all of the second oxidations (one of which is metal centered) have an identical rate constant of 2.7 × 10^{-2} cm/s. It is interesting to note from Table VI that a correlation appears to exist between the porphyrin ring basicity of the first six complexes and the magnitude of the rates of both the first oxidation and the first reduction. In the former case the rates monotonically increase with increasing basicity while, in the latter case, a decrease in rates is observed. However, the differences are very small, and if these are taken as a whole, one may say that all of the rate constants are virtually identical.

Summary. In conclusion, we have shown that nickel tetraalkylporphyrins and chlorins may be oxidized by two oxidation steps or reduced in a single electron-transfer step similar to the case for (TPP)Ni. It was found that three different mechanisms can occur for oxidations of the different porphyrin complexes. In contrast, only one electrode mechanism governs the reductions.

There is a dramatic shift in the first oxidation potential when one goes from (TPP)Ni, to (TRP)Ni, and then to (TMeC)Ni. A similar 200–210 mV negative shift in potentials is found on going from other metalloporphyrin to metallochlorin systems and can easily be rationalized by the differing energies of the HOMO's and the LUMO's (which have a change in symmetry from D_{4h} to C_{2v}), as well as by a reduction in the total aromatic stabilization of the chlorin relative to the porphyrin complex. It is more difficult, however, to explain the 200-mV negative shift in potential for the three (TRP)Ni^{II} complexes with respect to (TPP)Ni^{II}. The fact that there is no intramolecular electron transfer producing nickel(III) with the tetraalkylporphyrins may indicate that there is an additional stabilization mechanism that is operative. Aggregation has been found in solutions of (TMeC)Ni^{II},[7] and the structure of the conducting (TMeP)Ni^{II}I system indicates that these porphyrins can stack, thus enabling intermolecular interactions to take place. The fact that (TEtP)Ni^{II}, (TPrP)Ni^{II}, and (TMeC)Ni^{II} do not form aggregates might be explained on the basis of steric factors.

Acknowledgment. The support of the National Science Foundation (Grant CHE 8215507) is gratefully acknowledged.

Registry No. ((*p*-Cl)TPP)Ni, 57774-14-8; [((*p*-Cl)TPP)Ni]$^{-}\cdot$, 88669-53-8; [((*p*-Cl)TPP)Ni]$^{+}\cdot$, 88669-49-2; [((*p*-Cl)TPP)Ni]$^{2+}$, 88669-58-3; (TPP)Ni, 14172-92-0; [(TPP)Ni]$^{-}\cdot$, 88669-50-5; [(TPP)Ni]$^{+}\cdot$, 29484-62-6; [(TPP)Ni]$^{2+}$, 57208-12-5; (TMeP)Ni, 67067-51-0; [(TMeP)Ni]$^{-}\cdot$, 88669-54-9; [(TMeP)Ni]$^{+}\cdot$, 78965-41-0; [(TMeP)Ni]$^{2+}$, 88669-59-4; (TEtP)Ni, 75706-99-9; [(TEtP)Ni]$^{-}\cdot$, 88669-55-0; [(TEtP)Ni]$^{+}\cdot$, 88669-51-6; [(TEtP)Ni]$^{2+}$, 88669-60-7; (TPrP)Ni, 15245-21-3; [(TPrP)Ni]$^{-}\cdot$, 88669-56-1; [(TPrP)Ni]$^{+}\cdot$, 88703-06-4; [(TPrP)Ni]$^{2+}$, 88669-61-8; ((*p*-Et$_2$N)TPP)Ni, 88669-48-1; [((*p*-Et$_2$N)TPP)Ni]$^{-}\cdot$, 88669-57-2; [((*p*-Et$_2$N)TPP)Ni]$^{+}\cdot$, 88669-52-7; [((*p*-Et$_2$N)TPP)Ni]$^{2+}$, 88669-62-9; (TMeC)Ni, 75758-44-0; [(TMeC)Ni]$^{-}\cdot$, 88685-58-9; [(TMeC)Ni]$^{+}\cdot$, 88685-57-8; [(TMeC)Ni]$^{2+}$, 88685-59-0; TBAP, 1923-70-2; TBA(PF$_6$), 3109-63-5.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 67. Reductions of Hydroxylamine Derivatives by Vitamin B_{12s} (Cob(I)alamin)[1]

P. N. BALASUBRAMANIAN and E. S. GOULD*

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Vitamin B_{12s} (cob(I)alamin), the Co(I) derivative of vitamin B_{12}, reduces substituted hydroxylamines to the corresponding amines. Specific rates for the reductions of nine alkylated hydroxylamines and hydroxylaminesulfonic acids have been measured and their acid dependencies, in the range 0.01–0.11 M H^+, examined. Reactions of the alkylated hydroxylamines, and that of NH_3OH^+ itself, proceed at rates independent of $[H^+]$, indicating that partition of B_{12s} into protonation levels is not significant in our systems. When rates proportional to $[H^+]$ are observed, as in the reductions of NO_3^- and $HON(SO_3)_2^{2-}$, protonation of the oxidant appears to be occurring. Reduction of NH_3OH^+ to NH_4^+ is considerably slower than that of NO_3^- to NH_4^+ under corresponding conditions, indicating the NH_3OH^+ is not an intermediate in the latter conversion. The 2:1 stoichiometry of the reactions at hand is not altered by additions of alcohols (which have previously shown to divert $NH_2\cdot$ radicals), implying that these reductions, unlike the Cr(II)–NH_3OH^+ reaction, are heterolytic. It is proposed that these reactions proceed via nucleophilic substitution by Co(I), followed by rapid Co(III)–Co(I) comproportionation. The observed kinetic patterns suggest that initial attack occurs predominantly at oxygen for N-alkylated hydroxylamines and *N*-sulfonic acids, but at nitrogen for O-alkylated hydroxylamines and NH_2OSO_3H. The 4e reduction of acetophenone oxime by B_{12s} yields both $C_6H_5CH(CH_3)NH_2$ and $C_6H_5CH(CH_3)OH$. The amine almost certainly arises via initial attack at the C=N double bond of the protonated oxime, whereas the carbinol probably results from substitution at oxygen. Because of competing hydrolysis of the oxime in the medium used, we cannot estimate the relative importance of the two reductive paths.

A sufficient number of redox studies[2] involving vitamin B_{12s}, the cobalt(I) derivative of vitamin B_{12}, have been carried out to demonstrate that this species is a powerful and versatile reductant. We have reported[3] that cob(I)alamin reduces nitrate rapidly and cleanly to NH_4^+ at pH 1.5–2.5, that the overall rate of this net transfer of eight electrons is determined by the initial step, and that the reduction of HNO_2 under the same conditions is, as expected, more rapid than that of NO_3^-. The hydroxylammonium ion, NH_3OH^+, in which the oxidation number of nitrogen is −1, may be considered a logical intermediate in the overall conversion to NH_4^+. If so, NH_3OH^+ should likewise be reduced more rapidly by B_{12s} than is NO_3^-. We find, on the contrary, that it is reduced more slowly and, further, that its reduction is accelerated by N-methylation.

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(1) Support of this work by the National Science Foundation (Grant No. 8022881) is gratefully acknowledged.

(2) See, for example: (a) Lexa, D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1976**, *98*, 2652. (b) Itabashi, E.; Parekh, H. V.; Mark, H. B., Jr. *Anal. Lett.* **1978**, *B11*, 515. (c) Kaufmann, E. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7051. (d) Ryan, D. A.; Espenson, J. H.; Meyerstein, D.; Mulac, W. A. *Inorg. Chem.* **1978**, *17*, 3725. (e) Espenson, J. H.; Gjerde, H. B. *Ibid.* **1980**, *19*, 3549. (f) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc. A* **1968**, 2886.

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

Table I. Stoichiometries of the Reactions of Cob(I)alamin with Hydroxylamine Derivatives[a]

oxidant (Ox)	$10^5 \times$ $[Co^I]$, M	$10^5 \times$ [Ox], M	$10^5\Delta$-$[Co^I]$,[b] M	$\Delta[Co^I]/\Delta[Ox]$
NH_3OH^+	6.20	1.58	3.21	2.03
$CH_3NH_2OH^+$	6.20	1.40	3.07	2.19
$CH_3ONH_3^+$	4.00	1.26	2.48	1.97
	6.00	0.91	1.93	2.10
	6.00	1.34	2.88	2.14
	8.00	2.14	4.53	2.10
$(CH_3)_2NHOH^+$	4.40	1.44	2.90	2.01
	6.20	2.40	4.48	1.87
	6.20	1.11	2.28	2.05
$(C_2H_5)_2NHOH^+$	4.40	1.46	2.85	1.95
	6.20	2.33	4.61	1.98
	8.00	3.40	6.20	1.82
	8.00[c]	2.40	4.40	1.84
	8.00[c]	3.30	6.21	1.88
	6.40[d]	2.44	4.55	1.87
	8.60[d]	3.80	6.95	1.83
	8.00[e]	3.30	6.39	1.94
	8.10[e]	3.80	6.96	1.83
NH_2OSO_3H	6.20	1.24	2.44	1.97
	6.20	0.65	1.54	2.35
	6.20	0.89	1.70	1.92
	4.44	1.29	2.80	2.16
	8.00	1.29	3.00	2.30
	8.00	2.03	4.04	1.98
$C_6H_5C(=NOH)CH_3$	8.65	1.48	5.56	3.75
	8.60	0.99	4.08	4.09
	6.40	0.80	3.37	4.20

[a] Cob(I)alamin was generated by reduction of hydroxocobalamin hydrochloride with zinc amalgam. Reductions were carried out in 0.040 M $HClO_4$ (see Experimental Section and ref 3). [b] Determined spectrophotometrically at 387 nm. [c] Reaction in 10% (v/v) methanol. [d] Reaction in 20% (v/v) ethanol. [e] Reaction in 20% (v/v) 2-propanol.

The present contribution describes experiments dealing with the reductions, by cob(I)alamin, of a variety of substituted hydroxylamines.

Experimental Section

Materials. Alkylated hydroxylamines (available as their hydrochlorides or hydrosulfates (Aldrich)), hydroxylamine-*O*-sulfonic acid (Aldrich), and hydroxocobalamin hydrochloride (Sigma) were used as received. Lithium perchlorate, for use in kinetic experiments, was prepared as described.[4] The potassium salt of hydroxylamine-*N*,*N*-disulfonic acid, $HON(SO_3K)_2$, was prepared by the method of Rollefson[5] and was recrystallized from water three times to remove traces of nitrite. A portion of the disulfonate was converted to the tripotassium salt, $[K^+]_3[ON(SO_3)_2]^{3-}$, by recrystallization from aqueous KOH, and the tribasic salt was then hydrolyzed to the potassium salt of the monosulfonic acid, $HONH(SO_3K)$, by a modification of the procedure of Degener and Seel.[6] Acetophenone oxime was prepared by the action of hydroxylamine on the parent ketone in aqueous NaOH.[7] All redox reactions were carried out under N_2 in distilled water that had been previously boiled and purged with O_2-free nitrogen for at least 4 h. Cob(I)alamin was generated in solution by reduction, using zinc amalgam, of the cobalt(III) complex, hydroxocobalamin hydrochloride, as described.[3]

Stoichiometric Studies. The stoichiometries of seven of the more rapid reactions in 0.040 M $HClO_4$, taking the Co^I complex in excess, were determined by adding a measured deficiency of oxidant to the Co^I solution, waiting 30–80 min for completion of the reaction,[8] and then measuring the decrease in absorbance at 387 nm. This decrease, after a suitable "blank" correction for the slow loss of Co^I in the absence of the coreagent, was compared to that observed when B_{12s} was treated with excess oxidant. Representative results appear in Table I. Very nearly 2 mol of Co^I reacts with each mole of the substituted hydroxylamines, whereas 1 mol of acetophenone oxime consumes nearly 4 mol of Co^I.

Kinetic Studies. Rates were estimated from measurements of decreases in absorbance at 387 nm using a Cary 14 recording spectrophotometer. The difficulty in transferring dilute solutions of cob(I)alamin led us to employ the procedure of Loar,[9] in which B_{12s} was generated directly in the optical cell.[3] Since B_{12s} reacts avidly with traces of oxygen in the hydroxylamine solution, it was advisable that the added volume of the latter reagent be minimal. Acidities were regulated by addition of known concentrations of $HClO_4$ while the total ionic strength was kept near 0.11 M by addition of $LiClO_4$.[10,11] Reactions were generally first order each in Co^I and oxidant but were carried out under pseudo-first-order conditions with the oxidant in at least 10-fold excess. Conversions were followed for at least 5 half-lives. Rate constants from successive half-life values within a run agreed to within 5%, and average values did not differ significantly from those obtained from slopes of plots of absorbance differences against reaction times. Specific rates from replicate runs checked to better than 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The kinetic traces obtained from reaction of acetone oxime, $(CH_3)_2C{=}NOH$, with cob(I)alamin departed significantly from the usual exponential (pseudo-first-order) curves, for during the early stages the decrease in rate was much less marked than would result from depletion of the reductant. It appears here that hydrolysis of the oxime to acetone and NH_3OH^+ is competing with the redox reaction of interest[12] and that NH_3OH^+ is reduced somewhat more rapidly than the oxime. This reaction was not pursued.

Reduction of Acetophenone Oxime. This reaction was carried out on a preparative scale in order to identify the products. Cob(I) alamin was present in catalytic quantities and was regenerated in situ by the action of zinc amalgam.[13] The oxime (6.4 mmol) was dissolved in 5 mL of 40% methanol, and the solution was made 0.3 M in $HClO_4$ and 1.2×10^{-4} M in Co(I). The preparation was stirred at room

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

(5) Rollefson, G. K.; Oldershaw, C. F. *J. Am. Chem. Soc.* **1932**, *54*, 977.

(6) (a) Degener, E.; Seel, F. *Z. Anorg. Allg. Chem.* **1956**, *285*, 129. (b) Oblath, S. B.; Markowitz, S. S.; Novakov, T.; Chang, S.-G. *Inorg. Chem.* **1983**, *22*, 579. Hydrolysis of the di- to the monosulfonate was carried out at pH 4 and 100 °C. The monosulfonate was recrystallized three times to remove traces of disulfonate.

(7) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 4th ed.; Wiley: New York, 1956; p 254. For evidence that the phenyl rather than the methyl group in this oxime lies trans to OH, see, for example: Donaruma, L. G.; Heldt, W. Z. *Org. React.* (*N.Y.*) **1960**, *11*, 17.

(8) Stoichiometric studies of the very slow reactions in this series could not be carried out since loss of Co(I), by a combination of spontaneous decay and oxidation by traces of air slowly leaking in the vessel, became competitive with the primary reaction, thus complicating interpretation of the results. At the other extreme, reaction with the exceedingly active *O*-sulfonic acid, NH_2OSO_3H, was complete in less than 2 min.

(9) See ref 6 of: Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330. More specifically, solutions of the cobalt(III) complex, hydroxocobalamin hydrochloride, were acidified and then reduced under nitrogen in the optical cell, using a small weighed quantity of zinc amalgam and a 7-mm Teflon-coated magnetic stirrer. For the subsequent kinetic runs, the spectrophotometer beam was positioned above the level of the amalgam. Stirring was discontinued just before addition of the oxidant. Acetophenone oxime, which is only slightly soluble in water, was added as its solution in methanol; the small methanol content of the resulting solution (<4% by volume) was assumed to be without significant effect upon the specific rate of reduction.

(10) We[3] and others[11] have reported gradual losses of acidity, presumably resulting from the Co^I-catalyzed reaction of zinc with H^+. We find that this loss can be minimized by preparing the amalgam at room temperature, drying it at room temperature, and storing it near 0 °C. Nevertheless, the behavior of the amalgam in this respect must be considered capricious, and the stability of acid solutions in contact with it in the presence of B_{12s} should be checked for each new amalgam preparation.

(11) Schrauzer, G. N.; Deutsch, E.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 2441.

(12) In a single run using conditions similar to those in our redox studies (0.04 M $HClO_4$ + 0.06 M $LiClO_4$, 25 °C, reaction monitored at 280 nm) acetone oxime was found to undergo hydrolysis at a specific rate near 0.002 s^{-1}, i.e., on a time scale close to that for reduction of hydroxylamine by B_{12s} (rate constant 0.006 s^{-1} with $[NH_3OH^+] = 1.8 \times 10^{-3}$ M). Under the same conditions, reduction of acetone by cob(I)alamin was found to proceed immeasureably slowly.

(13) Reduction of the oxime by direct action of metal requires much more rigorous conditions than those employed here and may therefore be neglected. See, for example: Lycan, W. H.; Puntambaker, S. V.; Marvel, C. S. "Organic Synthesis"; Wiley: New York, 1943; Collect. Vol. II, p 318.

Table II. Representative Kinetic Data for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with Hydroxylamine and Hydroxylamine-*N,N*-disulfonate[a]

oxidant (Ox)	$10^4 \times$ [Ox], M	[H^+], M	k_{obsd}[b]	k_2[c]
NH_3OH^+[d]	8.96	0.04	3.8	4.2
	17.9	0.04	7.7	4.3
	35.8	0.04	12.8	3.6
	36.4	0.04	13.5	3.7
	36.4	0.04[e]	16.0	4.4
	36.2	0.01	14.7	4.1
	36.2	0.02	14.7	4.1
	36.2	0.06	14.6	4.0
	36.2	0.10	15.2	4.2
$HON(SO_3)_2^{2-}$	19.7	0.066	1.11	0.56
	40.6	0.066	2.2	0.54
	77.6	0.066	4.5	0.58
	39.4	0.011	1.16	0.29
	39.0	0.022	1.27	0.33
	37.6	0.044	1.61	0.43
	37.6	0.066	2.2	0.58
	39.4	0.088	2.5	0.64
	39.0	0.110	2.9	0.74

[a] Reactions were carried out at 25.0 °C; the supporting electrolyte was $LiClO_4$ ($\mu = 0.11$). $[Co^I]_0 = 6.0 \times 10^{-5}$ M throughout. [b] Pseudo-first-order rate constants (in $s^{-1} \times 10^3$) = $-d[Co^I]/dt[Co^I]^{-1}$. [c] Second-order rate constants (in $M^{-1}\ s^{-1}$) = k_{obsd}/[ox]. [d] Added as the hydrochloride. [e] $\mu = 0.25$ M ($LiClO_4$ + $HClO_4$).

temperature under N_2 with an excess (7.66 g) of zinc amalgam, adding 31 mmol of deaerated $HClO_4$ (in portions) to replace H^+ consumed in the reaction. When the Co(I) color persisted (about 20 h after initiation), the acidic preparation was decanted from the unreacted amalgam and then extracted with 100 mL of ether. The aqueous layer was then made basic and extracted with a second 100-mL portion of ether. The two ether extracts were separately dried over anhydrous Na_2SO_4, and the ether was removed from both by rotary evaporation. The residue from the acid extraction exhibited an infrared spectrum corresponding to that of *sec*-phenethyl alcohol, $C_6H_5CH(CH_3)OH$. The (smaller) residue from the basic extrction was titrated with $HClO_4$ and was found to consume 1.44 mmol of the latter, corresponding to a yield of 23% α-phenylethylamine. The basic aqueous layer gave a strong positive Nessler test for ammonia.[14,15]

Results and Discussion

The reaction of cob(I)alamin with substituted hydroxylamines (the first six oxidants in Table I) is seen to consume two molecules of Co^I per molecule of oxidant, indicating that, in each instance, conversion to the amine (reaction 1) predominates, as has been established for reactions of hydroxylamine with the 1e reductants, Cr(II),[16] Ti(III),[17] U(III),[18] Cu(I),[19] and V(III).[20]


(1)

Representative kinetic data, applying to the reaction of NH_3OH^+ and that of the disulfonate, $HON(SO_3)_2^{2-}$, are given in Table II. Note that the specific rate of reduction of the hydroxylammonium ion remains constant within the acidity range studied whereas the reduction of the disulfonate is markedly acid dependent. Specific rates for all oxidants in this series are summarized in Table III.

Table III. Specific Rates for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with Derivatives of Hydroxylamine

oxidant	k[a]	oxidant	k[a]
NH_3OH^+	4.1	$CH_3NH_2OCH_3^+$	0.49
$CH_3NH_2OH^+$	7.3	NH_2OSO_3H[b]	$>2 \times 10^4$
$(CH_3)_2NHOH^+$	39	$HONHSO_3^-$	10.0[H^+]
$(C_2H_5)_2NHOH^+$	48	$HON(SO_3)_2^{2-}$	0.20 + 5.4[H^+]
$CH_3ONH_3^+$	24	$C_6H_5C(=NOH)CH_3$	70[H^+]

[a] Second-order specific rates in $M^{-1}\ s^{-1}$. Reactions were carried out at 25.0 °C, $\mu = 0.11$ ($LiClO_4$-$HClO_4$). [b] [H^+] = 0.040 M.

Reactions of each of the alkylated hydroxylamines, like that of hydroxylamine itself, are seen to proceed at rates independent of pH for [H^+] values between 0.01 and 0.1 M. This invariance assures us that neither the oxidant nor the reductant undergoes significant partition between protonation levels within the relatively narrow acidity range considered. The latter conclusion is in accord with the pK_A values of the protonated hydroxylamines, which are comparable to that of the parent species (pK_A = 6.1),[21,22] but is inconsistent with a pK_A near 1 reported by Lexa and co-workers[2a,23] for cob(I)alamin in 1.6 M aqueous *p*-toluenesulfonate. Moreover, we find the electronic spectrum of B_{12s} to be invariant between pH 1 and 2. We therefore suspect that pK_A for protonation of B_{12s} (assuming that it occurs) has been significantly shifted in our medium (0.1 M ClO_4^-) to a value well outside the pH range examined.[24,25]

The activated complex for reduction of each of the alkylated hydroxylamines has the composition (Co^I + amine + H^+). This is consistent with a mechanism in which B_{12s} attacks the protonated hydroxylamine and, alternatively, with attack on the nonprotonated hydroxylamine by the protonated form of Co^I (a species that is presumed to have some hydride-like character).[26] We believe the first of these possibilities to be much more likely. If attack by Co^I–H on the free base were predominant, it would occur at a bimolecular rate constant (obtained by multiplying the tabulated values in Table III by the ratio $K_A^{Co(I)}/K_A^{amine}$, near $10^6\ M^{-1}\ s^{-1}$. The latter value appears to be unreasonably high for a nucleophilic substitution (see below) taking place on an unactivated first-row element attached to a relatively ineffective leaving group.

The argument just presented suggests a choice between paths for the reduction of nitrate by B_{12s}, a reaction found[3] to be first order in H^+. Assuming a mechanism similar to that for reduction of the N–O compounds in the present study, we tend to favor a sequence in which B_{12s} reacts with molecular HNO_3 rather than one featuring reaction of the protonated

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(14) Swift, E. H. "A System of Chemical Analysis"; Prentice-Hall: Englewood Cliffs, NJ, 1940; p 203.

(15) Attempts to estimate the yields of *sec*-phenethyl alcohol and α-phenylethylamine from reaction mixtures resulting from our kinetic experiments, using gas–liquid chromatography or high-pressure liquid chromatography, were unsuccessful. We thank T. Molloy, G. Powell, and Dr. M. Gangoda for help in these endeavors.

(16) Schmidt, W.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1984.

(17) (a) Stahler, A. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 4732. (b) Bray, W. C.; Simpson, M. E.; MacKenzie, A. A. *J. Am. Chem. Soc.* **1919**, *41*, 1363.

(18) Adamcikova, L.; Treindl, L. *Collect. Czech. Chem. Commun.* **1978**, *43*, 1844.

(19) (a) Kurtenacker, A.; Werner, F. *Z. Anorg. Allgem. Chem.* **1927**, *160*, 333. (b) Tomat, R.; Rigo, A. *Electroanal. Chem. Interfacial Electrochem.* **1975**, *59*, 191.

(20) Tomat, R.; Rigo, A. *J. Inorg. Nucl. Chem.* **1974**, *36*, 611.

(21) Sillen, L. G. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*, 159. Note that NH_2OCH_3 (pK_A = 4.6)[22] is a significantly weaker base than the N-alkylated hydroxylamines. However, in the range of acidities studied, it too is converted essentially completely to its protonated form.

(22) Vodrazka, Z. *Chem. Listy* **1952**, *46*, 208; *Chem. Abstr.* **1952**, *46*, 11045*a*.

(23) Lexa, D.; Saveant, J. M.; Zickler, J. *J. Am. Chem. Soc.* **1977**, *99*, 2786.

(24) Rubinson, K. A.; Parekh, H. V.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.* **1983**, *22*, 458. These authors record a pK_A value of 1.5 for protonation of B_{12s} in 0.5 M KCl. However, their data (as summarized in their Figure 1) do not appear to support such a value, for the plot of their measured potentials for the B_{12r}–B_{12s} conversions vs. pH is linear and devoid of discontinuities between pH 5.0 and 0.5.

(25) There is evidence that apparent pK_A values of vitamin B_{12} derivatives are unusually sensitive to variations in ionic media. Thus, pK_A of B_{12r} has been reported as 2.9 in 1.6 M *p*-toluenesulfonate[2a] and 1.96 in 0.11 M $LiClO_4$.[23]

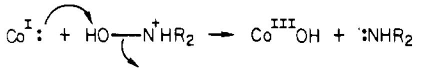
(26) See, for example: Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1.

form of B_{12s} with NO_3^-. With nitrate, as with acetophenone oxime (Table III), the $[H^+]$ dependency observed may be considered simply to reflect the circumstance that protonation of an oxidant usually converts it to a more effective electron acceptor.[27,28]

A related point emerges from comparison of the specific rate for reduction of NH_3OH^+ (4.1 M^{-1} s^{-1}) to values for reduction of NO_3^- to NH_4^+ (120 and 520 M^{-1} s^{-1} at 0.0063 and 0.025 M H^+).[3] Since reduction of hydroxylamine is clearly slower than that of nitrate, NH_3OH^+ cannot be a significant intermediate in the reduction of NO_3^- to ammonia by B_{12s}. If we assume that the latter reduction passes through N(−I), we must entertain the possibility that another, less usual, species at that oxidation level (e.g., NH_2^+ or a cobalt-bound nitrene) intervenes. Further examination of this point is obviously needed.

The reductions of hydroxylamine by Cr(II)[16] and by Ti(III)[29] have been shown to be homolytic, both of these passing through NH_2 (or $NH_3^{+\cdot}$), an intermediate that may be diverted by addition of olefins or alcohols to the reaction mixture. In contrast, the stoichiometry of the reduction of $(C_2H_5)_2NHOH^+$ by cob(I)alamin is seen (Table I) to be unaffected by high concentrations of methanol, ethanol, or 2-propanol, indicating that this reduction and, by implication, that of hydroxylamine itself are heterolytic reactions. This conclusion is not at all astonishing in view of the extraordinary nucleophilic potency of B_{12s}[11] and the ready accessibility of an oxidation state 2 units higher.

We may then represent the reduction of substituted hydroxylamines in acidic solution schematically by the simple two-step sequence (2)–(3). The second (comproportionation)



$$Co^{I}: + HO-\overset{+}{N}HR_2 \rightarrow Co^{III}OH + :NHR_2 \qquad (2)$$

$$Co^{III}OH + Co^{I} \xrightarrow[\text{rapid}]{H_3O^+} 2Co^{II}OH_2 \qquad (3)$$

step (3) is taken to be rapid in accord with the results of Espenson and co-workers,[2c,d] which point to a specific rate near 10^8 M^{-1} s^{-1} in strongly acidic solutions.

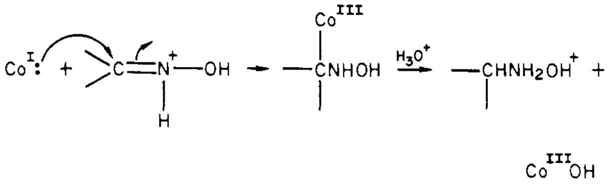
A key point in this study concerns the site of attack (oxygen vs. nitrogen) by Co^I. The identity of the Co^{II} product, which appears to be aquocob(II)alamin in all cases, is not informative here, for ligands occupying axial positions at Co^{II} centers are doubtlessly exceedingly substitution labile[30] and the cobalt(II) product resulting from the primary reaction would be expected to undergo almost immediate aquation. Analogy with the $Cr(II)-NH_3OH^+$ system, where attack at oxygen has been demonstrated,[16] must be drawn with the reserve in view of the homolytic nature of the latter reaction. Nevertheless, in the substitution step (2), we have indicated an attack at oxygen. This is almost certainly the case with NH_3OH^+ itself and with the N-alkylated hydroxylamines, for increased branching at the nitrogen atom is seen to accelerate the reaction, whereas if nitrogen were the site of attack, such branching should strongly retard. A similar conclusion probably applies to the *N*-sulfonates, $HONHSO_3^-$ and $HON(SO_3)_2^{2-}$, for here too the nitrogen is protected by branching. The lower specific rate for the disulfonate may arise simply from the greater repulsion between the negatively charged oxidant and the electron-rich attacking site of Co(I), whereas the H^+ catalysis observed with both sulfonates reminds us that protonation of a leaving group in nucleophilic substitution invariably facilitates its departure.

We suspect, on the other hand, that attack on the O-methylated species, $CH_3ONH_3^+$, occurs at nitrogen, for N-methylation of this cation, converting it to $CH_3NH_2OCH_3^+$, is seen to lower the rate of reduction 50-fold. Moreover, it is conceivable that the very sluggish reduction of the latter derivative may proceed by a combination of both paths.

The very rapid reduction of the *O*-sulfonic acid, for which our attempted estimates of specific rate yield only a lower limit, almost certainly proceeds by attack at nitrogen, for this oxidant, unlike any of the others in this series, features the unusually effective leaving group $-OSO_3H$.[31] This reaction may then be considered analogous to a large number of nucleophilic substitution reactions of this species that have been studied by Krueger and co-workers.[32]

Consideration of reduction of acetophenone oxime is complicated by uncertainty as to the ratio of reaction products. When the reduction is carried out under preparative conditions, 23% of the oxime is converted to α-phenylethylamine, $C_6H_5CH(CH_3)NH_2$, but the extended reaction period used in this experiment, during which time the oxime remains in strongly acid solution, assures us that hydrolysis of the oxime to acetophenone and NH_3OH^+ competes with the primary reduction. Reductions of the hydrolysis products yield *sec*-phenethyl alcohol and NH_4^+, both of which are found in the reaction mixture. Since the amine cannot be formed from these products, nor from the imine $C_6H_5C(CH_3){=}NH$ (which would undergo rapid hydrolysis at the low pH used), it must be considered a primary product and the observed 23% may be taken as a lower limit under conditions prevailing in the much more rapid kinetic runs.

It is likely that formation of the amine is initiated by attack by Co^I on the C=N double bond, in a manner analogous to the attack on C≡N in the known reaction between B_{12s} and saturated nitriles.[33]



$$Co^{I}: + {>}C{=}\overset{+}{N}(H)-OH \rightarrow -\overset{Co^{III}}{C}NHOH \xrightarrow{H_3O^+} -CHNH_2OH^+ + Co^{III}OH \qquad (4)$$

$$>CHNH_2OH^+ + Co^{I} \xrightarrow{H_2O} >CHNH_3^+ + Co^{III}OH \qquad (5)$$

$$2Co^{III}OH + 2Co^{I} \xrightarrow{2H_3O^+} 4Co^{II}OH \qquad (6)$$

Since the rate law for this reaction exhibits a straightforward H^+ dependence (Table III), it appears that the rate is determined by the initial step. If so, step 5, involving the intervention of a second Co^I molecule, may be taken to be considerably more rapid than (4). This would be the case if the

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(27) Exceptions to this general statement involve inner-sphere oxidants in which lead-in sites can be blocked off by protonation. See, for example: Loar, M. K.; Thomas, J. C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 2877.

(28) Since this system does not exhibit kinetic saturation with respect to H^+ at pH 1, we may infer its pK_A values to be substantially less than unity. This conclusion is in accord with p*K* values near 0, which have been estimated for several simple oximes. See, for example: Hall, N. F. *J. Am. Chem. Soc.* **1930**, *52*, 5115. Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 349.

(29) Albisetti, C. J.; Coffman, D. D.; Hoover, F. W.; Jenner, E. L., Mockel, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 1489.

(30) The lability of axial substituents in cob(III)alamin derivatives has been demonstrated by: Thusius, D. *J. Am. Chem. Soc.* 1971, *93*, 2629. It is expected that ligand exchange in the corresponding Co(II) complexes, for which ligand field stabilization is much less marked, will be, if anything, even more rapid.

(31) Since the pK_A of hydroxylamine-*O*-sulfonic acid has been reported as 1.48 (Candlin, J. P.; Wilkins, R. G. *J. Am. Chem. Soc.* **1965**, *87*, 1490), this oxidant is partitioned into protonated and nonprotonated forms in the pH range here considered. Reduction is immeasurably rapid throughout.

(32) (a) Krueger, J. H.; Sudbury, B. A., Blanchet, P. F. *J. Am. Chem. Soc.* **1974**, *96*, 5733. (b) Krueger, J. H.; Blanchet, P. F.; Lee, A. P.; Sudbury, B. A. *Inorg. Chem.* **1973**, *12*, 2714. (c) Krueger, J. H.; Blanchet, P. F. *Ibid.* **1974**, *13*, 719. (d) Sudbury, B. A.; Krueger, J. H. *Ibid.* **1974**, *13*, 1736.

(33) See, for example: Fischli, A. *Helv. Chim. Acta* **1978**, *61*, 2560.

specific rate for reduction of the indicated branched hydroxylamine were comparable to that found here for $(CH_3)_2NHOH^+$.

Although a portion of the second organic product, $C_6H_5CH(CH_3)OH$, doubtless arises from hydrolysis of the oxime and reduction of the resulting ketone, we cannot exclude the possibility that some of this alcohol results from an alternative reductive sequence beginning with attack at the N–O bond (7). If this route is significant, the close adherence to monomial kinetics again requires that the initial step (7) be slower than succeeding steps. In particular, the specific rate for reduction of acetophenone to the alcohol must exceed that for reduction of the oxime to the rapidly hydrolyzed imine. Although the latter condition appears to be in accord with experiment,[34] additional work is needed to evaluate the extent to which this path contributes.

$$\mathrm{Co^{I}\colon} + \mathrm{HO(H)N^{+}{=}C}< \; \rightarrow \mathrm{Co^{III}OH} + \mathrm{NH{=}C}< \qquad (7)$$

$$>\mathrm{C{=}NH} \xrightarrow{\mathrm{H_3O^+}} >\mathrm{C{=}O} \xrightarrow[\mathrm{H^+}]{\mathrm{Co^I}} >\mathrm{CHOH} \qquad (8)$$

Acknowledgment. The authors are indebted to Professor Harry B. Mark, Jr., for helpful discussions.

Registry No. NH_4^+, 14798-03-9; $C_6H_5CH(CH_3)NH_2$, 98-84-0; $C_6H_5CH(CH_3)OH$, 98-85-1; NO_3^-, 14797-55-8; $(CH_3)_2C{=}NOH$, 127-06-0; $C_6H_5COCH_3$, 98-86-2; $NH_2OH{\cdot}HClO_4$, 15588-62-2; $CH_3NHOH{\cdot}HClO_4$, 88905-37-7; $CH_3ONH_2{\cdot}HClO_4$, 28219-79-6; $(CH_3)_2NOH{\cdot}HClO_4$, 88905-38-8; $(C_2H_5)_2NOH{\cdot}HClO_4$, 88905-39-9; NH_2OSO_3H, 2950-43-8; $C_6H_5C({=}NOH)CH_3$, 613-91-2; $HON(SO_3)_2^{2-}{\cdot}2K^+$, 21049-67-2; $CH_3NHOCH_3{\cdot}HClO_4$, 88905-40-2; $HONHSO_3^-{\cdot}K^+$, 13768-26-8; hydroxocobalamin hydrochloride, 15041-07-3; cob(I)alamin, 18534-66-2.

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(34) Preliminary experiments by P.N.B. indicate that acetophenone is reduced by cob(I)alamin at a specific rate near 12 $M^{-1}\ s^{-1}$ in 0.088 M $HClO_4$ at 25 °C. The observed rate constant for reduction of the oxime at this acidity is 6.2 $M^{-1}\ s^{-1}$, of which a maximum of 77%, or 4.8 $M^{-1}\ s^{-1}$, pertains to the alcohol-generating path.

Contribution from the Energy Systems Group,
Rockwell International Corporation, Canoga Park, California 91304

Electrochemical Studies of Graphite Oxidation in Sodium Carbonate Melt

GARY B. DUNKS

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The oxidation of spectroscopic grade graphite in sparged beds of sodium carbonate employing air, nitrogen, and carbon dioxide was investigated at 900 °C by using electrochemical techniques. Evidence for the formation of metallic sodium suggested that a first step in the oxidation process was the reduction of sodium ion by graphite. The positive centers thus generated in the graphite matrix apparently reacted with oxyanions in the melt to produce carbon monoxide. The oxidation rate of a graphite electrode using carbon dioxide containing sparge gas was increased by application of positive potentials and decreased by application of negative potentials, which supports such an ionic mechanism. The initial rates of graphite oxidation using nitrogen or carbon dioxide sparge were approximately equal and were 6.5 times slower than the rate using air. Sequences of reactions are proposed for the oxidation of graphite using air, carbon dioxide, and nitrogen sparge gases in sodium carbonate melt.

Introduction

Alkali-metal carbonates are effective catalysts for the gasification of carbonaceous materials including coal. The mechanisms through which these gasification processes proceed however are not well understood.[1] In previous studies directed toward the elucidation of the mechanism of graphite oxidation in sparged beds of molten sodium carbonate, oxidation rates were determined as functions of oxygen and carbon dioxide concentrations of the sparge gas, melt temperature, sulfate concentration, graphite loading, and graphite surface area.[2–4] Subsequently, electrochemical measurements showed that oxide, peroxide, and superoxide ions and possibly the complex ions peroxycarbonate and peroxydicarbonate exist in molten sodium carbonate and how the concentrations of the melt species changed with perturbations of the oxygen and carbon dioxide concentrations of the sparge gas.[5]

The results of work in which the relative concentrations of melt species were monitored electrochemically during graphite oxidation in molten sodium carbonate using air, carbon dioxide, and nitrogen sparge gases are reported here.

Experimental Section

Materials. Air ("breathing air": 20.9% oxygen, 0.03% carbon dioxide, and 78.1% nitrogen), oxygen (99.993%), carbon dioxide (99.99%), nitrogen (99.999%), and calibration gas mixtures were obtained from and analyzed by Airco.

Sodium carbonate (Baker anhydrous reagent grade, 99.5%) contained nitrogen compounds (N, 0.001%), phosphorus (PO_4, 0.01%), silica (SiO_2, 0.005%), sulfur (SO_4, 0.003%), and iron (Fe, 5 ppm).

The graphite was spectroscopic grade SP2-Z powder (>80% graphitic) prepared from petroleum coke with use of a proprietary binder and heat treated at 3000 °C (Union Carbide Corp.). The total ash content was <2 ppm; impurities present were iron (0.3 ppm), magnesium (0.2 ppm), and silicon (0.4 ppm). Prior to use, the graphite was sieved with 80-mesh (0.0180-cm) and 100-mesh (0.0150-cm) screens. All of the experiments were performed with the −80 to +100 mesh fraction, which had a specific surface area of 1.01 m^2/g (BET, nitrogen, or krypton adsorption measured by Micromeritics Instrument Corp., Norcross, GA 30071). Graphite electrodes (0.32 × 30.5 cm cylinders) were ACKSP spectroscopic grade containing <6 ppm impurities and <1 ppm ash (Union Carbide Corp.). The graphite electrodes were lowered into the cell and suspended on platinum lead wires.

Apparatus. The apparatus (described in detail previously[5]) consisted of an electrochemical cell contained in a tube furnace. A three-electrode system was used in which the working electrode consisted of a rectangular gold sheet (1 × 0.5 × 0.025 cm) spot welded to 0.05-cm (diameter) gold lead wire and allowed to extend 1 cm into the melt providing an effective geometric surface area of 1.16 cm^2. The counterelectrode was a gold-foil cylinder (4 × 7 cm) that rested on the bottom of the crucible and was connected by a 0.05-cm (diameter) gold lead wire. The reference electrode consisted of a 0.05-cm (diameter) gold wire that dipped into the melt within an alumina tube that rested on the bottom of the crucible. The melt within the tube was in contact with a slow stream (40 mL/min) of oxygen (33%) and carbon dioxide (67%). This reference electrode has been described in detail.[6] All parts of the apparatus contacting the molten sodium

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