Kinetic and Mechanistic Investigations of the Reduction by Radicals of Nitro to Hydroxyamino Groups in a Cobalt(III) Cage Compound

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A compound containing both a hydroxyamino and a nitro group in a cobalt(III) cage complex was detected and isolated in a $DQ^{\ddagger}$ (1,1′-ethylene-2,2′-bipyridinium radical cation) reduction of the corresponding symmetric dinitro compound, $[Co(diNOsar)]^{3+}$ (diNOsar=1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane). The nitro group of this compound was reduced to the hydroxyamino group by $\dot{S}O_2^-$, $MDQ^{\ddagger}$ (1,1′-ethylene-4,4′-dimethyl-2,2′-bipyridinium radical cation), and $PDQ^{\ddagger}$ (1,1′-trimethylene-2,2′-bipyridinium radical cation). Rate constants for the various processes were obtained.

Sargeson et al.[1,2] have synthesized and developed the chemistry of a large number of macrocyclic metal cage compounds. The cobalt(III) cage complex containing two nitro groups $[Co(diNOsar)]^{3+}$ (**1**, X=Y=NO_2)[3] has interesting and unique redox properties. Compounds in various states of reduction between nitro and amino groups have been prepared by reductions with electrodes,[4] zinc dust,[1] and dithionite.[5] When the dithionite ion is used in excess, $[Co^{III}(diNOsar)]^{3+}$ is reduced to $[Co^{II}(diNOsar)]^{2+}$ and the latter is then followed by a reduction of the nitro to hydroxyamino groups with a concomitant oxidation of cobalt(II) to cobalt(III):[5]

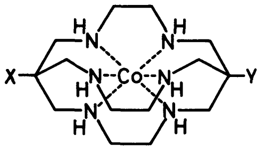
$$[Co^{III}(diNOsar)]^{3+} \xrightarrow{e^-} [Co^{II}(diNOsar)]^{2+} \qquad (1)$$

$$[Co^{II}(diNOsar)]^{2+} \xrightarrow{7e^-} [Co^{III}(diHAsar)]^{3+} \qquad (2)$$

Dithionite ion is a very strong reductant of the formal redox potential −0.66 V at pH 7.[6] If we choose various reductants,[7] DQ^+ (**2a**, $E°=-0.35$ V), MDQ^+ (**2b**, −0.49 V), and PDQ^+ (**2c**, −0.55 V), it would be possible to obtain an intermediate compound in the formation process of $[Co^{III}(diHAsar)]^{3+}$ (**1**, X=Y=NHOH) from $[Co^{III}(diNOsar)]^{3+}$. Therefore, we decided to study the kinetics and to examine the products of this interesting reaction using the above radicals as well as SO_2^- ions which are effective reductants from dithionite ions. The kinetics of a one-electron reduction of $[Co(diNOsar)]^{3+}$ with viologen radicals as in Reaction 1 were reported previously.[8]

Experimental

Materials. $[Co(diNOsar)](ClO_4)_3\cdot H_2O$ was prepared as described previously.[5,9] Its absorption spectrum in water (λ_{max}=474 nm (ε=159 $M^{-1}cm^{-1}$) and λ_{max}=345 nm (ε=128 $M^{-1}cm^{-1}$)) was in agreement with that described in the literature.[5] 1,1′-Ethylene-2,2′-bipyridinium dibromide, $(DQ)Br_2$, was obtained from Chemical Services. 1,1′-Ethylene-4,4′-dimethyl-2,2′-bipyridinium dibromide hydrate, $(MDQ)Br_2\cdot H_2O$, and 1,1′-trimethylene-2,2′-bipyridinium dibromide hydrate, $(PDQ)Br_2\cdot H_2O$, were prepared by the method of Homer and Tomlinson.[10] The other chemicals used were the purest commercial products. The viologen radicals (DQ^+, MDQ^+, and PDQ^+) were prepared by adding 0.95 equivalent of sodium dithionite to the oxidized viologens (DQ^{2+}, MDQ^{2+}, and PDQ^{2+}). $[Co(sep)]^{2+}$ was generated in situ by Zn/Hg reduction of $[Co(sep)]^{3+}$.[11] Aquapentacyanoferrate(II), $[Fe(CN)_5H_2O]^{3-}$, was prepared in situ by dissolving $Na_3[Fe(CN)_5NH_3]$ in water.



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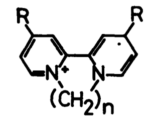

2a $DQ^{\ddagger}$ (n=2, R=H)
2b $MDQ^{\ddagger}$ (n=2, R=CH_3)
2c $PDQ^{\ddagger}$ (n=3, R=H)

Fig. 1.

Kinetics. All kinetic measurements were carried out using a Gibson-Dionex stopped-flow spectrophotometer interfaced with an OLIS data-collecting system. The reactions with viologen radicals were followed by the loss of the radical at 760 nm, 25 °C, an ionic strength (*I*) of 0.50 M (1 M=1 mol dm^{-3}) with Na_2SO_4, and pH=7.8—8.2 (Tris-H_2SO_4 buffer, Tris=tris(hydroxymethyl)aminomethane) in an argon atmosphere. The molar absorption coefficients used were $\varepsilon_{760}=2.7\times10^3$ $M^{-1}cm^{-1}$ (DQ^+) and $\varepsilon_{760}=2.9\times10^3$ $M^{-1}cm^{-1}$ (MDQ^+).[7] The viologen radical (6.0×10^{-5}—2.9×10^{-4} M) was used in excess over the cobalt(III) complex (1.0×10^{-5}—5.0×10^{-5} M). Dithionite reductions were carried out at pH 6.3 (0.1 M MES buffer, MES=2-(*N*-morpholino)ethane sulfonic acid) and pH 10.8 (0.02 M borate buffer), at 25 °C and *I*=0.50 M (Na_2SO_4). The cobalt(III) complex decomposed slowly at pH 10.8; therefore, neutral solutions of cobalt(III) complex in Na_2SO_4 were mixed with dithionite solutions at pH 11.1 (0.04 M borate buffer). The reactions were followed at the absorption maximum 505 nm of this complex at pH 10.8. Dithionite (5.0×10^{-3}—4.0×10^{-2} M) was used in excess over cobalt(III) complex (3.0×10^{-4}—5.0×10^{-4} M).

Product Analyses. Viologen radicals and dithionite ion were used in five-to fifteen-fold excess over the cobalt(III) complex (1×10^{-4}—5×10^{-4} M). After the reactions were quenched by introducing air (reaction time was about half an hour at room temperature), the solutions were poured onto a CM-Sephadex C-25 (Na^+ form) column. The column was washed with water and the products were separated using different concentrations of NaCl solutions. Spectral measurements were carried out using a Cary 14 spectrophotometer and a Hitachi 260-50 IR spectrophotometer. Cyclic voltammetry was carried out in an argon atmosphere in an aqueous Tris-H_2SO_4 buffer (pH 7.8) with a BAS Model CV-1B Instrument. A three-electrode system was composed of a Pt auxiliary electrode and a Pt working electrode against a Ag/AgCl (3 M NaCl) reference electrode. Voltammograms were recorded on a Houston Instruments Omnigraphic 100 X-Y recorder at scan rate of 20—200 mV s^{-1}.

Results and Discussion

Product Analyses. When a viologen radical was mixed with $[Co(diNOsar)]^{3+}$, Reaction 1 was observed, being followed by a slow process. Stoichiometry determinations and kinetics were carried out on the MDQ^+ system where the slow process was sufficiently fast to be followed before an occurrence of a spontaneous decay of MDQ^+. Stoichiometric titrations monitored at an MDQ^+ radical peak showed $[MDQ^+]/[Co(III)]=8.0\pm0.1$ for the overall reaction; therefore a 7:1 stoichiometry was required for the second stage. The same result was obtained from the absorbance change in stopped-flow traces during the reaction; the ratio of the amplitude for the second stage and the first stage was 7.0 ± 0.2 at 760 nm. The same stoichiometry was obtained in the PDQ^+ reduction.

When an excess of MDQ^+ was used over the cobalt(III) complex (at least 15 times), three products were separated on a Shephadex column. A pale-green species was eluted with a 0.1 M NaCl solution and was identified as MDQ^{2+}. A trace amount of a yellow species was eluted with a 0.4 M NaCl solution, but was not identified. A third orange species was eluted with a 0.5 M NaCl solution and was identified as $[Co(diHAsar)]^{3+}$ (>90%).

In the DQ^+ system the slow process could not be followed due to a spontanious decay of this radical. When an excess of DQ^+ was used over the cobalt(III) complex (ten times), four products were separated on the column. The first, a yellow species, was eluted with a 0.05 M NaCl solution and was found to be an air-oxidation product of DQ^+ ($\lambda_{max}=419$ nm), the yellow color being faded gradually. The same phenomenon has been reported in the O_2 oxidation of DQ^+ in methanol.[12] This is not the same species as that which arises from the oxidation of DQ^+ by hydrogen peroxide ($\lambda_{max}=453$ nm at pH 8). We have not identified these species. The second, a pale-brown species, was eluted with a 0.2 M NaCl solution and identified as DQ^{2+} which results from the oxidation of DQ^+ by cobalt(III). The third, an orange species,was eluted with a 0.4 M NaCl solution and identified as $[Co(diHAsar)]^{3+}$. It was isolated as a hydrogen chloride salt when it was eluted with 1 M HCl, evaporated to dryness, and washed with acetone. The IR spectrum showed the absence of an $-NO_2$ group. The fourth, an orange species, was eluted with a 0.5 M NaCl solution. The absorption spectrum in water has a $\lambda_{max}=473$ nm ($\varepsilon=150\pm20$ M^{-1} cm^{-1}) and there was no absorption maximum near 340 nm. It was isolated as a hydrogen chloride salt and its IR spectrum showed the presence of an $-NO_2$ group (1550 and 1350 cm^{-1}). From these results the fourth species was identified as $[Co(HANOsar)]^{3+}$ which contains a hydroxyamino and a nitro group (**1**, X=NHOH, Y=NO_2; analytical data for a hydrogen chloride salt, Found: C, 26.75; H, 6.10; N, 17.38%. Calcd for $[Co(C_{14}H_{33}O_3N_8)]Cl_4\cdot4H_2O$: C, 26.51; H, 6.53; N, 17.67%).

When a five-fold excess of DQ^+ was used over the cobalt(III) complex, an additional orange species was found on the top of the column. This was eluted with a 0.5 M NaCl solution and identified as the starting material, $[Co(diNOsar)]^{3+}$, by the IR and absorption spectra. This was easily recovered as a perchlorate salt.

These cobalt(III) complexes were also distinguished from each other using $[Fe(CN)_5H_2O]^{3-}$; with $[Co(diNOsar)]^{3+}$ a brown material, insoluble in water, is formed and with $[Co(diHAsar)]^{3+}$ a violet material is precipitated. Analytical data for the latter show the formula, $[Co(diHAsar)Fe(CN)_5]\cdot4H_2O$ (Found: C, 33.78; H, 5.62; N, 28.08%. Calcd: C, 34.39; H, 6.39; N, 27.45%). The IR spectrum shows the presence of -CN groups (2050 and 1620 cm^{-1}). $[Co(HANOsar)]^{3+}$ reacted with $[Fe(CN)_5H_2O]^{3-}$ to form a reddish violet species soluble in water ($\lambda_{max}=490$ nm). The absence of a nitroso group in $[Co(HANOsar)]^{3+}$ was confirmed by a Liebermann reaction[13] in which nitroso groups react with phenol to form deep-red species in sulfuric acid. These three complexes were also characterized by cyclic voltammetry. $[Co(diNOsar)]^{3+}$ and $[Co(diHAsar)]^{3+}$ showed quasi-reversible one-electron waves at +0.0 and −0.26 V vs. NHE, respectively. $[Co(HANOsar)]^{3+}$ showed a one-electron wave near −0.1 V, intermediate between those of $[Co(diNOsar)]^{3+}$ and $[Co(diHAsar)]^{3+}$. These values are in good agreement with those found in the literature.[4]

$[Co(sep)]^{2+}$ was also used as a reductant, its redox potential (−0.30 V) is slightly higher than that of DQ^+. When a five-fold excess of $[Co(sep)]^{2+}$ was used over $[Co(diNOsar)]^{3+}$, three orange species were separated on the column; these were identified as $[Co(sep)]^{3+}$, $[Co(HANOsar)]^{3+}$, and $[Co(diNOsar)]^{3+}$.

$[Co(HANOsar)]^{3+}$ was further reduced by MDQ^+ and dithionite. Two reactions were monitored in the dithionite reduction—a decrease in absorbance followed by an increase in absorbance at 480 nm. Stoichiometric titrations at 760 nm with MDQ^+ showed $[MDQ^+]/[Co(III)]=4.0\pm0.1$. This is in agreement with the $3e^-$ reduction for the second stage in which

Table 1. Rate Constants for Reduction of [Co(diNOsar)]$^{3+}$ by Dithionite at pH 10.8$^{a)}$

$[S_2O_4^{2-}]_0/10^{-3}$ M	First Stage$^{b)}$ k_{obsd}/s^{-1}	Second Stage$^{c)}$ k_{obsd}/s^{-1}	Third Stage $k_{obsd}/10^{-3}\,s^{-1}$
7.0	0.91	0.042	1.3
14.3	1.30	0.073	1.9
20.0	1.61	0.083	2.2
30.0	1.90	0.108	2.1
40.0	1.89	0.129	2.1

a) 25 °C, I=0.50 M (Na_2SO_4), $[Co(III)]_0=5.0\times10^{-4}$ M, and λ=505 nm. b) Plots of k_{obsd} vs. $[S_2O_4^{2-}]_0^{1/2}$ were linear with zero intercept and k_1 was obtained as $(2.9\pm0.2)\times10^5\,M^{-1}\,s^{-1}$ using $K_d=1.4\times10^{-9}\,M^{-1}$ for the dissociation of $S_2O_4^{2-}$ to SO_2^-. D. O. Lambeth and G. Palmer, *J. Biol. Chem.*, **248**, 6095 (1973). c) Plots of k_{obsd} vs. $[S_2O_4^{2-}]_0^{1/2}$ were linear with zero intercept and k_2 was obtained as $(1.6\pm0.2)\times10^4\,M^{-1}\,s^{-1}$.

[Co(diHAsar)]$^{3+}$ was produced.

When dithionite was used at pH 10.8 with [Co(diNOsar)]$^{3+}$, only [Co(diHAsar)]$^{3+}$ was produced. There was no evidence of further reductions of hydroxyamino to amino groups.

From the above observations it is considered that the following reactions occur successively after Reaction 1:

$$[Co^{II}(diNOsar)]^{2+} \xrightarrow{3e^-} [Co^{III}(HANOsar)]^{3+} \tag{3}$$

$$[Co^{III}(HANOsar)]^{3+} \xrightarrow{e^-} [Co^{II}(HANOsar)]^{2+} \tag{4}$$

$$[Co^{II}(HANOsar)]^{2+} \xrightarrow{3e^-} [Co^{III}(diHAsar)]^{3+} \tag{5}$$

Kinetics. Balahura et al.$^{5)}$ have examined the dithionite reduction of [Co(diNOsar)]$^{3+}$ at pH 6.3. We have also measured this system at pH 10.8 and obtained similar results for the first and second stages (Table 1). A third very slow reaction, whose rate was independent of the concentrations of dithionite, may represent the decomposition of the cobalt(III) complex. The second-order rate constants are $(2.9\pm0.2)\times10^5\,M^{-1}\,s^{-1}$ ($3.5\times10^5\,M^{-1}\,s^{-1}$ at pH 6.3$^{5)}$) for Reaction 1 and $(1.6\pm0.2)\times10^4\,M^{-1}\,s^{-1}$ ($1.6\times10^4\,M^{-1}\,s^{-1}$ at pH 6.3$^{5)}$) for Reaction 2. This result is surprising because it is known that [Co(diNOsar)]$^{3+}$ is converted to a deprotonated species [Co(diNOsar-H)]$^{2+}$ (pK_a=8.85)$^{8)}$ whose redox potential for the Co(III)/Co(II) couple shifts to a more negative value.$^{14)}$ The rate-determining step of the reduction of the nitro to hydroxyamino groups in the cobalt(II) complex does not require hydrogen ions.

Dithionite reduction of [Co(HANOsar)]$^{3+}$ was carried out at pH 6.3 (0.1 M MES buffer), 25 °C and I= 0.50 M (Na_2SO_4). The rate constants obtained are $k_4=(2.1\pm0.4)\times10^5\,M^{-1}\,s^{-1}$ for Reaction 4 and $k_5=(8.4\pm0.6)\times10^3\,M^{-1}\,s^{-1}$ for Reaction 5 (Table 2). Rates for Reactions 3 and 5 in the dithionite system are obviously comparable, suggesting that the attack of an electron on the $-NO_2$ group is rate determining and that the following intramolecular electron-transfer reactions and further reductions of nitroso groups are very fast ($\leqslant\geqslant$ denotes sar),

Table 2. Rate Constants for Reduction of [Co(HANOsar)]$^{3+}$ by Dithionite$^{a)}$

$[S_2O_4^{2-}]_0/10^{-3}$ M	First Stage$^{b)}$ k_{obsd}/s^{-1}	Second Stage$^{c)}$ k_{obsd}/s^{-1}
5.0	0.68	0.022
10.0	0.72	0.030
20.0	1.4	0.046
30.0	1.6	0.053

a) 25 °C, I=0.50 M (Na_2SO_4), pH 6.3 (0.1 M MES buffer), $[Co(III)]_0=3.0\times10^{-4}$ M, and λ=480 nm. b) Plots of k_{obsd} vs. $[S_2O_4^{2-}]_0^{1/2}$ were linear with zero intercept and k_4 was obtained as $(2.1\pm0.4)\times10^5\,M^{-1}\,s^{-1}$ for the SO_2^- reduction. c) Plots of k_{obsd} vs. $[S_2O_4^{2-}]_0^{1/2}$ were linear with zero intercept and k_5 was obtained as $(8.4\pm0.6)\times10^3\,M^{-1}\,s^{-1}$ for the SO_2^- reducion.

Table 3. Rate Constants for Reduction of [Co(diNOsar)]$^{2+}$ and [Co(HANOsar)]$^{2+}$ by MDQ$^+$

$[Co(III)]_0$	$[MDQ^+]_0$	k_{obsd}	k_2 or k_5
10^{-6} M	10^{-4} M	s^{-1}	$10^4\,M^{-1}\,s^{-1}$
[Co(diNOsar)]$^{2+}$			
10	1.03	—	1.36$^{b)}$
10	1.50	—	1.13$^{b)}$
[Co(HANOsar)]$^{2+}$			
2	0.90	1.28	1.4
2	1.30	3.05	2.3
2	1.50	3.96	2.6
17	1.43	—	1.7$^{c)}$

a) 25 °C, I=0.50 M (Na_2SO_4), pH 7.8 (0.1 M Tris-H_2SO_4 buffer) and λ=760 nm. b) Obtained from plots of $\ln[A_t/(A_t-A_\infty)]$ vs. t (Eq. 8). c) Obtained from plots of $\ln[A_t/(A_t-A_\infty)]$ vs. t (Eq. 9).

$$O_2N \leqslant Co^{II} \geqslant NO_2^- \xrightarrow{\text{fast}} O_2N \leqslant Co^{III} \geqslant NO \xrightarrow{\text{fast}} \tag{6}$$

$$HOHN \leqslant Co^{II} \geqslant NO_2^- \xrightarrow{\text{fast}} HOHN \leqslant Co^{III} \geqslant NO \xrightarrow{\text{fast}} \tag{7}$$

We also determined the rate constants for the MDQ$^+$ reductions of nitro to hydroxyamino groups in [Co(diNOsar)]$^{2+}$ and [Co(HANOsar)]$^{2+}$. Since the decay of MDQ$^+$ radical was monitored, the rate constants were obtained using the following equations, respectively:

$$\ln[A_t/(A_t-A_\infty)] = ([MDQ^+]_0-7[Co(II)]_0)k_2t + \ln[MDQ^+]_0/7[Co(II)]_0 \tag{8}$$

$$\ln[A_t/(A_t-A_\infty)] = ([MDQ^+]_0-3[Co(II)]_0)k_5t + \ln[MDQ^+]_0/3[Co(II)]_0 \tag{9}$$

where [ ]$_0$ represents the initial concentration of the given species and A_t and A_∞ denote the absorbances at time t and infinity, respectively. The plots of $\ln[A_t/(A_t-A_\infty)]$ vs. t for each system gave a linear relation for at least 3 half-lives. The second-order rate constant, k_2 or k_5, was calculated from the slope of this straight line. The results are shown in Table 3. Reaction-rate constants are similar to those for the dithionite system. Attempts to detect an intermediate compound containing a nitroso group (-NO) were unsuccessful. However, we cannot completely rule out the possibility of the formation of a nitroso group since in these systems a small amount of cobalt(III) complex was separated which could not be identified.

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3) diNOsar=1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-[6.6.6]icosane; HANOsar=1-hydroxyamino-8-nitro-3,6,10,13,-16,19-hexaazabicyclo[6.6.6]icosane; diHAsar=1,8-bis(hydroxyamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; sar=3,6,-10,13,16,19-hexaazabicyclo[6.6.6]icosane; sep=1,3,6,8,10,13,16,-19-octaazabicyclo[6.6.6]icosane; DQ^{+}=1,1′-ethylene-2,2′-bipyridinium radical cation; MDQ^{+}=1,1′-ethylene-4,4′-dimethyl-2,2′-bipyridinium radical cation; PDQ^{+}=1,1′-trimethylene-2,2′-bipyridinium radical cation.

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