

Table III. Data for the $\text{Cu}^{\text{II}}(\text{H}_4\text{C})^{2-} + \text{IrCl}_6^{2-}$ Reaction Using the Pulsed-Flow Instrument^a

velocity, m/s		$10^4 t_{1/2}$, s	velocity, m/s		$10^4 t_{1/2}$, s
	abs ^b			abs ^b	
8.37	0.0503	1.8	7.83	0.0502	1.8
4.68	0.0455	2.0	9.11	0.0499	1.7
6.26	0.0435	1.6	6.99	0.0468	1.6

^a $A_0(\text{IrCl}_6^{2-}) = 0.2155$, $A_0(\text{Cu}^{\text{II}}(\text{H}_4\text{C})^{2-}) = 0.0043$, $A_\infty = 0.0228$, $[\text{Cu}(\text{II})] = [\text{Ir}(\text{IV})] = 1.47 \times 10^{-5}$ M, $\lambda = 490$ nm, 25.0°C , $\mu = 0.1$ M (NaClO_4), pH 8.00. ^b Absorbance corrected for media effects.

and so an empirical scheme has been developed which is based on a linear dependence of the absorbance quotient, $(A - A_\infty)/(A_0 - A_\infty)$, on the first half-life of a known system.^{14,31} On this basis the values of $t_{1/2}$ in Table III were determined. The average half-life for this reaction is $(1.7 \pm 0.3) \times 10^{-4}$ s. The observed second-order rate constant is $k_{12} = 4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, since the initial concentration of the reactants is 1.47×10^{-5} M. This value is almost a factor of 4 larger than the value calculated from eq 15 which gives k_{12}^{calcd} equal to $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ on the basis of $k_{11} = 6.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_{22}(\text{Ir}^{\text{IV,III}}\text{Cl}_6^{2-,3-}) = 2.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$,³² $\log K_{12} = 6.95$, and $f = 0.096$. On the other hand the observed k_{12} value is a factor of 10 less than the diffusion-limiting rate constant for 2-,2-reactants. As discussed elsewhere³³ for a series of Cu(II) peptides reacting with IrCl_6^{2-} , the value of $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

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corresponds to a limiting rate constant expected for a model in which axial substitution of water in the $\text{Cu}^{\text{II}}(\text{H}_4\text{C})^{2-}$ complex is the rate-determining step. Although the behavior of IrCl_6^{2-} with $\text{Cu}^{\text{II}}(\text{H}_4\text{C})^{2-}$ is only a factor of 4 different from the Marcus predictions, the behavior is consistent with that of other copper(II) peptides with IrCl_6^{2-} where the reaction does not correspond to an outer-sphere electron-transfer process.³³

Conclusions

The macrocyclic peptide ligand helps to stabilize the copper(III) complex both thermodynamically and kinetically. The reduction potential of 0.48 V for $\text{Cu}^{\text{III,II}}(\text{H}_4\text{C})^{1-,2-}$ is less than that predicted for four deprotonated peptide donors alone and the tightness of the metal cavity appears to favor the higher oxidation state.

The redox decomposition reactions are much slower than those of corresponding open-chain peptide complexes of copper(III). The kinetic results for the acid decomposition suggest that ligand substitution in equatorial positions is involved prior to the redox steps and that the macrocyclic ligand makes these processes more difficult.

The electron-exchange reactions for $\text{Cu}^{\text{III,II}}(\text{H}_4\text{C})^{1-,2-}$ are rapid, and the value of $6.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ calculated for the self-exchange agrees with other Cu(III,II) self-exchange rate constants.

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Registry No. $\text{Cu}^{\text{III}}(\text{H}_4\text{C})^-$, 76721-70-5; $\text{Cu}^{\text{II}}(\text{H}_4\text{C})^{2-}$, 74185-28-7; IrCl_6^{2-} , 16918-91-5.

Contribution from the Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556

Anion Radical Oxidation of Nickel(II) Macrocyclic Complexes. Pulse Radiolysis of (2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene)nickel(II) in Sodium Bromide Solution

P. MORLIERE and L. K. PATTERSON*

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The oxidation of $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ [$\text{CR}+4\text{H} = 2,12\text{-dimethyl-}3,7,11,17\text{-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15\text{-triene, } \alpha \text{ isomer}$] by Br_2^- and subsequent chemistry of Ni(III) intermediates have been studied by pulse radiolysis. The initial electron transfer is diffusion controlled and results in an initial product which exhibits characteristics of a Ni(III)- Br^- adduct. The stability of this adduct, especially in acidic media, is dependent on bulk bromide concentration, demonstrating an equilibrium process of the form $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons \text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2 + \text{Br}^-$, with $K_{\text{eq}} = 360 \text{ M}^{-1}$. The pK of dissociation for the aquated species is 4.0 ± 0.8 . At pH > 5 displacement of the bound bromide is first order in $[\text{OH}^-]$ with a rate constant of $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Disappearance of the $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ intermediate is also pH dependent, suggesting amine dissociation in the ligand and formation of an unstable ligand radical leading to a final product with increased ligand unsaturation.

Introduction

The interest in transition-metal complexes with uncommon and frequently unstable oxidation states and their associated chemistry has grown considerably during recent years. Such complexes are mentioned as intermediates in both catalytic reactions and biological processes.¹ A special group of these are the nickel(II) complexes with macrocyclic ligands which form species of high stability.² Electrochemical oxidations

of the Ni(II) metal center in these complexes have been reported for various macrocyclic ligands in nonaqueous solvents where the lifetimes of Ni(III) complexes can be quite long.²⁻⁵ This large stability permits detailed characterization of Ni(III) compounds by EPR and optical spectroscopy. With a few exceptions, Ni(III) complexes are generally short-lived in aqueous solutions, and only a limited number of investigations have been reported.⁶⁻⁸

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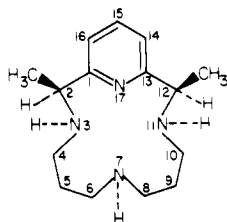
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Oxidized transition-metal ions in macrocyclic complexes have been evoked as intermediates in reactions with Br_2 or HNO_3 which introduce double bonds in the macrocyclic ligand.⁹⁻¹¹ Such transformations via oxidized metal centers should exhibit smaller activation barriers than transformations involving a direct ligand oxidation. It follows that an understanding of the real time behavior of aqueous Ni(III) species could contribute significantly to the elucidation of mechanisms for oxidation of macrocyclic structures. Pulse radiolysis techniques are particularly suitable for the investigation of unstable oxidation states of metal complexes in aqueous media. Reducing species (e_{aq}^-) and oxidizing radicals ($\cdot\text{OH}$, Br_2^- , Cl_2^- , $(\text{SCN})_2^-$), may be generated in very short times when ionizing radiation is absorbed in aqueous media. We have chosen to apply these techniques to the study of $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ oxidation (where $\text{CR}+4\text{H} = 2,12$ -dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, α isomer)



by Br_2^- anion radicals. The Br_2^- radical has several advantages in a study of this kind. It has been shown to be a powerful oxidant toward metallic ions and behaves cleanly in reactions with metallic complexes in the sense that no reactions other than oxidation of the metallic ions, e.g., hydrogen abstractions from the ligand, have been previously reported.¹² Further, its reactions may be investigated over a wide pH range (3–11) without interference from other species like $\cdot\text{H}$, $\cdot\text{OH}$, or O^- . The $\text{CR}+4\text{H}$ ligand system also makes it an attractive choice for study. The high symmetry limits the number of possible sites eventually involved in alteration reactions of the ligand. Additionally, a family of nickel(II) compounds derived from this ligand with various degrees of unsaturation have been previously synthesized and characterized.^{4,13}

From such information, it should be possible to observe any introduction of double bonds into the macrocyclic ligand and to determine the mechanism of the ligand dehydrogenation via Ni(III) intermediates.

Experimental Section

Radiolytic Procedures. Optical pulse radiolysis measurements were made with a computerized system similar to that described earlier.^{6a,14,15} Absorbance data are presented in dimensions of an extinction coefficient by the parameter ϵ' calculated from the function

$$\epsilon' = (\text{Abs})K/G(\text{dose})$$

where Abs is the absorbance for a given pulse and K is chosen such that ϵ' for $(\text{SCN})_2^-$ in the same cell is equal to $7600 \text{ M}^{-1} \text{ cm}^{-1}$ at 472

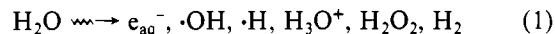
nm in N_2O -saturated solutions.¹⁶

Materials and Synthesis. The complex was prepared as the perchlorate salt $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})(\text{ClO}_4)_2$ according to a literature procedure.¹³ Three recrystallizations were carried out from distilled water. The infrared spectrum is in good agreement with that previously reported.⁴

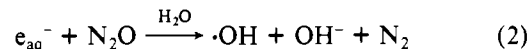
Other materials were of reagent grade and were used without further purification. Water for the radiolysis experiments was obtained from a Milli-R015 Millipore filtering system. Adjustment of pH lower than 5 and higher than 9 was obtained with perchloric acid or sodium hydroxide. In the pH range 5–9, phosphate buffer was used, the pH being adjusted by addition of perchloric acid or sodium hydroxide. Borate buffer was also used in the range 8.7–8.8.

Results and Discussion

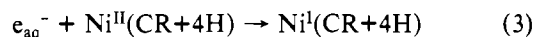
Formation of Br_2^- Anion Radical. The radiolysis of water may be represented by reaction 1. In very dilute nitrogen-



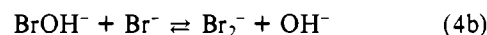
saturated solutions, the initial yields are $G_{e_{\text{aq}}^-} = G_{\cdot\text{OH}} \sim G_{\text{H}_3\text{O}^+} = 2.65$, $G_{\cdot\text{H}} = 0.6$, $G_{\text{H}_2} = 0.45$, and $G_{\text{H}_2\text{O}_2} = 0.75$ (G = number of radicals formed/100 eV of energy deposited in solution).¹⁷ In the presence of nitrous oxide, hydrated electrons are converted into $\cdot\text{OH}$ radicals via reaction 2 with a rate constant



of $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁸ Hydrated electrons may also react with protons to give $\cdot\text{H}$ atoms with a rate constant of $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.¹⁸ Even in the extreme limit of these experiments, at pH 3.1 in N_2O -saturated solutions, less than 10% of hydrated electrons are lost via the reaction with protons. Because of the high reactivity of hydrated electrons toward the nickel(II) macrocyclic complex



which occurs with a rate constant $k_3 = 3.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, a concentration $\leq 2 \times 10^{-4} \text{ M}$ $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ must be used in N_2O -saturated solutions to ensure that less than 3% of hydrated electrons reduce Ni(II). Under the conditions used, Ni(I) species were not present in high enough concentration to interfere with the reactions of interest. In solutions containing bromide ions reaction 4 occurs with an overall rate



constant $k_4 \geq 8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at $\text{pH} \leq 11$.¹⁹ The competing hydroxyl radical reaction with $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ which proceeds with a rate constant of $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is avoided by using a ratio $[\text{Br}^-]/[\text{Ni}^{\text{II}}(\text{CR}+4\text{H})] \geq 50$. Under our standard conditions ($[\text{Br}^-] = 10^{-2} \text{ M}$), essentially all hydroxyl radicals are transformed into Br_2^- with $\tau_{1/2} \leq 0.1 \mu\text{s}$. At lower Br^- concentration ($[\text{Br}^-] = 10^{-3} \text{ M}$) doses ≤ 0.6 krd are used to avoid loss of Br_2^- anion radical by disproportionation which occurs with a rate constant of $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹²

The radical yield in aqueous solution will depend on the concentration of solutes acting as spur scavengers which alter interactions among primary water radicals. In N_2O -saturated solutions the yield of $\cdot\text{OH}$ radical via reaction 2 and spur scavenging of $\cdot\text{OH}$ by Br^- according to reaction 4 combine to give a total yield of ~ 6.1 for Br_2^- compared to the sum of the primary yields in dilute solutions (~ 5.3).¹⁶ Such concentration dependences must be taken into account when both kinetic and

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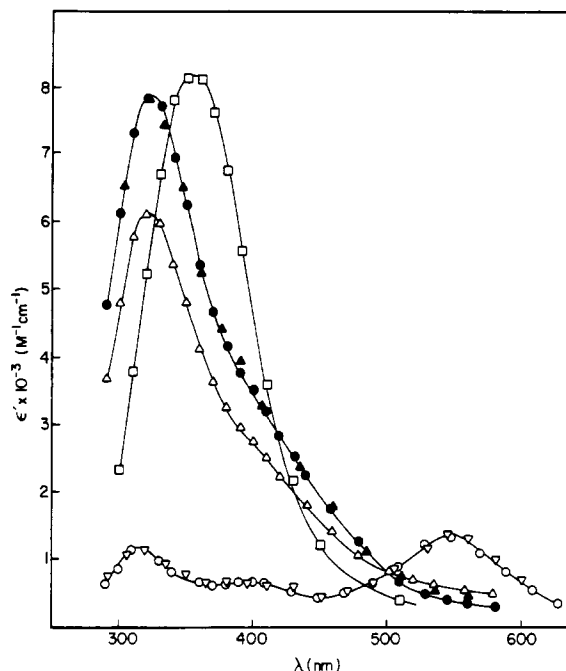
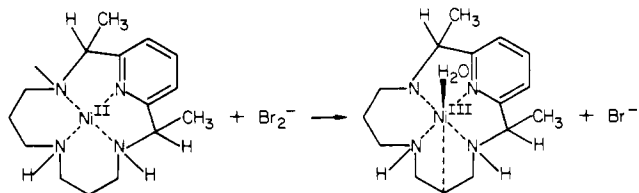


Figure 1. Transient spectra produced by Br_2^- oxidation of $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ in N_2O -saturated, neutral buffered solution (pH 7, $[\text{Na}_2\text{HPO}_4] = [\text{NaH}_2\text{PO}_4] = 2.5 \times 10^{-4} \text{ M}$), in neutral unbuffered solution (pH 5.5), and in basic solution (pH 9.3). $[\text{Br}^-] = 10^{-2} \text{ M}$ and $[\text{Ni}^{\text{II}}(\text{CR}+4\text{H})] = 10^{-4} \text{ M}$. The curves represent spectra measured at different intervals after the pulse: (\square) 0.4 μs at pH 7, (Δ) 6 μs at pH 7, (\bullet) 6 μs at pH 5.5, (\circ) 750 μs at pH 7, (∇) 1.5 ms at pH 5.5. \blacktriangle is a spectrum (Δ) corrected for the fast second reaction at pH 7 in buffered solution.

spectral parameters are considered. Hence in nitrous oxide saturated solutions containing bromide ions, the only radicals participating in reaction with the nickel(II) macrocyclic complex are Br_2^- anion radical and $\cdot\text{H}$ atoms with a initial relative yield $\sim 10/1$.

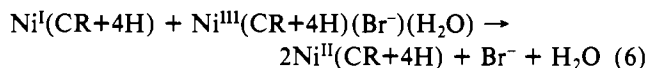
Behavior of Intermediates Generated from $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ Reaction with Br_2^- . In the pH range 3–9 the first observed reaction is the disappearance of Br_2^- and simultaneous formation of a transient oxidation product strongly absorbing in the 300–400-nm region. The spectrum of this intermediate is unaffected by acid concentrations over the range of our measurements and is given in Figure 1. Previous works have reported the oxidation of other nickel(II) macrocyclic complexes by anion radicals (Br_2^- , Cl_2^- , and $(\text{SCN})_2^-$).^{6–8} In each case initial oxidation transient products exhibited spectra with intense absorption in the 300–400-nm region. From similarities with spectra obtained by electrochemical oxidation in acetonitrile^{6,8} and from conductivity measurements,⁸ the formation of intermediates of the type $\text{Ni}^{\text{III}}(\text{L})(\text{X}^-)$ has been suggested ($\text{X}^- = \text{Br}^-$, Cl^- , or SCN^-). Unfortunately no spectrum associated with electrochemical oxidations of $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ has been reported. However comparison between the spectral behavior of our intermediate and that of the oxidation transients for other nickel(II) macrocyclic complexes leads to the suggestion that the first observed reaction is



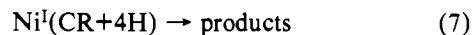
(5)

In the $\text{Ni}(\text{II})$ complex, the coordinated water molecules are not drawn; indeed Karn et al. have shown that at room temperature ($\sim 20^\circ \text{C}$) the planar $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ and the octahedral $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ complexes are present in a ratio of about 1:1. The spectral evidence strongly suggests a center of symmetry in the $\text{Ni}(\text{III})$ compound, hence the inclusion of coordinated water in that structure. The course of this reaction was monitored by following changes in optical absorption at 360 and at 300 nm where the spectra of Br_2^- and the transient complex differ significantly. At both wavelengths pseudo-first-order kinetics were observed and the rate constant was determined by changing $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ concentration. The resulting value of $k_5 = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was found to be independent of the pH. This is in good agreement with data previously reported for other nickel(II) complexes.^{6–8} The intermediate produced by Br_2^- reaction is too short-lived to be trapped for ESR characterization as has been possible for some nickel(III) complexes.^{6,20,21} Hence attempts to further identify this first transient were based on its redox properties.

$\text{Ni}(\text{III})$ species are known to participate in redox reactions with reducing agents, e.g., Ni^+ , Fe^{2+} , or I^- .^{6,7} Kinetics of the redox reactions for some of these reducing agents with the assumed $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ intermediate were measured to characterize the oxidation state of the nickel ion and the presence of Br^- ion in the axial position. At pH ≤ 5 the half-life of the intermediate is sufficiently long to allow such reactions to be monitored. Indeed the most straightforward reaction to study here is the potential reduction of $\text{Ni}(\text{III})$ by $\text{Ni}(\text{I})$ generated in N_2 -saturated solutions (reaction 6). In



N_2 -purged solutions containing bromide, e_{aq}^- and Br_2^- are both produced. The hydrated electrons may react with H^+ or with the complex ($k_{e_{\text{aq}}^- + \text{H}^+} = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_3 = 3.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). At pH 4.8 with $[\text{Ni}^{\text{II}}(\text{CR}+4\text{H})] = 10^{-4} \text{ M}$, $\sim 7\%$ of hydrated electrons are lost via the reaction with protons; then at pH 4.8 in 10^{-2} M Br^- and N_2 -purged solutions the G value for $\text{Ni}(\text{I})$ species from (3) is then equal to $G_{e_{\text{aq}}^-}$, e.g., ~ 2.5 , and the G value for $\text{Ni}(\text{III})$ species is equal to $G_{\text{Br}_2^-}$, i.e., ~ 3.1 . In fact there is evidence that reaction 6 must compete with reaction 7 which was found to be a second-order



reaction with $2k_7 = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. At 290 and 320 nm, dose-dependent decays of absorption are observed. If this decay corresponds only to reaction 7 without involving reaction 6, the absorption at the end of the decay should be the sum of absorptions from the products of reaction 7 and of the remaining absorption of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$. As the final absorption is considerably lower than this sum, we can assume that reaction 6 does take place. However due to the complexity of the combined reactions, only an order of magnitude rate constant for reaction 6 in the range of 10^8 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ may be given. This value is in good agreement with data previously reported for electron transfer to Ni^{III} with a different macrocyclic ligand.⁶

A redox reaction between the proposed intermediate $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ and ferrous ions was also observed. At pH 3.5 ferrous ions, in concentrations below the limit for direct reaction with e_{aq}^- or $\cdot\text{OH}$,^{18,19} enhanced the natural decay of the intermediate $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ observed in the absence of reducing agents. This reaction exhibited good first-order behavior over the Fe^{2+} concentration of 1×10^{-3}

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Table I. Rate Constants of the Reaction following the Formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ in Neutral Solutions^a

pH	$10^5 \times$ [Ni ^{III} (CR+4H)], M	$10^3 \times$ [Br ⁻], M	$10^4 \times$ [NaH ₂ PO ₄] or $10^4 \times$ [Na ₂ HPO ₄], M	$10^4 \times$ [Na ₂ B ₄ O ₇], M	<i>k</i>	dose, krd
4.5	10	10			$2.2 \times 10^2 \text{ s}^{-1}$	~0.6-2.0
4.8	2	10			$2.3 \times 10^2 \text{ s}^{-1}$	~1.3
4.8	2	1			$2.2 \times 10^2 \text{ s}^{-1}$	~1.3
4.8	2	7.5			$2.5 \times 10^2 \text{ s}^{-1}$	~1.3
4.8	2	12			$2 \times 10^2 \text{ s}^{-1}$	~1.3
4.8	2	17.5			$1.85 \times 10^2 \text{ s}^{-1}$	~1.3
4.8	10	10			$2.5 \times 10^2 \text{ s}^{-1}$	~0.6-2.0
5.1	10	10	5		$2.4 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
5.5	10	5			$6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	~0.6-2.5
5.5	10	10			$6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	~0.6-2.5
5.5	10	25			$6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	~0.6-2.5
5.5	10	10	5		$3.8 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
6.1	10	10	5		$4.4 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
6.5	10	10	5		$5.7 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.0	10	10	1		$5.2 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.0	10	10	2.5		$5.5 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.0	10	10	5		$6.0 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.0	10	10	10		$6.5 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.0	10	5	5		$5.5 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.0	10	25	5		$4.9 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
7.8	10	10	5		$6.5 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
8.2	10	10	5		$6.0 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
8.7	10	10			$2.6 \times 10^4 \text{ s}^{-1}$	~0.25
8.7	10	10			$3.3 \times 10^4 \text{ s}^{-1}$	~0.5
8.7	10	10			$5.3 \times 10^4 \text{ s}^{-1} \text{ b}$	~1.3
8.7	10	10			$6.6 \times 10^4 \text{ s}^{-1} \text{ b}$	~2.0
8.7	10	10		1	$2.5 \times 10^5 \text{ s}^{-1}$	~0.25
8.7	10	10		1	$2.15 \times 10^5 \text{ s}^{-1}$	~1.2
8.7	10	10		1	$2.4 \times 10^5 \text{ s}^{-1}$	~1.6
8.7	10	10		1	$2.55 \times 10^5 \text{ s}^{-1}$	~2.0
8.7	10	10	5		$9.5 \times 10^4 \text{ s}^{-1}$	~0.25
8.7	10	10	5		$9.8 \times 10^4 \text{ s}^{-1}$	~1.2
8.7	10	10	5		$1.05 \times 10^5 \text{ s}^{-1}$	~2.0

^a All solutions were N₂O saturated. ^b Rate constants determined from the 2-3 first half-lives.

to 4×10^{-3} M. As expected for reactions involving charged species, the rate constant of the reaction increased with ionic strength. So that data over a wide ionic strength range could be obtained, NaBr concentration was varied from 4×10^{-3} to 2×10^{-2} M. A linear dependence of $\log k_{\text{Fe}^{2+}+\text{Ni}(\text{III})}$ on $\mu^{1/2}$ was obtained, according to the classical relationship²²

$$\log k - \log k_0 = Z_A Z_B \mu^{1/2}$$

where Z_A and Z_B stand for the charges of reactants. As may be seen in Figure 2, the slope of this plot yields a value equal to 4.1. This gives a value $Z_A Z_B$ of essentially 4, indicating a charge of 2 for the Ni(III) intermediate in agreement with proposed $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$. The rate constant k_0 extrapolated to zero ionic strength is equal to $1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Along with conductivity⁸ and spectral data, the experiments described here confirm the assignment of the $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ transient in the pH range 3-9 as per reaction 5.

Reactions of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$. The behavior of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ has been investigated over the range pH 3-8.7. As may be seen, the reactions of this intermediate are highly pH dependent and the chemistry varies considerably at the extreme limits of this range.

In the pH range 4.8-8.7 the formation of a second transient was observed. The spectrum of this intermediate is included in Figure 1 and exhibits absorptions at 320, 400, and 550 nm. The transformation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ into this second transient is characterized by an isosbestic point at 490

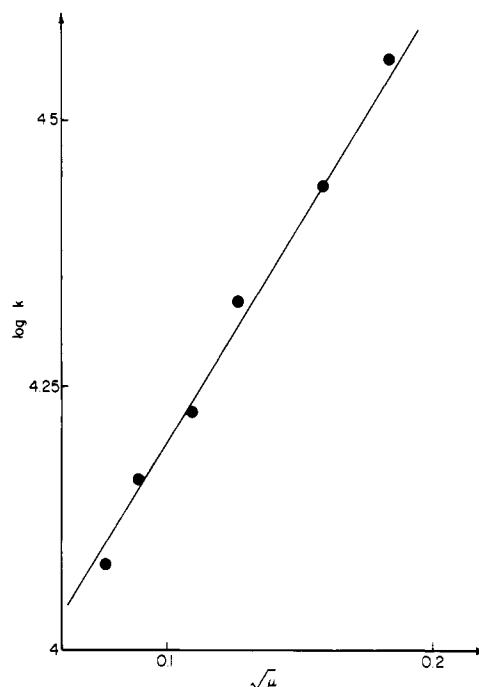


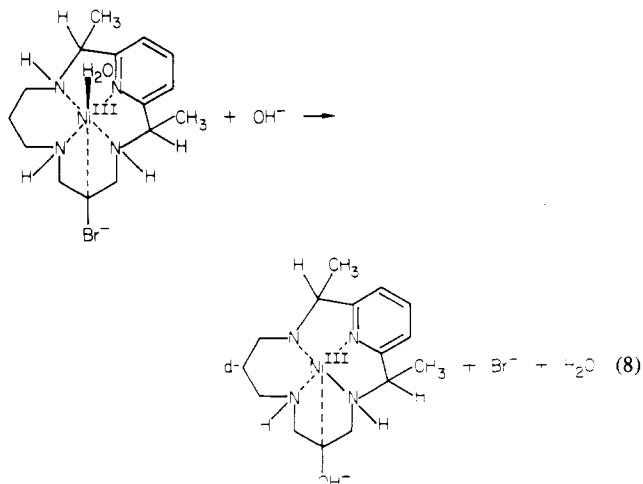
Figure 2. Ionic strength effect on the reaction of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ and Fe^{2+} at pH 3.5. $[\text{Ni}^{\text{III}}(\text{CR}+4\text{H})] = 10^{-4}$ M, $[\text{Br}^-] = (0.5-2.0) \times 10^{-2}$ M, and $[\text{Fe}^{2+}] = (1-4) \times 10^{-3}$ M.

nm, showing the conversion between the two transients. The kinetic data as a function of pH are given in Table I. In unbuffered neutral solutions (pH 5.5), the reaction follows

(22) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution" Oxford University Press, London, 1947.

second-order kinetics and is independent of Br^- concentrations. At pH 8.7 without buffer and at low dose (0.25 krd), the reaction obeys first-order kinetics. With higher doses (up to 2 krd) the first-order fit exhibits small distortions. Increasing the dose over this range increases the initial rate constant from 2.5×10^4 to $6.6 \times 10^4 \text{ s}^{-1}$. With addition of buffer to this system, kinetic behavior changes significantly. In buffered solutions (pH 5.1–8.8) the fit is predominantly first order and the decay is not dose dependent. As can be seen in Table I, higher rate constants were determined in phosphate-buffered than in unbuffered solutions at the same pH. At pH 8.7 in phosphate- and in borate-buffered solutions, the first-order fit is quite good. However, it is of interest to notice that the rates in phosphate- and borate-buffered solutions at the same pH are themselves different. As may be seen in Table I, the effect of the buffer concentration on the rate constant is not very important and no significant effect of Br^- concentration was observed (pH 7). Due to long time distortions in the first-order fit, some of the rates reported in Table I are the rate constants taken from the first 2–3 half-lives. Despite the differences between the rates in buffered and unbuffered solutions, the spectra at the end of the reactions are absolutely identical.

To explain the pH-dependent behavior of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ species in this pH range, one must reconsider the initial radiolytic reactions. In water radiolysis, protons are generated with a yield essentially equivalent to that for e_{aq}^- . Subsequently the hydrated electrons are scavenged by N_2O via reaction 2 and the protons initially produced are "neutralized" by OH^- produced in this reaction. Reaction 4, it may be noted, generates OH^- ions with a yield equal to that for Br_2^- . Hence in the pH range 5–9, dose-dependent pH shifts due to those primary radical redox processes are possible. At pH 8.7 in unbuffered solutions, this shift is sufficient to explain the observed variations in the rate constants with the dose. If the pH shift is small at low dose (0.25 krd), it is more important to the overall kinetics at high dose (2 krd); with high dose the initial reaction rate is greater than at low dose but decreases as the reaction proceeds. From all these data one may suggest that the second reaction is

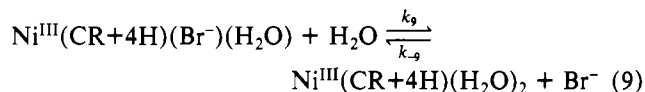


where the letter d indicates a distortion of the complex. Deprotonation of the coordinated water with simultaneous elimination of Br^- or substitution of Br^- by OH^- with simultaneous elimination of water could lead to the nonplanar $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ complex. Then the absorption at 550 nm may be attributed to d-d transitions in an unsymmetrical complex.^{6,8} The distortion observed in the first-order fit at high dose in unbuffered solutions (pH 8.7) is consistent with the interaction between radiolytically generated OH^- and the $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ transient. At pH 5.5 in unbuffered solutions, $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ and OH^- are produced

in almost the same concentrations, and the expected second-order behavior is observed. It may be noted that the second-order rate constant determined at pH 5.5 in unbuffered solutions ($k_8 \approx 6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and the second-order rate constant calculated from the pseudo-first-order rate constant measured at pH 8.7 in unbuffered solutions at low dose ($k_8 \approx 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are very similar. In the pH range 5–9 in buffered solutions, the high observed rates and the distortions in the first-order fitting lead us to suggest that an interaction with the buffer is involved. No important changes of the rates with various buffer concentration (10^{-4} – 10^{-3} M) were observed (Table I, pH 7). Hence it appears that the interaction with the buffer must be very complex.

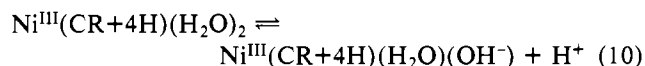
In previous work formation of a second intermediate absorbing at 550 nm ($\epsilon \sim 1500 \text{ M}^{-1} \text{ cm}^{-1}$) was observed following Br_2^- oxidation of $\text{Ni}(\text{II})$ complexes with 14-member tetraaza macrocyclic ligands.^{6–8} The same intermediate was observed in oxidation by $\cdot\text{OH}$ radicals of these complexes. Here oxidation of $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ by $\cdot\text{OH}$ radicals gives a first transient absorbing in the near-UV region and at 550 nm, but the UV absorption is higher and the visible absorption smaller than the absorptions of the intermediate $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ observed following the oxidation by Br_2^- . Experiments in progress suggest that in addition to $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ formation, some hydrogen abstraction from the ligand or $\cdot\text{OH}$ addition to the pyridine ring to give a ligand radical could be involved.

At pH values below 4.0, an additional mode of kinetic behavior was observed. Immediately following oxidation by Br_2^- , a small first-order decay in the 320-nm absorption is evident. The rate constants are given in Table III and may be seen to increase with Br^- concentration. The absorption at the end of this reaction also increases with Br^- concentration until at the limit, $[\text{Br}^-] \geq 10^{-2}$, no change in the initial absorption is observable. Such Br^- dependence strongly suggests an equilibrium of the form



The experimental rate constant k_{expd} for a reaction of this type is, of course, equal to $k_9 + k_{-9}[\text{Br}^-]$. The experimental rate constants were plotted as a function of Br^- concentration, and a straight line was obtained (see Figure 3). Rate constant k_9 equal to $7.2 \times 10^2 \text{ s}^{-1}$ and k_{-9} equal to $2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ were determined, and an equilibrium constant $K_9 = k_{-9}/k_9 = 360 \text{ M}^{-1}$ was calculated. A spectrum of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ has been calculated from the spectrum obtained at the end of this reaction, by using 10^{-3} M Br^- and the equilibrium constant K_9 (see Figure 4).

In the range pH 4–5 there is a transition in the kinetics between those obtained at low pH explained by equilibrium 9 and at high pH consistent with reaction 8. At pH 4.5 and 4.8, the reaction following the formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{OH}^-)$ leads to the species $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ but this reaction is too fast to be consistent simply with reaction 8. The rate constants are reported in Table I, and the very small variations with Br^- concentrations may be noted. The behavior in this pH region is best described by interaction of equilibrium processes 9 and 10. The spectrum at the end of



the reaction and at low Br^- concentrations (10^{-3} M) is nearly identical with the spectrum of $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ determined at higher pH. Then we can conclude that, in the pH range 4.5–4.8, the intermediate $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})(\text{OH}^-)$ is temporarily formed, leading by water elimination to the

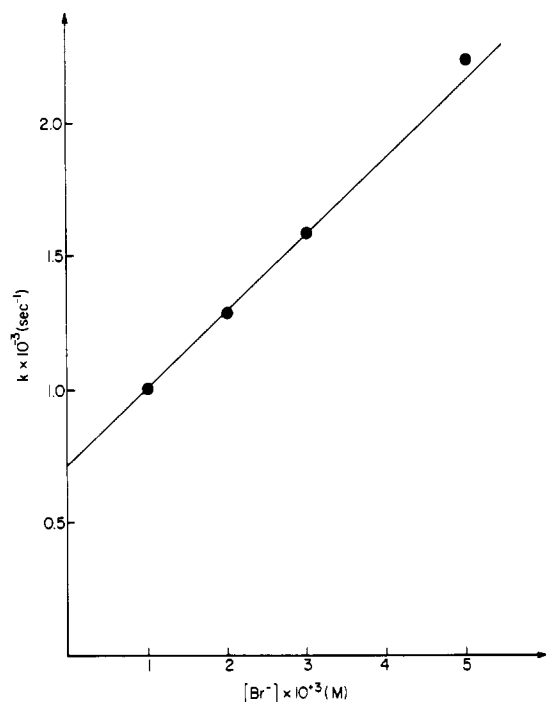


Figure 3. Influence of Br^- concentration on the first reaction following the formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ at pH 3.1.

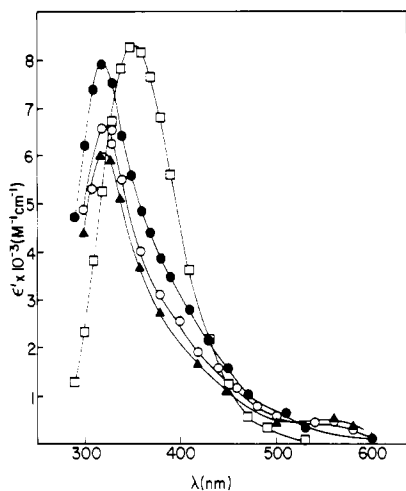


Figure 4. Transient spectra produced by Br_2^- oxidation of $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ at pH 3.1. $[\text{Br}^-] = 10^{-3} \text{ M}$ and $[\text{Ni}^{\text{II}}(\text{CR}+4\text{H})] = 2 \times 10^{-4} \text{ M}$. The spectra were recorded at various intervals after the pulse: (\square) 1.2 μs , (\bullet) 30 μs , (\circ) 3 ms. They may be assigned to Br_2^- (\square), $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ (\bullet), and a mixture of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ and $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ (\circ). The spectrum \blacktriangle is a calculated spectrum of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$, assuming an equilibrium constant $K_9 = 360 \text{ M}^{-1}$ (see text).

$\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ intermediate. No formation of the $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ being observed at pH 3.1, we conclude that the deprotonation of coordinated water is not effective at this pH. In the pH range 4.5–4.8, the initial absorption at 320 nm also increases with Br^- concentration in this pH range and may be explained by the displacement of equilibrium 9 toward the formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$. As reaction 9 involves only small changes in the 320-nm absorption and its rate is only slightly faster than the rate determined from the overall decay at 320 nm, it is not possible to clearly isolate this step. We do not, therefore, introduce a large error when assuming that the experimental rate constant ($2.2 \times 10^2 \text{ s}^{-1}$) at low Br^- concentration is equal to k_{10} . It is not possible to observe a true equilibrium between $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ and $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})(\text{OH}^-)$.

Table II. Rate Constants of the Reaction following the Formation of $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)^a$

pH	$10^4 \times [\text{Ni}^{\text{II}}(\text{CR}+4\text{H})], \text{ M}$	$10^2 \times [\text{Br}^-], \text{ M}$	$10^4 \times [\text{Na}_2\text{HPO}_4]$ or $10^4 \times [\text{NaH}_2\text{PO}_4], \text{ M}$	$k, \text{ s}^{-1}$
4.8	1	1		8.2
5.1	1	1	5	9
5.5	1	1	5	1.1×10
6.3	1	1	5	2.6×10
7.8	1	1	5	9.2×10
8.2	1	1	5	9.6×10
9.2	1	1		2.6×10^2
9.5	1	1		4.5×10^2
10	1	1		1.5×10^3
10.5	1	1		4×10^3

^a All solutions were N_2O saturated.

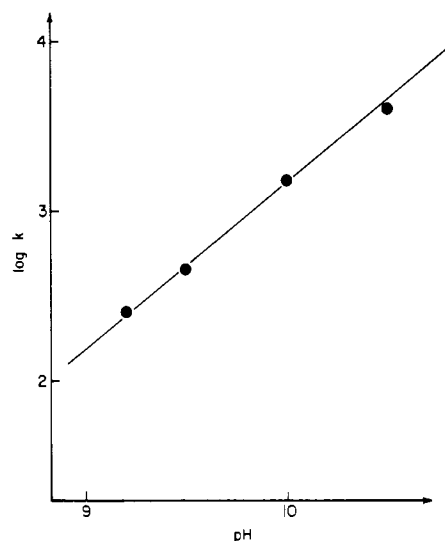


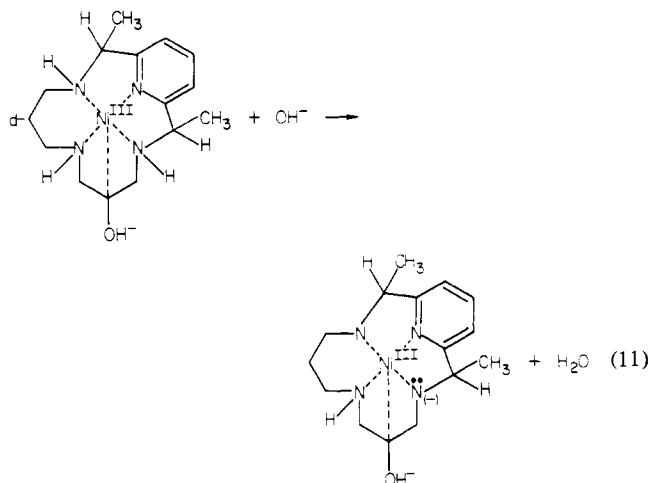
Figure 5. Plot of pH vs. the logarithm of the first-order rate constant of the reaction of $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ in N_2O -saturated solutions. $[\text{Br}^-] = 10^{-2} \text{ M}$ and $[\text{Ni}^{\text{II}}(\text{CR}+4\text{H})] = 10^{-4} \text{ M}$.

However, from these measurements one may estimate pK_{10} to be 4 ± 0.8 . This is well within the range for such acid–base equilibrium previously reported for Co^{III} ion with similar ligands²³ and for $\text{Ni}^{\text{III}}\text{Me}_2[14]-4,11\text{-dieneN}_4$.⁸

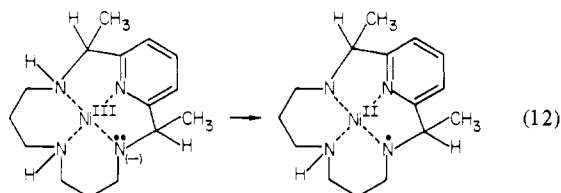
At pH > 9 the intermediate $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ is no longer observed. The first transient exhibits the same spectrum as $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$, and it is clear that the $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ intermediate becomes highly unstable in this pH region. Such instability may be due to OH^- coordination at the axial positions in either the parent compounds or the Ni(III) intermediate.

Decay of the Intermediate $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$. In the pH range 4.8–10.5, the last reaction observed is the decay of the intermediate $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ absorbing at 550 nm. First-order kinetics were observed, and the rate constants are given in Table II. Due to difficulties of adapting the pulse radiolysis monitoring system to measurements of weakly absorbing transients at long time ($t > 200 \text{ ms}$) periods, some of these data are subject to a degree of uncertainty, especially at low pH where the rates become very small. A strong pH dependence can be observed throughout. At pH > 8.5 the measured rate constant increases in proportion to changes in OH^- concentration (see Figure 5). This observation suggests reaction 11 with a rate constant $k_{11} = 1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ on

(23) D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).

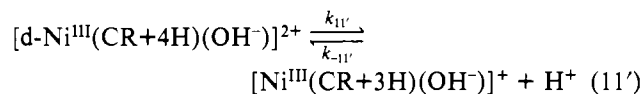


the assumption that the intermediate $[\text{Ni}^{\text{III}}(\text{CR}+3\text{H})(\text{OH}^-)]^{2+}$ is shorter lived than $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$. A fast electron transfer (eq 12) from the macrocyclic ligand anion to the metal center might be suggested, leaving an unstable ligand radical, from which products are formed via reaction 13. Similar pathways for degradation have been suggested for other Ni(III) macrocycles.^{6,8} Whether protonation of the OH^- ion occurs in the axial position following the electron transfer (eq 12) is not known; no assumptions regarding these axial positions are made in the mechanism suggested. No further



intermediate appeared in conjunction with the disappearance of $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ during this last reaction, even at pH 10.5 where the highest rate constant ($k_{11} = 4 \times 10^3 \text{ s}^{-1}$) was measured. Reactions 12 and 13 therefore must be significantly faster than reaction 11.

In neutral solutions (pH 4.8–8.2) the rate constant increases with increasing pH and a stabilization of the rate is observed around pH ~ 8 (see Table II). However at pH ≤ 8.2 the rates are too high to involve a direct reaction of OH^- with intermediate and reaction 11 must be rewritten as



The value of the equilibrium constant $K_{11'}$ for such an acid-base dissociation would be very small. With the assumption of the steady-state approximation for $[\text{Ni}^{\text{III}}(\text{CR}+3\text{H})(\text{OH}^-)]^{2+}$, the rate law for $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ disappearance is

$$\frac{-d[\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)]}{dt} = \frac{k_{11}k_{12}}{k_{-11'}[\text{H}^+] + k_{12}} [\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)]$$

This rate law is in good agreement with the experimental data, i.e., an increasing rate with increasing pH and stabilization around pH 8. Around pH 8, $k_{-11'}[\text{H}^+] \ll k_{12}$ and the experimental rate constant k_{exptl} is then equal to k_{11} . Taking into account a direct reaction of OH^- (reaction 11) at this pH, we find $k_{11} \approx 70 \text{ s}^{-1}$. Around pH 6.5, where an inflection point is implied (see Table II), $k_{\text{exptl}} \approx k_{11'}/2$ and $k_{-11'}[\text{H}^+]$ is then

Table III. Rate Constants of the Reactions following the Formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})$ in Acidic Solutions^a

pH	$10^5 \times [\text{Ni}^{\text{III}}(\text{CR}+4\text{H})], \text{ M}$	$10^2 \times [\text{Br}^-], \text{ M}$	$10^{-3} \times k_9, k_9^b, \text{ s}^{-1}$	k^c	dose, krd
3.1	2	0.1	1	5.5 s^{-1}	~ 1.4
3.1	2	0.2	1.3		~ 1.4
3.1	2	0.3	1.58		~ 1.4
3.1	2	0.5	2.2	4.6 s^{-1}	~ 1.4
3.1	10	3	d	$6.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	10	3	d	$9.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6
3.1	10	6	d	$5.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	10	6	d	$8.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6
3.1	10	10	d	$3.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	10	10	d	$6.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6
3.1	10	30	d	$2.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	10	30	d	$5.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6
3.1	3.2	5	d	$4.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	3.2	5	d	$6.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6
3.1	7.2	5	d	$3.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	7.2	5	d	$5.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6
3.1	17	5	d	$2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 2.5
3.1	17	5	d	$4.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	~ 0.6

^a All solutions were N_2O saturated. ^b Identified as k_9 (see text). ^c Last observed reaction (see text). ^d Not observable.

equal to k_{12} . From data obtained at pH 10.5, we set $k_{12} > 4 \times 10^3 \text{ s}^{-1}$; then $k_{-11'}$ must be higher than $1.25 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. From these rate constants we find $K_{11'} = k_{11'}/k_{-11'} < 6 \times 10^{-9} \text{ M}$. Such an equilibrium constant appears reasonable for the weak acidity of coordinated amino groups. The largely base-assisted decay of $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$ indicates that the acid character of the ligand might be enhanced by the high charge of the metal center. Increase of acidity in ammonia and amino groups when coordinated to tripositive or quadripositive metal ions has been reported.²⁴

Secondary Reactions of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})$ Intermediates in Acidic Solutions. The reactions following formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ and $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ appear to be very complicated in acidic solutions (pH 3.1). At low Br^- concentration ($\sim 2 \times 10^{-3} \text{ M}$), first-order decay kinetics were observed at 320 nm with a rate constant equal to 5.5 s^{-1} . No changes in the half-life were observed when the dose was changed. This first-order behavior may be attributed to a reaction of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ similar to that observed for $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$, i.e., formation of a ligand anion (eq 11'), subsequent formation of a ligand radical (eq 12), and formation of products (eq 13). With the assumption of such comparable behavior, the rate constant 5.5 s^{-1} appears very high. One can explain this high value if the equilibrium constant $K_{11'}$ is greater for $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ than for $\text{d-Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$. The absence of an anion in the axial position in $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$ might increase the positive charge on the metal center, leading to a shift of electron density from the macrocycle to Ni(III) and a more labile nitrogen-hydrogen bond. As the Br^- concentration increases, the rate constant is expected to decrease, equilibrium 9 being displaced toward the formation of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})(\text{Br}^-)$. Indeed, with $5 \times 10^{-3} \text{ M Br}^-$, a rate constant of 4.6 s^{-1} was measured.

At higher Br^- concentrations ($> 5 \times 10^{-3} \text{ M}$), modifications of the kinetic behavior were observed. The fit of the 320-nm decay becomes predominantly second order, but the half-life dose dependence is somewhat distorted (Table III). A small decrease of the rate constant is observed when the $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ concentration is increased. As may be seen this second-order rate constant also decreases with Br^- concentration, especially at high dose. All of these data suggest that, at high Br^- concentration and in acidic solution, the behavior

(24) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions and Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974.

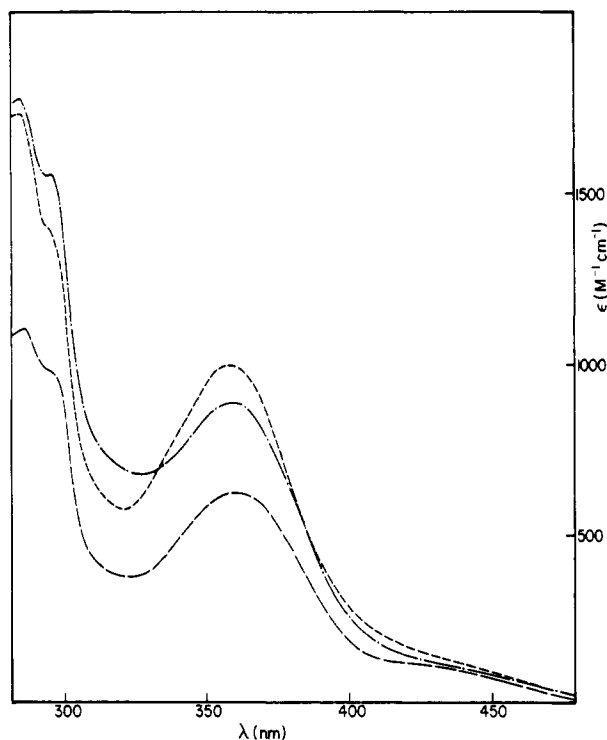
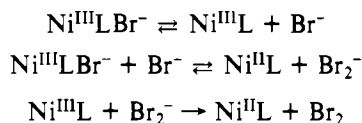


Figure 6. Differential spectra after γ -ray irradiations of 2×10^{-4} M $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ and 10^{-2} M Br^- and N_2O -saturated solutions at different pH: (---) pH 10, (-·-) pH 5.5, (—) pH 3.

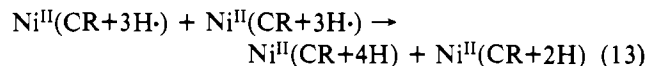
is very complex. Whitburn and Laurence⁷ suggested, in acidic solutions, oxidation of Br^- by Ni^{III} .



Such a mechanism predicts second-order kinetic behavior and an overall rate constant dependent on $[\text{Br}^-]$ and $[\text{Ni}^{\text{II}}]$. The transient behavior of $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$ parallels the predictions of their mechanism. However, this process may not be the only one involved. Reactions via a ligand radical may also take place. Only at very low pH, where the protonation of the ligand anion is faster than the electron transfer

from the anion to the metal center, the ligand radical formation can be completely avoided. Pulse radiolytically it is not possible to generate only Br_2^- at such low pH and no further investigations are possible. However, it clearly appears that the order of reaction and the rate constant themselves are significantly influenced by equilibrium 9.

Final Products of Reaction. Due to the difficulty of adapting the pulse radiolysis monitoring system to measurements of weakly absorbing transients at long time, we were not able to obtain well-defined final spectra by pulse radiolysis. However residual absorptions were observed in the UV region (280 nm) and the near-UV region (350 nm). So that data on final products could be obtained, differential spectra were recorded with use of a Cary 219 spectrophotometer after irradiations with a γ source. Aqueous solutions containing 2×10^{-4} M $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ and 10^{-2} M bromide were irradiated to convert 20–30% of the starting material. The differential spectra after irradiation at different pH values are shown in Figure 6. The final products of reaction are stable; no change of the absorption with time or with opening of the cell to the atmosphere were observed. The absorption at 360 nm with a shoulder at 450 nm is typical of the $\text{Ni}^{\text{II}}(\text{CR}+2\text{H})$ complexes reported by Barefield.⁴ Taking into account the absorption of the starting material $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$ ($\epsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda > 330 \text{ nm}$), the yield for $\text{Ni}^{\text{II}}(\text{CR}+2\text{H})$ formation in neutral or basic solutions is about 50%. This yield is consistent with a termination step (13) involving disproportionation of the ligand. In acidic



solutions the apparent yield in $\text{Ni}^{\text{II}}(\text{CR}+2\text{H})$ is lower. This is in agreement with the suggestion above that complex side reactions may occur in acidic solutions.²⁵

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Registry No. $\text{Ni}^{\text{II}}(\text{CR}+4\text{H})$, 53537-59-0; Br_2^- , 12595-70-9; $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{Br}^-)(\text{H}_2\text{O})$, 76011-06-8; $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{OH}^-)$, 76011-07-9; $\text{Ni}^{\text{III}}(\text{CR}+4\text{H})(\text{H}_2\text{O})_2$, 76011-08-0; Fe^{2+} , 15438-31-0.

(25) One of the reviewers has suggested an alternative termination step (13'), $\text{Ni}^{\text{III}} + \text{R}\cdot$. We cannot eliminate this possible pathway, given that $k_{13'} \gg k_{13}$, allowing for apparent overall first-order behavior.