 \pm 0.3$ M^{-1}. Analogous treatment of the $DCOO^-$ rates yields the lower limiting rate, $(8.7 \pm 0.3) \times 10^{-3}$ s^{-1}, and, as expected, very nearly the same K_{assn}, 2.3 ± 0.3 M^{-1}.

As indicated in Table IV, the reduction of B_{12a} with 0.08 M formate is retarded moderately by 1 M acetate and by 10^{-3} M thiocyanate but severely by 10^{-3} M imidazole. The effectiveness of these added nucleophiles as inhibitors thus follows the same order as the association constants for axial substitution of these species at the Co(III) center of hydroxocobalamin.[15]

The observed kinetic saturation characterizing this reaction, in conjunction with its inhibition by strongly coordinating nucleophiles, points to a path initiated by axial coordination of formate to Co(III) in B_{12a}. The kinetic isotope effect, k_H/k_D = 1.8, resulting from substitution of DCO_2^- for HCO_2^-, falls slightly

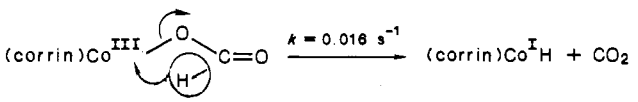
Table V. Attempted Reductions of B_{12a} (Hydroxocobalamin) with Formyl Species[a]

red (concn, M)[b]	pH	$10^3 k$, s^{-1}
HCOOH (0.081)	3.8	3.2
 (0.033)	4.1	0.18
 (0.033)	4.1	<0.03
 (0.014)	3.9	<0.3
 (0.30)	4.8	0.01
HC(=O)—COOH (1.0)	3.1	<0.12
(0.40)	3.9	0.24
 (0.45)	4.9[c]	<0.001

[a] Reactions were carried out under N_2 at 25 °C in the absence of added buffer (unless otherwise indicated); μ = 1.0 M. [b] Solutions were made by half-neutralization of the indicated acid using NaOH. [c] Phthalate buffer.

below that for the internal redox of Co(III)-bound hypophosphite (2.1–2.3)[2] and lies remarkably close to that for the Cannizzaro reaction of benzaldehyde (1.8),[16] a reaction that is considered to involve intramolecular hydride migration from a formyl group.[17] Our experiments thus support a mechanism represented as sequence (6)–(9). The indicated association constant for the

$$(\text{corrin})Co^{III}(H_2O) + HCO_2^- \underset{-H_2O}{\overset{K = 4.6\ M^{-1}}{\rightleftharpoons}} (\text{corrin})Co^{III}(OCHO) \quad (6)$$



(7)

$$(\text{corrin})Co^{I}H \xrightarrow{pK_A < 0} (\text{corrin})Co^{I} + H^+ \quad (8)[18]$$

$$(\text{corrin})Co^{III}(H_2O) + (\text{corrin})Co^{I} \xrightarrow{k = 10^7} 2(\text{corrin})Co^{II} + H_2O \quad (9)$$

B_{12a}–formate complex (4.6 M^{-1}) is obtained by multiplying the apparent value at pH 3.80, where 65% of the added formate is in the anionic form, by $^{100}/_{65}$. The very high rate for the final comproportionation step is that reported by Ryan and co-workers[19] for pH near 4.

Note that the present transformation, unlike the reaction of the hypophosphito complex of $(NH_3)_5Co^{III}$,[2] requires no external hydroxide, suggesting that the extra electrostatic push needed to drive hydride into the coordination sphere of Co(III) is no longer needed for B_{12a}, the Co(III) center of which is known to be far more substitution-labile than that in the $(NH_3)_5$-substituted complex.[20]

(13) During this refinement, K_A, the acidity constant for formic acid, was held at the recorded[9] value, 2.95×10^{-4} M, whereas the parameters k and K_{Co} were allowed to "float". An alternate path entailing the reaction of un-ionized formic acid with the deprotonated form of B_{12}, is also consistent with rate law 4. Refinement based on this mechanism yields the same value of K_{Co} but a much larger k value, 2.3×10^3 s^{-1}. This path is taken to be negligible, since a redox reaction of this type should be favored by protonation of the oxidant and deprotonation of the reductant, rather than by the reverse process.

(14) Rubinson, K. A.; Parekh, H. V.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.* **1983**, *22*, 458.

(15) See, for example: Pratt, J. M. *Inorganic Chemistry of Vitamin B_{12}*; Academic: London, 1972; p 172.

(16) Wiberg, K. B. *J. Am. Chem. Soc.* **1954**, *76*, 5371.

(17) Hauser, C. R.; Hamrick, P. J., Jr.; Stewart, A. T. *J. Org. Chem.* **1956**, *21*, 260.

(18) See, for example: Pillai, G. C.; Gould, E. S. Inorg. *Chem.* **1986**, *25*, 4740.

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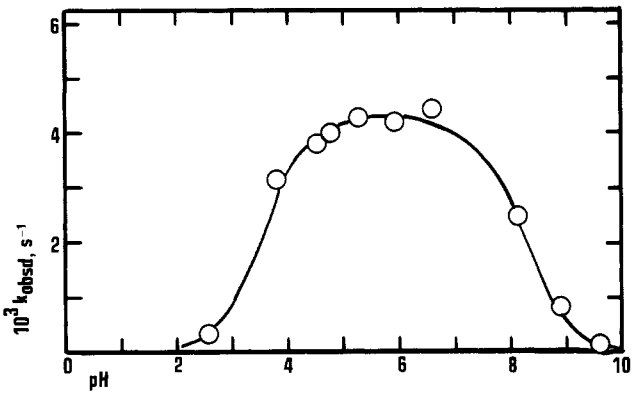
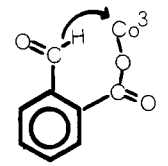


Figure 1. Variation, with pH, of the specific rate of reduction of vitamin B_{12a} (hydroxocobalamin) (2.7×10^{-4} M) with formate at 25 °C and μ = 1.0 M ($LiClO_4$). Reactions were carried out under N_2 in solutions buffered by phthalate, acetate, phosphate, and borate (see Table III). The solid line represents pseudo-first-order rate constants, calculated from eq 4, with $[formate]_t$ taken as 0.0810 M, K_{Co} as 6.15×10^{-9} M, and K_A as 2.95×10^{-4} M; the circles represent experimental values.

Attempts to apply this reaction to other formyl species led to results summarized in Table V, which emphasize the unique effectiveness of formate. The other carboxylates would be expected to coordinate with B_{12a} in the same manner as formate and acetate, but the formyl group is generally not properly positioned for migration to Co^{III}. Modest activity is observed in the case of *o*-formylbenzoic acid, which may react through a somewhat strained transition state I (featuring a seven-membered ring). The



complex of glyoxylic acid, HC(=O)COOH, appears to offer a more favorable orientation for internal hydride migration, but reaction here may be inhibited by conversion of this acid by hydration to its *gem*-diol form ($>C{=}O + H_2O \rightarrow >C(OH)_2$), a transformation that is known to be very nearly complete under our conditions.[21]

Reduction of B_{12a} by ascorbic acid is found to be rapid, but the biphasic profiles observed for this reaction, in conjunction with the known ability of this reductant to undergo both 1e and 2e oxidations,[22] indicate the operation of a different, and more complex, mechanism for this process.

Acknowledgment. We thank Arla White for technical assistance.

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Contribution from the Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, and Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR, Bologna, Italy

Electron- and Energy-Transfer Processes Involving Excited States of Lanthanide Complexes: Evidence for Inner-Sphere and Outer-Sphere Mechanisms

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The interaction of the luminescent excited states of the Eu_{aq}^{3+} and Tb_{aq}^{3+} ions, the $[Eu{\subset}2.2.1]^{3+}$ and $[Tb{\subset}2.2.1]^{3+}$ complexes, and the $[Eu{\subset}2.2.1]^{3+}$-$2F^-$ and $[Tb{\subset}2.2.1]^{3+}$-$2F^-$ ion pairs with $M(CN)_6^{z-}$ complexes (M = Cr(III), Fe(II), Co(III), Ru(II), Os(II)) has been studied in aqueous solution by luminescence lifetime measurements. Some measurements on solid samples precipitated from the aqueous solutions have also been performed. Depending on the specific lanthanide-species/cyanide-complex system, the lifetime of the luminescent lanthanide species is quenched (by an energy- or electron-transfer mechanism), unaffected, or enhanced. The enhancement is attributed to substitution of H_2O molecules in the coordination sphere of the lanthanide ion by cyanide complexes that are unable to cause energy- or electron-transfer quenching. The lower values obtained for the quenching constants of exergonic energy- and electron-transfer processes than those for diffusion are attributed to poor electronic factors (nonadiabatic behavior). The results can be accounted for by making the reasonable assumption that the precursor complex has a different structure depending on the lanthanide species involved: (i) for the aquo ions, water molecules can be replaced by the cyanide complex to yield an intimate ion pair; (ii) for the $[Ln{\subset}2.2.1]^{3+}$ complexes, a CN-bridged ion pair can be formed, as previously suggested on the basis of spectroscopic (intervalence-transfer band) results; (iii) for the $[Ln{\subset}2.2.1]^{3+}$-$2F^-/M(CN)_6^{z-}$ systems, only outer-sphere ion pairs can be involved in the quenching process.

Introduction

The study of processes involving electronically excited states can make an important contribution to elucidating reaction mechanisms and understanding the role played by nuclear and electronic factors in determining reaction rates. This is particularly true in the field of coordination chemistry, where the numerous studies carried out in the last few years on photoinduced electron-transfer processes[2-5] have strongly improved the original Marcus-Hush theory[6-7] and have focused on some important unresolved problems.[8-9]

Electronic energy transfer via an exchange mechanism[10] (eq 1, where an asterisk denotes electronic excitation) is a process quite

$$*A + Q \rightleftarrows *A\cdots Q \rightleftarrows A\cdots *Q \rightleftarrows A + *Q \qquad (1)$$

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(10) The Coulombic mechanism is generally not effective for coordination compounds, because in most cases Laporte- and/or spin-forbidden excited states are involved.[11,12]

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