inhibits the general-acid-catalyzed dissociation pathway. Within the reaction complex, the increased electron density on the peptide nitrogen caused by solvent-assisted bond weakening permits unhindered proton transfer to occur. This is reflected by the low value obtained for the intrinsic energy barrier $\lambda/4$.

The product work term (W_P) is 17.4 kcal mol^{-1} and is calculated from C and the acid-dissociation constant ($10^{-7.7}$ M) of $Ni(H_{-1}G_3)$.[3] Formation of the reaction complex from the products ($Ni(H_{-1}G_3)$, B) would require bringing the products together with coordination of the peptide linkage. The large value of W_P is a reflection of the poor coordinating ability of the protonated peptide nitrogen.

Acknowledgment. This investigation was supported by the National Science Foundation (Grant CHE74-00043) and the Public Health Service (Grant No. GM 12152 from the National Institute of General Medical Sciences).

Registry No. $Ni(H_{-2}G_3)^-$, 31011-65-1; $[Ni(H_{-2}G_3)Im]^-$, 78393-22-3; $[Ni(H_{-2}G_3)(\alpha\text{-pic})]^-$, 78393-23-4.

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Formation of Nitrosyltricyanonickelate ($NiNO(CN)_3^{2-}$) in a Direct NO^- Displacement Reaction[1]

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Received April 6, 1981

Kinetic and stoichiometric studies of the formation of the violet complex $NiNO(CN)_3^{2-}$ when trioxodinitrate ($Na_2N_2O_3$) decomposes in the presence of $Ni(CN)_4^{2-}$ show that the process is controlled by release of the intermediate species HNO from $HN_2O_3^-$. Nitrosyltricyanonickelate is formed by direct displacement of CN^- by NO^-, in competition with dimerization of the intermediate to form N_2O. The proportion of NO^- that is trapped by $Ni(CN)_4^{2-}$ is pH dependent, increasing from 3.6% at pH 9.27 to ca. 30% at pH 10.75 with $Ni(CN)_4^{2-}$ in twofold excess over $Na_2N_2O_3$. In the additional presence of NH_2OH (tenfold excess), a three-way competiton for NO^- is established in which reduction to N_2 predominates and in which trapping of NO^- by $Ni(CN)_4^{2-}$ is reduced to 1.27% at pH 10.82. A NO^- intermediate known to be produced in the reaction between NO and NH_2OH is also shown to form $NiNO(CN)_3^{2-}$ by a direct displacement interaction with $Ni(CN)_4^{2-}$. The trapping efficiency of $Ni(CN)_4^{2-}$ for NO^- from this source is less than that for NO^- from $HN_2O_3^-$ decomposition. This difference is ascribed to a probable difference in the electronic states of NO^- ions formed in the two cases.

Introduction

In 1948 Nast and Proeschel[2,3] demonstrated that the deep violet product of the reaction between $K_2Ni(CN)_3$ and NO in liquid ammonia is identical with the complex ion produced by the action of hydroxylamine on $K_2Ni(CN)_4$ in alkaline aqueous solution. The product complex is $NiNO(CN)_3^{2-}$ and was postulated to have a tetrahedral rather than square-planar configuration.[2] Nast et al.[3] proposed that the disproportionation of hydroxylamine produces HNO, which is then deprotonated, and that NO^- directly displaces CN^- in $Ni(CN)_4^{2-}$ (eq 1-3). Nast, Nyul, and Grziwok[4] proposed that the yellow to violet color change accompanying postulated reaction 3 could be used as a sensitive test for the intermediacy of HNO or NO^-. They applied it, with apparently positive results, to the alkaline hydrolyses of three hydroxylamine sulfonates. Kinetic evidence for the intermediacy of HNO (or NOH) in one of these cases, the hydrolysis of hydroxylamine *N*-sulfonate, was later reported by Ackerman and Powell.[5]

$$2NH_2OH = NH_3 + HNO + H_2O \qquad (1)$$

$$HNO + OH^- = NO^- + H_2O \qquad (2)$$

$$Ni(CN)_4^{2-} + NO^- = NiNO(CN)_3^{2-} + CN^- \qquad (3)$$

The decomposition of trioxodinitrate ($Na_2N_2O_3$) has been assumed to yield HNO (or NOH) since the time of its discovery by Angeli,[6] an assumption that has been verified by isotope labeling.[7] If displacement reaction 3 occurs, $Na_2N_2O_3$ decomposition in the presence of $K_2Ni(CN)_4$ should produce the characteristic violet color of $NiNO(CN)_3^{2-}$. Veprek-Siska et al. observed such a reaction (eq 4) and employed it in development of a colorimetric analytical method for trioxodinitrate.[8] Otherwise, Nast's proposed test for HNO appears to have recieved little attention, although Hughes and Nicklin[9] applied it in a study of the autoxidation of hydroxylamine.

$$N_2O_3^{2-} + Ni(CN)_4^{2-} = NiNO(CN)_3^{2-} + NO_2^- + CN^- \qquad (4)$$

Veprek-Siska and Lunak have reported kinetic studies of the NH_2OH-$Ni(CN)_4^{2-}$ reaction in the presence of O_2[10] and in an inert atmosphere.[11] They conclude that displacement of CN^- by NO^- does not occur in either case, that trapping of NO^- cannot account for the observations of Hughes and Nicklin,[9] and that Nast's proposed test[4] for NO^- is not valid. In the oxidative case they postulate coordination of a fully deprotonated hydroxylamino species NO^{3-}, followed by its

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oxidation to NO^- within the Ni^{2+} coordination sphere. In inert atmosphere, they propose the two step mechanism shown in eq 5 and 6 They also report a reaction between nitrosyltricyanonickelate and hydroxylamine (eq 7).

$$Ni(CN)_4^{2-} + NH_2OH = Ni(NH_2OH)(CN)_3^- + CN^- \quad (5)$$

$$Ni(NH_2OH)(CN)_3^- + NH_2OH + OH^- = NiNO(CN)_3^{2-} + NH_3 + 2H_2O \quad (6)$$

$$NiNO(CN)_3^{2-} + NH_2OH + CN^- = Ni(CN)_4^{2-} + N_2 + H_2O + OH^- \quad (7)$$

Nast's proposed tetracyanonickelate test for HNO[4] depended initially upon the interpretation of hydroxylamine disproportionation as occurring via eq 1. However, whereas NH_3, N_2, and N_2O are the observed products of NH_2OH decomposition over widely varying conditions, Veprek-Siska and Lunak[11] report that no trace of N_2O can be detected in the presence of $Ni(CN)_4^{2-}$, although it would be an expected product if the intermediate HNO (or NO^-) were to experience a competiton between reactions of dimerization and $Ni(CN)_4^{2-}$ trapping. Indeed, they report reaction conditions under which (6) and (7) establish a steady-state $NiNO(CN)_3^{2-}$ concentration, the rates of N_2 and NH_3 production are equal, and the net process appears to be tetracyanonickelate-modulated hydroxylamine decomposition.

Lunak and Veprek-Siska have also investigated the NH_2OH disproportionation reaction.[12] They find it to be first order in NH_2OH, in agreement with earlier investigators,[13] a circumstance that argues against reaction 1 as an elementary process. They report a strong dependence of decomposition rate upon the purity of reagents employed, in particular KOH, and suggest that hydroxylamino complexes of catalyzing metal ions at trace concentration levels rather than nitrosyl hydride are the principal intermediates.

In addition to $NiNO(CN)_3^{2-}$, the nitrosyl complexes $CrNO(CN)_5^{3-}$[14] and $MnNO(CN)_5^{3-}$[15] have been prepared by treatment of the corresponding cyano complexes with alkaline hydroxylamine. The net reaction in each case is replacement of CN^- by NO^-, but it has not been suggested that direct insertion occurs. In both cases, the M-N-O bonds are known to be linear.[16,17] The complex ion $NiNO(CN)_3^{2-}$ has been shown to be mononuclear;[18] the NO stretching frequency is reported to be 1780 cm^{-1},[19] a value that suggests a linear $N{\equiv}O^+$ configuration. Although no detailed structural study has been reported, it seems most likely that this anion is a tetrahedral Ni(0) complex. In this paper we report experiments demonstrating that despite the probable NO^+ character of this compound, $NiNO(CN)_3^{2-}$ can be produced by direct replacement of CN^- by NO^- in $Ni(CN)_4^{2-}$.

Experimental Section

$K_2Ni(CN)_4$ was synthesized by the reaction of KCN with $NiSO_4 \cdot 6H_2O$ and was twice crystallized from water.[20] $Na_2N_2O_3$ was synthesized as reported previously.[9] Reagent grade $NH_2OH \cdot HCl$, $NaClO_4$, and borate buffer components were used without further purification. Commercial NO was purified by repeated passage over molecular sieve 5A at 113 K, followed by pumping at 77 K. Commercial CF_4 employed as chromatographic internal reference gas was deoxygenated by passage over BASF R3-11 catalyst.

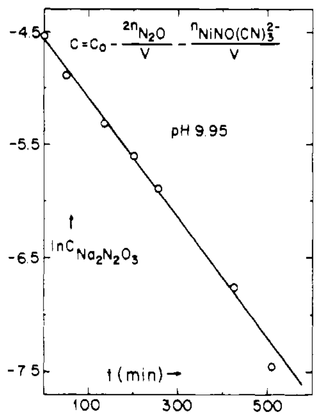

Figure 1. First-order rate plot for trioxodinitrate decomposition in the presence of $Ni(CN)_4^{2-}$ (pH 9.95, T = 25.0 °C, $[Ni(CN)_4^{2-}]_0$ = 0.0216 M). $[Na_2N_2O_3]$ was calculated according to eq 11.

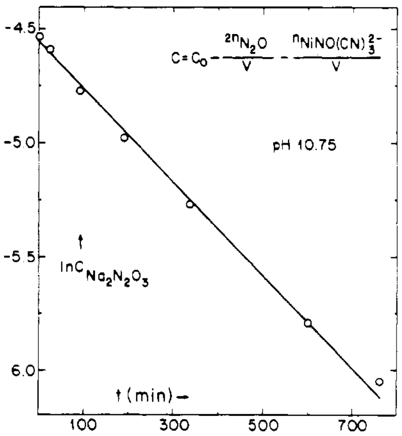

Figure 2. First-order rate plot for trioxodinitrate decomposition in the presence of $Ni(CN)_4^{2-}$ (pH 10.75, T = 25.0 °C, $[Ni(CN)_4^{2-}]_0$ = 0.0216 M). $[Na_2N_2O_3]$ was calculated according to eq 11.

All experiments were carried out under oxygen-free conditions, either by deaeration with N_2 or He or by vacuum line degassing techniques or both. Gas analyses were carried out chromatographically by use of CF_4 as internal reference and a vacuum line interface method described elsewhere.[21]

For studies of the $Na_2N_2O_3$–$K_2Ni(CN)_4$ system, the rate of change of $[NiNO(CN)_3^{2-}]$ was followed by continuous monitoring at λ = 498 nm with a Cary 14 spectrophotometer, employing the value 427 M^{-1} cm^{-1} for the molar absorption coefficient, as reported by Veprek-Siska and Lunak.[10] The rate of production of N_2O was followed with use of a reaction vessel described elsewhere.[22] A 16.0-mL solution of $K_2Ni(CN)_4$ in borate buffer in the main vessel and 4.0 mL of a solution of $Na_2N_2O_3$ in aqueous NaOH in the entry port position were degassed separately. Reaction was then initiated by causing the latter solution to drain into the main vessel, and purified CF_4 gas was admitted at measured partial pressure. Rapid phase mixing was provided by mechanical vibration (see ref 22), and the gas phase was sampled at intervals for analysis. The chromatographically measured ratio of N_2O/CF_4, appropriately corrected for solubility and for sample withdrawal, could then be used to calculate the moles of N_2O released. The compositions of the two solution components were chosen to provide the final desired pH upon combination, as determined by separate experiments and verified by direct measurement. Temperature-controlled water circulating continuously through the thin

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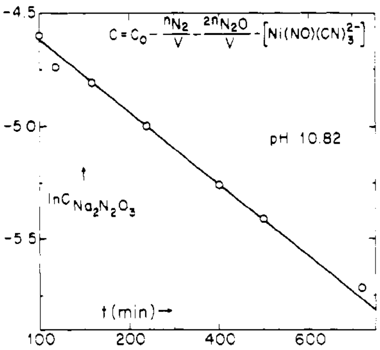

Figure 3. First-order rate plot for trioxodinitrate decomposition in the presence of both $Ni(CN)_4^{2-}$ and NH_2OH (pH 10.82, $T = 25.0$ °C, $[Ni(CN)_4^{2-}]_0 = 0.0216$ M, $[NH_2OH] = 0.0960$ M). $[Na_2N_2O_3]$ was calculated according to eq 12.

outer jacket of the reaction vessel served to maintain a temperature of 25.0 ± 0.1 °C.

The manner of initiation of reaction on the vacuum line, described above, resulted in small solution transfer losses, which account for the fact that the first-order rate plots to be described int the next section (Figures 1–3) miss initial concentration intercepts by 2–3%. Also, addition of a small volume of basic $Na_2N_2O_3$ solution to a larger volume of solution which is initially at pH lower than the desired final value may be expected to result in a brief interval of abnormally rapid decomposition during mixing. Simulation calculations show that this would result in an apparent initial slight loss and later recovery of linearity, a feature that appears in the results and has been accorded a slight weighting factor in determining the slopes of first-order plots.

When the only gas-reaction product was N_2O, gas-phase samples (dried by passage through a helical trap at dry-ice temperature) were collected by condensation at 77 K. In experiments in which NH_2OH reduction led to N_2 product, collection of gas samples containing N_2O, CF_4, and N_2 was necessarily carried out with the aid of a Toepler pump.

In studies of the NH_2OH–$Ni(CN)_4^{2-}$–NO system, no solution addition at the entry port was necessary. Buffered solutions of NH_2OH and $K_2Ni(CN)_4$ were separately deaerated, introduced to the vessel by syringe injection, then degassed. Reaction was initiated by addition of an NO–CF_4 mixture of known composition, at measured partial pressure. So that mass balances could be obtained, gas samples were analyzed for the four components CF_4, NO, N_2, and N_2O. Upon completion of the reaction, an aliquot of the solution phase was removed by syringe and held under an inert atmosphere while spectrophotometrically analyzed for $NiNO(CN)_3^{2-}$ concentration.

Results and Discussion

(1) $Na_2N_2O_3$ + $K_2Ni(CN)_4$. Decomposition of the monobasic anion $HN_2O_3^-$ (eq 8) is known to proceed at a pH-independent rate in the interval pH ca. 4–8,[7,23] followed normally by the rapid dimerization process eq 9, although in the presence of hydroxylamine there is a competing reduction reaction,[24] eq 10. In order to explore the possibility that $Ni(CN)_4^{2-}$ trapping may similarly compete with dimerization, it was necessary to conduct our experiments at pH >9 because of the high pK_a of HCN. Under these conditions we assume the intermediate to exist in the deprotonated form NO^-, conistent with the pK_a value 4.7 measured for an HNO species observed by pulse radiolysis.[25]

$$HN_2O_3^- = HNO + NO_2^- \tag{8}$$

$$HNO + HNO = N_2O + H_2O \tag{9}$$

$$HNO + NH_2OH = N_2 + 2H_2O \tag{10}$$

Table I. Initial Rates of Formation of $NiNO(CN)_3^{2-}$ in Solutions Containing $Na_2N_2O_3$ and $K_2Ni(CN)_4$ and Borate Buffer[a]

(1) $[Na_2N_2O_3] = 0.010$ M

$[Ni(CN)_4^{2-}]$, M	10^8R_0,[b] M s^{-1}	$10^6R_0/[Ni(CN)_4^{2-}]$, s^{-1}
0.0053	2.67	5.04
0.010	5.67	5.67
0.020	10.9	5.45

(2) $[Ni(CN)_4^{2-}] = 0.010$ M

$[Na_2N_2O_3]$, M	10^8R_0,[b] M s^{-1}	$10^6R_0/[Na_2N_2O_3]$, s^{-1}
0.0060	3.58	5.97
0.010	5.67	5.67
0.0218	7.50	3.44

[a] $I = 0.50$ M (maintained with $NaClO_4$); $T = 25.0$ °C. [b] $R_0 = d[NiNO(CN)_3^{2-}]/dt$, as determined from initial slope of concentration vs. time curve.

Initial rates of formation of $NiNO(CN)_3^{2-}$ in the presence of $Na_2N_2O_3$ were determined in a preliminary series of spectrophotometric experiments at pH 9.45, with the results shown in Table I. The method is subject to a number of uncertainties, particularly in relation to the rate of initial mixing, but within these limitations it is clear that the rate of initial formation of the nitrosyl complex increases with the concentrations of both reagents, is probably proportional to the concentration of $Ni(CN)_4^{2-}$, and may also be proportional to the concentration of $Na_2N_2O_3$ (i.e., of $HN_2O_3^-$).

Kinetics experiments were carried out, following N_2O production by vacuum line–GC techniques and $NiNO(CN)_3^{2-}$ production (in separate systems of identical composition) by spectrophotometry. With the assumption that the rate-controlling process is reaction 8 but that the (deprotonated) HNO formed in this reaction is consumed by a combination of dimerization reaction 9 and a competing displacement reaction (3), the concentration of undecomposed $Na_2N_2O_3$ at any time t should be given by eq 11 where n_{N_2O} is total moles of N_2O released, and V is the volume of the solution phase. The logarithm of this combination of terms is found to provide good first-order rate plots, as illustrated in Figures 1 and 2. The final points in the two cases shown appear at 3.9 and $2.2t_{1/2}$, respectively. (Experimental uncertainty becomes substantial beyond t = ca. $3t_{1/2}$). The proportion of HNO that reacts with $Ni(CN)_4^{2-}$, i.e., the "trapping" ratio $n_{NiNO(CN)_3^{2-}}/(n_{NiNO(CN)_3^{2-}} + 2n_{N_2O})$, increases with pH and also shows a gradual increase with time during individual runs. (I.e., in the Figure 1 experiment, this ratio increases from 10.3% at 50 min to 14.8% at 510 min and has an "infinite" time value of 14.3%. Corresponding values for the Figure 2 experiment are 21.1% (10 min), 27.6% (760 min), and 28.1% ("infinite" time). These observations are consistent with the assumption of a small initial interval of relatively rapid N_2O production (see Experimental Section).)

$$[Na_2N_2O_3]_t = [Na_2N_2O_3]_0 - \left(\frac{2n_{N_2O}}{V}\right)_t - [NiNO(CN)_3^{2-}]_t \tag{11}$$

The fact that the combination of separately measured concentration terms (eq 11) corresponds closely to first-order kinetic behavior could hardly be expected if the products arise from mechanistically distinct processes. We conclude that the overall process is controlled by the release of HNO from $HN_2O_3^-$ (eq 8), followed by rapid, competing reactions of

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Table II. First-Order Rate Constants, Mass Balances, and Trapping Ratios for Complete $Na_2N_2O_3$ Decomposition in the Presence of $K_2Ni(CN)_4$ in 20.0 mL of Borate Buffer[a]

expt no.	pH	reactant $10^5(n_{Na_2N_2O_3})_0$	products $10^5 n_{N_2O}$	 $10^5 n_{NiNO(CN)_3^{2-}}$	$10^5 k_1$, s^{-1}	mass balance,[b] %	trapping ratio,[c] %
1	9.27	23.7	12.2	0.911	18.0	106.8	3.6
2	9.45	21.3	9.91	1.68	14.0	100.8	7.8
3[d]	9.95	21.7	19.50	3.18	8.8	101.8	14.3
4	9.95	22.6	10.96	3.28	8.9	111.5	13.0
5	9.99	22.3	9.67	2.84		99.5	12.8
6	10.05	20.9	8.97	3.79	7.4	104.0	17.4
7[e]	10.75	21.6	8.44	6.07	3.4	106.3	26.5
8	10.75	19.9	6.39	6.32		96.0	33.1

[a] $I = 0.25$ M; $[Ni(CN)_4^{2-}] = 0.0216$ M; $T = 25$ °C. [b] Mass balance = $(2n_{N_2O} + n_{NiNO(CN)_3^{2-}})/n_{Na_2N_2O_3}$. [c] Trapping ratio = $n_{NiNO(CN)_3^{2-}}/(n_{NiNO(CN)_3^{2-}} + 2n_{N_2O})$. [d] Figure 1. [e] Figure 2.

Table III. Experiments on $Na_2N_2O_3$ Decomposition in the Presence of both $Ni(CN)_4^{2-}$ and NH_2OH in Borate Buffer in a 20.0-mL Solution[a]

expt no.	pH	$10^5 \times (n_{Na_2N_2O_3})_0$	% completion	$10^5 n_{N_2}$	$10^5 n_{N_2O}$	$10^5 \times n_{NiNO(CN)_3^{2-}}$	$10^5 k_1$, s^{-1}	mass balance,[b] %	trapping ratio,[c] %
1	10.72	21.7	84			0.26	(3.4)[d]		(1.4)[d]
2	10.82	21.3	100	18.2	1.39	0.270	2.67	99.8	1.27
3	11.04	22.2	64	12.0	1.03	0.216	2.16		1.52
4	11.33	21.3	41	7.04	0.761	0.162	1.33		1.86

[a] $I = 0.25$ M; $[Ni(CN)_4^{2-}] = 0.0216$ M; $[NH_2OH] = 0.096$ M; $T = 25$ °C. [b] Mass balance = $(n_{N_2} + 2n_{N_2O} + n_{NiNO(CN)_3^{2-}})/n_{Na_2N_2O_3}$. [c] Trapping ratio = $n_{NiNO(CN)_3^{2-}}/(n_{N_2} + 2n_{N_2O} + n_{NiNO(CN)_3^{2-}})$. [d] Value of k_1 from Table II, used to estimate trapping ratio.

Table IV. Experiments on the Reaction between NO and NH_2OH in the Presence of $Ni(CN)_4^{2-}$ at 25 °C in a 20.0-mL Solution

expt no.	pH	$[NH_2OH]_0$, M	$[Ni(CN)_4^{2-}]_0$, M	react time t, min	$10^4 \times$ (moles of NO reacted)	10^4(moles of product) N_2	 N_2O	 $NiNO(CN)_3^{2-}$	mass balance,[a] %	trapping ratio,[b] %
1	12.0	0.332	0.224	500	16.8	7.60	10.6	0.0490	108	0.64
2	12.6	0.332	0.489	200	5.87	2.64	3.16	0.0222	99.2	0.83
3	12.7	0.332	0.108	300	3.59	1.76	2.18	0.0206	110	1.16
4	12.7	0.332	0.489	150	4.43	2.20	2.89	0.0211	115	0.95
5	13.3	0.332	0.108	45	2.26	1.07	1.35	0.0222	108	2.0
6	14	0.113	0.108	115	1.78	0.858	0.882	0.157	107	15.5
7	14	0.113	0.108	1080	4.63	2.19	2.39	0.169	103	7.2

[a] Mass balance = $(n_{N_2} + n_{N_2O} + n_{NiNO(CN)_3^{2-}})/n_{NO}$. [b] Trapping ratio = $n_{NiNO(CN)_3^{2-}}/(n_{N_2} + n_{NiNO(CN)_3^{2-}})$.

dimerization to produce N_2O (eq 9) and trapping by $Ni(CN)_4^{2-}$ to form $NiNO(CN)_3^{2-}$ (eq 3). Rate constants obtained in these and other instances, as well as mass balances and trapping ratios measured upon complete reaction in a total of eight experiments (Table II), provide further evidence.

Our assumption requires that n moles of $Na_2N_2O_3$ initially present produce n moles of NO^- during total decomposition. If no NO^- is diverted to solution products other than $NiNO(CN)_3^{2-}$ (e.g., hyponitrite), then $(n_{Na_2N_2O_3})_0$ should be matched by $(n_{NiNO(CN)_3^{2-}} + 2n_{N_2O})_{final}$. This expectation is corroborated by the mass balance data shown in Table II. The mean value of 103 ± 5% seems satisfactory in view of the experimental uncertainty of ca. 5% and the possibility of additional uncertainty in the value employed for E_{498} of $NiNO(CN)_3^{2-}$. Since nitrite is a product of $N_2O_3^{2-}$ decomposition, a solution containing $NiNO(CN)_3^{2-}$ was treated with added NO_2^- for 18 h; no gas product and no change in absorbance at 498 nm were observed.

The general level of agreement between k_1 values for $HN_2O_3^-$ decomposition in the presence and absence of $Ni(CN)_4^{2-}$ seems satisfactorily consistent with our assumption that this process is controlling. The rate constants reported in Table II are in good agreement with a spectrophotometric value previously reported[7] for pH 10 but are somewhat lower than the values reported by Hughes and Wimbledon.[23] A rate constant measured without $Ni(CN)_4^{2-}$ at pH 10.75 by the method employed in these experiments gave the value 3.9×10^{-5} s^{-1} in contrast to the value of 3.4×10^{-5} s^{-1} observed in the presence of $Ni(CN)_4^{2-}$ (experiment 7). It is possible that $HN_2O_3^-$ decomposition is somewhat retarded by the presence of the complex, but this could not be checked by direct spectrophotometry because of strong interference in the UV on the part of both $Ni(CN)_4^{2-}$ and $NiNO(CN)_3^{2-}$.

It is interesting to note in Table II that the trapping ratio, i.e., the proportion of total NO^- released that is converted to nitrosyl complex, is a pH-dependent quantity. Its increase is about tenfold over the modest pH range examined, and given this trend it is plausible to believe that trapping could become the nearly exclusive fate of NO^- ions produced in the presence of $Ni(CN)_4^{2-}$ in strong base, if other competing processes are absent. While this may account for the observations of Hughes and Nicklin[9] in their study of the autoxidation of of NH_2OH, it seems to us more likely that their results may be accounted for by the direct NH_2O^-–$Ni(CN)_4^{2-}$ reaction, which is known to be much faster in the presence of O_2 than in its absence.[10,11]

(2) $Na_2N_2O_3$ + $K_2Ni(CN)_4$ in the Presence of NH_2OH. It has been shown that $HN_2O_3^-$ decomposition is not kinetically affected by the presence of NH_2OH but that this molecule competes strongly for HNO (NO^-) in reduction reaction 10.[24] It is therefore of interest to determine whether an $HN_2O_3^-$–$Ni(CN)_4^{2-}$ system establishes a three-way competition for NO^- in the presence of NH_2OH. In a preliminary spectrophotometric experiment at pH 10.72 (experiment 1, Table III), we followed only the growth of nitrosyl complex in the presence of NH_2OH (tenfold stoichiometric excess) and found that its formation is greatly reduced relative to the ca. 30% trapping ratio level reported in Table II. A full-scale measurement of both kinetics and stoichiometry was then carried out under similar conditions (experiment 2), basing concentration and mass balance calculations this time on the assumed relation shown in eq 12. The measured mass balance of 99.8% and

$$[Na_2N_2O_3]_t = [Na_2N_2O_3]_0 - \frac{n_{N_2}}{V} - \frac{2n_{N_2O}}{V} - [NiNO(CN)_3^{2-}] \tag{12}$$

the linear first-order rate plot (Figure 3) corroborate the assumption. The very low trapping ratio of 1.27% and the fact that the product gas contains more than 90% N_2 as expected[24] show that hydroxylamine reduction predominates over both dimerization and $Ni(CN)_4^{2-}$ trapping under these conditions. The additional experiments 3 and 4 show that the trapping ratio increases slowly with pH under NH_2OH-competition conditions.

(3) $NH_2OH + NO + Ni(CN)_4^{2-}$. Hydroxylamine reacts with NO to yield N_2O and N_2 via a mechanism that has been shown to involve NO^- intermediacy.[24] At high pH the intermediate is quantitatively reduced to N_2. It is now known that the reactive hydroxylamine species in this reaction is the deprotonated form NH_2O^-,[26] hence the overall process is given by eq 13–15. With decreasing pH, the product ratio n_{N_2}/n_{N_2O}

$$NO + NH_2O^- \rightarrow HNO + HNO^- \tag{13}$$

$$HNO^- + NO \rightarrow N_2O + OH^- \tag{14}$$

$$NO^- + NH_2O^- \rightarrow N_2 + 2OH^- \tag{15}$$

is observed to fall because of a pH-dependent competition between reduction 15 and the dimerization reaction 9 or 16.

$$NO^- + NO^- + H_2O \rightarrow N_2O + 2OH^- \tag{16}$$

Experimental study of the possibility that $Ni(CN)_4^{2-}$ may compete for the NO^- produced in this reaction system is complicated by the fact that NH_2OH is reported to produce $NiNO(CN)_3^{2-}$ in a process that does not involve NO^- intermediacy[11] (reactions 5 and 6) and also by the possibility that nitrosyl complex may be destroyed by reaction 7. Direct reaction between NH_2O^- and $Ni(CN)_4^{2-}$ is reported to be slow at modest levels of basicity,[10] particularly in the nonoxidative case.[11] In a preliminary experiment at pH ca. 13, a degassed solution containing hydroxylamine and $Ni(CN)_4^{2-}$ was allowed to stand for 12 h. No visible sign of $NiNO(CN)_3^{2-}$ production was observed, but upon admission of NO to the system, the violet color characteristic of this species was observed with dramatic suddenness. Spectrophotometric examination proved it to be identical with the nitrosyl complex formed with $HN_2O_3^-$. Kinetic plots based upon P_{NO} measurements showed that the presence of $Ni(CN)_4^{2-}$ has no effect on the rate of the NH_2OH–NO reaction. (E.g., pseudo-first-order plots at $[NH_2OH] = 0.332$ M and $[Ni(CN)_4^{2-}] = 0.244$ M gave half-lives of 117 and 21.7 min at pH 12.0 and 12.6, respectively, compared with 125 and 22.0 min in the absence of $Ni(CN)_4^{2-}$.[26])

Results of experiments designed to evaluate $Ni(CN)_4^{2-}$ trapping of NO^- produced in the NH_2OH–NO reaction are summarized in Table IV. In each case the molar quantities of N_2 and N_2O reported are final values measured either shortly before or after complete exhaustion of the NO initially admitted; the molar quantities of nitrosyl complex were determined immediately thereafter. The exception to this procedure is experiment 7 in which the final measurement was carried out well beyond the time of reaction completion.

We first consider whether a significant proportion of the $NiNO(CN)_3^{2-}$ reported in Table IV could be accounted for in terms of NH_2OH insertion (reactions 5 and 6).[11] The rate of this process is reported to be strongly $[OH^-]$ dependent, and visual observation convinces us that below pH ca. 13 its contribution is negligible during the reaction times employed in our study. The conditions of experiment 6 (pH 14) were reproduced in a separate experiment, and no visible color change was observed after 100 min without addition of NO, leading us to conclude that the complex concentration levels in both this case and experiment 5 are due largely to NO^- trapping.

We confirmed reaction 7 by deliberate addition of strongly basic NH_2OH solution to a solution containing $NiNO(CN)_3^{2-}$; the violet color was observed to fade, and N_2 gas was detected as reaction product. Other observations gave a clear impression that the rate of this reaction increases with pH. So that its probable effect on the experiment carried out at the lowest pH 12 (experiment 1) could be assessed, a solution containing $NiNO(CN)_3^{2-}$ was made 0.332 M in NH_2OH and adjusted to pH 12, and its concentration was followed by monitoring at $\lambda = 498$ nm. This yielded a pseudo-first-order rate constant of 3.1×10^{-6} s^{-1}, i.e., a half-life of 62 h in comparison with that of 117 min observed for the NO–NH_2OH reaction at the same pH. The effect of reaction 7 on the observed nitrosyl complex yield at pH 12 is therefore very small. A similar experiment carried out at pH ca. 14 indicated a small increase in $[NiNO(CN)_3^{2-}]$ during initial stages, and it is thus possible that the trapping ratio reported for experiment 6 is slightly elevated by a nontrapping reaction. However, the principal effect on $[NiNO(CN)_3^{2-}]$ at high pH is due to its destruction in reaction 7, as is made clear by the reduction of apparent trapping ratio after 1080 min (experiment 7) compared with 115 min (experiment 6).

We are confident, then, that the $NiNO(CN)_3^{2-}$ concentrations reported at the lower pH levels provide an accurate reflection of NO^- trapping. At these levels, the product ratios $(n_{N_2} + n_{NiNO(CN)_3^{2-}})/n_{N_2O}$ are less than unity, as expected under conditions in which HNO dimerization may be significant,[24] although they are generally somewhat lower than observed in the absence of $Ni(CN)_4^{2-}$.[22,26] The trapping ratio defined for Table IV is based upon the sequence eq 13–15; if product ratios are used to apportion NO^- intermediate in a way that takes dimerization reaction 16 into account, in addition to reduction and trapping, somewhat lower values are obtained (e.g., 0.51% at pH 12). The trapping ratios reported in Table IV for pH 12–12.7 should therefore be taken as upper limit values. At high pH, product ratios $(n_{N_2} + n_{complex})/n_{N_2O}$ near or slightly greater than unity are observed as expected.[24,26] Mass balances in all cases are generally greater than 100%, a fact that we ascribe to hydroxylamine disproportionation. This is consistent with observations made in the absence of $Ni(CN_4^{2-}$,[24,26] but the effect appears to be somewhat greater, possibly because of transition metal catalysis.[12] Apportionment of NO^- for dimerization renders mass balance figures somewhat greater than the values shown in Table IV (e.g., 102% for experiment 2).

(4) Properties of NO^- from the Two Reaction Sources. Extrapolation of the three values of NO^- trapping ratio in Table III (experiments 2–4) yields an estimated value of 2.65% at pH 12. The upper limit value for the trapping ratio in the NO–NH_2OH reaction at pH 12 is 0.64% (Table IV, experiment 1). The differences of conditions between the two cases are all in directions that should favor NO^- trapping in the Table IV case over that of Table III.[27] We conclude that the

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(26) Wang, N-Y; Bonner, F. T., unpublished results.

(27) I.e.: $n_{NH_2OH}/n_{Ni(CN)_4^{2-}} = 1.5$ (Table IV), 4.4 (Table III); $n_{NH_2OH}/n_{NO^-} = 4.0$ (Table IV), 9.0 (Table III); $n_{Ni(CN)_4^{2-}}/n_{NO^-} = 2.7$ (Table IV), 2.0 (Table III).

data reflect a real difference in the properties of the NO^- intermediate produced in the NO–NH_2OH reaction and in $HN_2O_3^-$ decomposition. We have previously reported that at pH 8 the $HN_2O_3^-$ decomposition product is predominantly reduced to N_2 in the presence of excess NH_2OH, whereas the intermediate produced in the NO–NH_2OH reaction forms N_2O predominantly under similar conditions.[24] We have speculated that this difference may correspond to the tautomers HNO and NOH, and since recent NMR evidence suggests that $HN_2O_3^-$ is protonated at nitrogen[28] and therefore releases HNO, we believe it possible that NO abstracts a hydrogen atom from NH_2O^- (reaction 13) at oxygen to form NOH. Since HNO is known to have a singlet ground state while calculations show that the unobserved species NOH would have a triplet ground state,[29–32] the key to the differences of properties observed in our reaction settings may reside in a difference of multiplicity between the two postulated forms of NO^-.

Conclusion

This paper describes the first proven instance of synthesis of a nitrosyl complex by direct insertion of NO^- into the coordination sphere of a transition metal ion, as far as we are aware. However, our efforts to achieve similar NO^- displacement processes in $Au(CN)_2^-$, $Pd(CN)_4^{2-}$, and $Pt(CN)_4^{2-}$, employing $HN_2O_3^-$ as a source of NO^-, have not succeeded. While our combination of kinetic and stoichiometric results shows conclusively that NO^- does engage in direct reaction in the case of Ni(II), it appears likely that Veprek-Siska and Lunak are correct in concluding that the reaction between NH_2OH and $Ni(CN)_4^{2-}$ can proceed at high pH without NO^- intermediacy[10,11] and that NH_2OH disproportionation does not produce this intermediate.[12] The NO^- test proposed by Nast et al.[4] cannot be taken to be conclusive and must be applied with caution.

Registry No. $NiNO(CN)_3^{2-}$, 25703-99-5; $K_2Ni(CN)_4$, 14220-17-8; $Na_2N_2O_3$, 13826-64-7; NH_2OH, 7803-49-8; NO, 10102-43-9; N_2O, 10024-97-2; N_2, 7727-37-9.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 3. Formation, Acid-Catalyzed Decomposition, and Intramolecular Isomerization of Oxygen-Bonded ($\alpha\beta S$)-(Sulfito)(tetraethylenepentamine)cobalt(III) Ion and the Hydrolysis of Its Sulfur-Bonded Analogue[1]

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Received December 16, 1980

The rate of SO_2 uptake by ($\alpha\beta S$)-hydroxo(tetraethylenepentamine)cobalt(III) ion has been studied by stopped-flow technique over the ranges $5.15 \le pH \le 7.6$ and $0.005 \le [\text{total sulfite}] \le 0.2$ M ($I = 1.0$ M, 10–20 °C) in sulfite buffer medium. The rate and activation parameters for SO_2 addition to $[(\alpha\beta S)\text{-Co(tetren)OH}]^{2+}$ are $k(10\ °C) = (3.2 \pm 0.5) \times 10^8\ s^{-1}\ M^{-1}$, $\Delta H^{\ddagger} = -0.5 \pm 1.0$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -21.0 \pm 3.5$ cal K^{-1} mol^{-1}. Retardation by SO_3^{2-} and SO_4^{2-} is observed, which is ascribed to the formation of nonreactive ion pairs $[(\alpha\beta S)\text{-Co(tetren)OH}_2,X]^+$ with association constants of $125 \pm 25\ M^{-1}$ ($X = SO_3^{2-}$) and $27 \pm 3\ M^{-1}$ ($X = SO_4^{2-}$) at 10 °C and $I = 1.0$ M. The product of the SO_2 uptake reaction is shown by spectral studies to be an O-bonded sulfito intermediate. At 10 °C the protonated form of such a species, $[(\alpha\beta S)\text{-Co(tetren)OSO}_2H]^{2+}$ (pK = 3.3), eliminates SO_2 with $k = 550 \pm 80\ s^{-1}$, $\Delta H^{\ddagger} = 7.2 \pm 2.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -20.4 \pm 8.7$ cal K^{-1} mol^{-1}. The oxygen-bonded sulfito intermediate shows no tendency to undergo internal redox but slowly isomerizes to its sulfur-bonded analogue. This process is shown to be totally intramolecular and its rate parameters are $k(30\ °C) = (4.2 \pm 0.7) \times 10^{-4}\ s^{-1}$, $\Delta H^{\ddagger} = 13.5 \pm 0.9$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -29.6 \pm 3.0$ cal K^{-1} mol^{-1}. The sulfur-bonded isomer is also very stable to reduction of the cobalt(III) center, but it does undergo second-order base hydrolysis in the range $[OH^-] = 0.2$–0.8 M with $k(25\ °C) = (0.81 \pm 0.01) \times 10^{-4}\ s^{-1}\ M^{-1}$, $\Delta H^{\ddagger} = 27.6 \pm 0.7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 15.1 \pm 2.4$ cal K^{-1} mol^{-1}. At 90 °C and $[H^+] = 0.5$ M, there is evidence for slow acid-catalyzed hydrolysis ($k_{obsd} \sim 10^{-5}\ s^{-1}$), but a detailed study of this process was not made.

Introduction

Recent investigations in this laboratory show that O-bonded sulfito complexes are formed on the stopped-flow time scale by reaction of acidic aqueous sulfite with aquopentaammine-,[4] *cis*-[5] or *trans*-diaquobis(ethylenediamine)-,[6] or diaquo(2,2′,2″-triaminotriethylamine)cobalt(III)[1] complex ions. The kinetic data demonstrate in each case that formation of the O-bonded sulfito species may be attributed to nucleophilic attack by the Co–OH moiety of the deprotonated complex ions on dissolved SO_2. The O-bonded products are all unstable, rapidly and completely reverting to the original reactants at low pH (≤2). However, at higher pH values, a much slower

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