Evidence for Br_2^- Reaction with Ni(III) Macrocyclic Complexes: Br_2^- as a Possible Reducing Agent

P. MORLIERE and L. K. PATTERSON*

Radiation Laboratory, University of Notre Dame, Notre Dame, Ind. 46556, U.S.A.

Received November 9, 1981

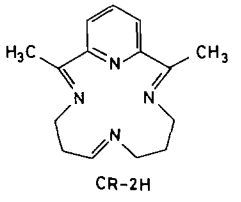
The anion radical, Br_2^-, has been widely used to produce metal complexes in unstable states by oxidation of the central metal ion [1]; we wish to report the novel behavior of a nickel(II) macrocyclic system in which the Ni(III) complex generated by Br_2^- oxidation may be reduced to the parent Ni(II) form by subsequent reaction with Br_2^-.

There are various literature reports [2–6] concerning oxidation of nickel(II) complexes by Br_2^- *via* the reaction:

$$[Ni(II)L]^{2+} + Br_2^- \rightarrow [Ni(III)L(Br^-)]^{2+} + Br^- \qquad (1)$$

However, the redox potential for the couple Br_2^-/Br_2 [7] would suggest the possibility that, for given complexes, actual reduction of Ni(III) by Br_2^- could occur. As studies of oxidation by Br_2^- have employed flash photolysis [6] or pulse-radiolysis techniques, [2–5] experiments have generally been conducted under pseudo-first order conditions ($[Br_2^-] \ll [Ni(II)L]$) where all Br_2^- reacts with parent complex and reduction of the resultant Ni(III) species by Br_2^- is not stoichiometrically possible.

In a recent report from our laboratory, [4] we described the pulse radiolytic formation and subsequent chemistry of Ni(III)(CR-2H)(Br^-) as per reaction (1) where CR-2H is a macrocyclic ligand of the form:



The value of k_1 was determined to be 1.1×10^{10} M^{-1} sec^{-1} by following kinetic behavior at 360 nm, the absorption maximum for Br_2^-. However, in the present study, initial concentrations of Br_2^- comparable to those of Ni(II)(CR-2H) in solution were generated pulse radiolytically [8]. Under these conditions, the loss ob Br_2^- *via* disproportionation must be taken into account

$$Br_2^- + Br_2^- \rightarrow Br_3^- + Br^- \qquad (2)$$

At pH = 3.2 where these experiments were performed, rate constants of $2k_2 = 4.2 \times 10^9$ M^{-1} sec^{-1} and 4.5×10^9 M^{-1} sec^{-1} were determined in solutions of $[Br^-] = 1 \times 10^{-2}$ M and 1×10^{-3} M respectively. Theoretical decays at 360 nm may be calculated from k_1 and k_2 and the extinction coefficients* for the various species involved. As may be seen in Fig. 1, the experimental decay considerably exceeds the decay predicted from the assumption that only reactions (1) and (2) are involved. Further, no previously described transformation of Ni(III)(CR-2H)(Br^-) [4] subsequent to reaction (1) may occur in this time scale to account for such behavior. The spectrum recorded at the end of this decay (Fig. 2) reveals no remaining absorption attributable to Br_2^- and no spectral evidence of any new species. Further, it also indicates a yield of Ni(III)(CR-2H)(Br^-) far less than expected for (1) and (2) alone. This data is consistent however, with a process involving both Ni(III)(CR-2H)(Br^-) and Br_2^- as reactants; and one may suggest the reaction

$$Ni(III)(CR\text{-}2H)(Br^-) + Br_2^- \rightarrow \\ Ni(II)(CR\text{-}2H) + Br_2 + Br^-, \qquad (3)$$

Laurence and Whitburn [6] have suggested such a reaction as part of an overall multistep mechanism to explain halide ion reactions with nickel(III) tetra-

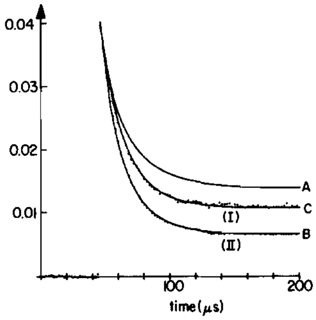


Fig. 1. Experimental decay of absorbance at 360 nm. Experimental points for (I) were recorded for $[Ni^{II}(CR\text{-}2H)]_0 = 4.3 \times 10^{-6}$ M, $[Br^-] = 1 \times 10^{-3}$ M and $[Br_2^-]_0 = 4.3 \times 10^{-6}$ M (scaling factor = 1) and experiments for (II) were recorded for $[Ni^{II}(CR\text{-}2H)]_0 = 4.3 \times 10^{-6}$ M, $[Br^-] = 1 \times 10^{-3}$ M and $[Br_2^-]_0 = 1.4 \times 10^{-6}$ M (scaling factor = 3). Curve A represents the decay calculated for reactions (1) and (2) for the conditions of experiment (II). Curves B and C represent the calculated decays involving reactions (1), (2), and (3) and associated with (I) and (II) respectively.

---

*Author to whom correspondence should be addressed.

*$\epsilon_{Ni^{II}(CR\text{-}2H)} = 900$ M^{-1} cm^{-1}, $\epsilon_{Ni^{III}(CR\text{-}2H)(Br^-)} = 4500$ M^{-1} cm^{-1}, $\epsilon_{Br_2^-} = 9500$ M^{-1} cm^{-1}, $\epsilon_{Br_2} \sim \epsilon_{Br_3} = 0$.

0020-1693/82/0000-0000/$02.75

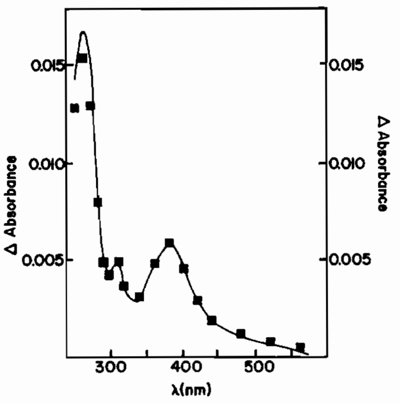


Fig. 2. (■) Absorptions recorded at the kinetic plateau ($\tau \sim$ 150 μs after the pulse) $[Ni^{II}(CR\text{-}2H)]_o = 3 \times 10^{-6}$ *M*, $[Br^-] = 1 \times 10^{-3}$ *M* and $[Br_2^-]_o = 3.6 \times 10^{-6}$ *M*. The solid curve represents the spectrum of 1.35×10^{-6} *M* $Ni^{III}(CR\text{-}2H)(Br^-)$, expected concentration from calculations involving reactions (1), (2) and (3).

azamacrocyclic complexes. However, this type of reduction has not been isolated from other reactions of Ni(III) species nor has a rate constant been reported. The redox potentials for Br_2^-/Br_2 in water and $Ni^{II}(CR\text{-}2H)/Ni^{III}(CR\text{-}2H)$ in acetonitrile are 0.43 [7] and 1.05 V [10] respectively. While some alteration in the latter is expected due to transfer to an aqueous system, reaction (3) appears to be thermodynamically feasible.

Using the rate law for competing reactions (1, 2, 3) calculated decays were fit to data at 360 nm using appropriate extinction coefficients, k_1, k_2 and an adjustable k_3. Over a range of dose, $[Br_2^-]_0 = 1.4$–4.3×10^{-6} *M*, starting material $[Ni(III)(CR\text{-}2H)] = 2$–$4.3 \times 10^{-6}$ *M* and bromide concentration, $[Br^-] = 1$–10×10^{-3} *M* sixteen sets of data were examined and fit using k_3 values of $1.02 \pm 0.07) \times 10^{10}$ M^{-1} sec^{-1}. The fits presented in Fig. 1 are representative of the agreement obtained. Attempts to fit the experimental decays with a parallel reaction with some unknown intermediate

$$Ni(II)(CR\text{-}2H)(Br^-) + Br_2^- \rightarrow \text{Intermediate X} \qquad (4)$$

were made by adjusting k_4 and the extinction coefficient of intermediate X. Such attempts were unsuccessful and the results incoherent.

The course of reaction was also monitored experimentally by following the transient growth at 265 nm, the absorption maximum of Br_3^-. Kinetic data were not fitted at this wavelength since Br_3^- is the main product of Br_2^- disproportionation and the equilibrium (5)

$$Br_2 + Br^- \rightleftarrows Br_3^- \qquad (5)$$

involves rates comparable [9] to those of the other processes occuring. This renders the transient growth extremely complicated. However, one may assume that equilibrium is approached at the end of the competing reactions (1)–(3). Plateau concentrations, values for transient growth of the species involved and associated absorption values at 265 nm were calculated* with this assumption, as value $K_5 = 15$ M^{-1} and k_1, k_2, k_3 given above. These are presented in Table I and may be seen to be in good agreement with experimental data. At bromide concentrations of 1×10^{-2} *M* the yield of Br_3^- arising from disproportionation alone is not sufficient to explain the data. This further supports the participation of reaction (3). At bromide concentrations of 1×10^{-3} *M* the contribution of Br_3^- is very small compared to Br_2 and the absorbance over the whole spectrum (Fig. 2) is consistent with the concentration of $Ni(III)(CR\text{-}2H)(Br^-)$ expected from the calculation.

The evidence presented strongly supports reduction of $Ni(III)CR\text{-}2H)(Br^-)$ by Br_2^- in competition with Ni(II)(CR-2H) oxidation by the same anion radical. One may expect that other similar cases will be observed.

TABLE I. Experimental and Calculated Absorptions at 265 nm for Various Concentrations of Participating Species.[a]

$[Ni^{II}(CR\text{-}2H)]_o$ $\times 10^6$ (*M*)	$[Br_2^-]$ $\times 10^6$ (*M*)	$[Br^-]$ $\times 10^3$ (*M*)	$[Ni^{III}(CR\text{-}2H)(Br^-)]$ $\times 10^6$ (*M*)	$[Br_3^-]$ $\times 10^8$ (*M*)	ΔAbs_{exp}	ΔAbs_{calc}
4	1.6	10	1.05	3.3	0.015	0.014
4	3.2	10	1.5	10.6	0.022	0.022
2	1.8	10	0.79	6.2	0.0127	0.012
2	4.3	10	0.98	21	0.0205	0.0195
2.1	1.5	1	0.81	0.48	0.010	0.010
2.1	2.8	1	0.98	1.3	0.012	0.0125
2.1	4.4	1	1.06	2.3	0.0125	0.014

[a] The concentrations of the absorbing species $Ni^{II}(CR\text{-}2H)$, $Ni^{III}(CR\text{-}2H)(Br^-)$ and Br_3^- are calculated from the rate law and assuming that equilibrium (5) is reached after 150 μs. The parameters used are k_1, k_2, k_3, given in the text, $K_5 = 15$ M^{-1} and the appropriate extinction coefficients*. Experimental absorptions are recorded in the time range 135–155 μs.

---

*$\epsilon_{Ni^{II}(CR\text{-}2H)} = 2700$ M^{-1} cm^{-1}, $\epsilon_{Ni^{III}(CR\text{-}2H)(Br^-)} = 15000$ M^{-1} cm^{-1}, $\epsilon_{Br_2^-} = 500$ M^{-1} cm^{-1}, $\epsilon_{Br_2} \cong 0$ M^{-1} cm^{-1}, $\epsilon_{Br_3^-} = 36000$ M^{-1} cm^{-1}.

Acknowledgement

The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2202 from the Notre Dame Radiation Laboratory.

References

1 A. B. Ross and P. Neta, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., 65* (1979).

2 P. Marathamuthu, L. K. Patterson and G. Ferraudi, *Inorg. Chem., 17*, 3157 (1978).

3 P. Morliere and L. K. Patterson, *Inorg. Chem. 20*, 1458 (1981).

4 P. Morliere and L. K. Patterson, submitted to *Inorg. Chem.*

5 M. Jaacobi, D. Meyerstein and J. Lilie, *Inorg. Chem., 18*, 429 (1979).

6 K. D. Whitburn and G. S. Laurence, *J. Chem. Soc., Dalton Trans., 1*, 139 (1979).

7 A. Henglein, *Radiat. Phys. Chem., 15*, 151 (1980).

8 The pulse radiolysis set up and Br_2^- production were earlier described (ref. 2,3 and references therein).

9 D. Wong and B. Di Bartolo, *J. Photochem., 4*, 249 (1975).

10 F. V. Lovecchio, E. S. Gore and D. H. Busch, *J. Amer. Chem. Soc., 96*, 3109 (1974).