Finally the stability constant for the addition of gly to Ni(trien)$^{2+}$ can be calculated as the ratio of $k_{gly}^{NiT}$ to $k_b$, which yields a value of $1.1 \times 10^4$. This must be compared to the stability constant of Ni(gly) of $6.03 \times 10^5$.[17] Although not as pronounced as the phen system, a significant decrease in stability is seen which must be due to the presence of trien.

It is interesting to note that the reaction between Ni(trien)$^{2+}$ and phen does not show an order dependence upon ligand concentration as glycine does. Ni(trien)$^{2+}$ provides the same amount of steric hindrance in both cases and molecular models show that the phen ring system does not interfere with chelation any more than the amine nitrogen of glycine. Yet eq 8, which assumes the steady-state approximation, can be used to describe the formation kinetics of the phen reaction. This means that $k_{-1}$ is small compared to $k_2$ or of about the same size as $k_2$ such that species I does not build up in concentration. The opposite is true for the glycine reaction: $k_{-1}$ is large compared to $k_2$. The reason for the different type of behavior is due to the difference in dissociation rates, $k_{-1}$, estimated by nickel–acetate and nickel–pyridine dissociation. The rate of nickel–acetate dissociation is $5 \times 10^3$ s$^{-1}$ [21] while that of nickel–pyridine is only 38 s$^{-1}$,[22] a decrease in rate of 130 which is too great to be compensated for by a decrease in $k_2$ due to steric hindrance. The effect of trien in decreasing the rate of ring closure is not great enough to decrease $k_2$ to the point where it is less than $k_{-1}$ when a stable dentate site bonds initially; however, it is great enough to drop $k_2$ well below $k_{-1}$ when a labile one bonds first. Thus the type of dentate sites available or the attacking ligand help determine the mechanism of the formation reaction when ring closure is very sluggish.

It must be noted that if the amine end of glycine bonded to nickel first, the $k_{-1}$ value would be sufficiently low so that ring closure would not be much smaller than $k_{-1}$ and the equilibrium type of mechanism would not be seen. This study provides evidence which supports the conclusion that the carbonyl group of amino acids bonds first in complex formation.

**Registry No.** Ni(trien)$^{2+}$, 24653-01-8; phen, 66-71-7; gly, 56-40-6.

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# Hydroxyl Radical Reactions with the Nickel(II) Macrocyclic Complexes Ni$^{II}$CR, Ni$^{II}$(CR-2H), and Ni$^{II}$(CR+4H). Generation of Ligand Radicals and Nickel(III) Species

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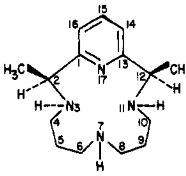
Reactions of hydroxyl radicals with the three closely related nickel(II) macrocylic complexes Ni$^{II}$(CR-2H), Ni$^{II}$(CR)(H$_2$O)$_2$, and Ni$^{II}$(CR+4H) have been studied by pulse radiolysis. With use of spectral data from the Ni(III) forms of these complexes and the behavior of radiolytically generated intermediates toward O$_2$, it has been found that both Ni(III) species and ligand radicals may be produced. The reaction of Ni$^{II}$CR(H$_2$O)$_2$ with ·OH gives evidence for formation of ligand radical alone. By contrast ·OH attack on Ni$^{II}$(CR-2H) and Ni$^{II}$(CR+4H) produces Ni(III) intermediates as well as ligand radicals through competitive pathways. The generation of a Ni(III) intermediate appears to parallel the absence of solvent binding at axial positions in the parent Ni(II) complexes. Such behavior may be linked to steric effects and/or electronic considerations.

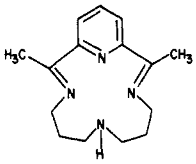
## Introduction

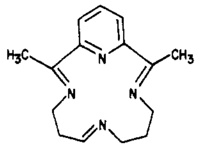
Anion radicals (e.g., Br$_2^-$, Cl$_2^-$, (CNS)$_2^-$) generated by pulse radiolysis have been shown to be useful tools in the study of redox processes in macrocyclic complexes, particular attention being given to Ni(II) systems.[1-5] Such investigations have provided considerable information on the behavior of Ni(III) intermediates with regard to mechanisms of formation, ligand binding at axial positions, and product formation. The initial event in all such reactions with anion radicals is taken to be oxidative attack on the central metal atom. Subsequent behavior has been shown to depend on both the nature of the ligand and solution conditions.

The precursor to the anion radical is the hydroxyl radical, ·OH, generated directly by water radiolysis. This radical is a powerful oxidant toward metal ions; but, by contrast with anion radicals such as Br$_2^-$, has the potential for hydrogen abstraction or addition to the ligand. There are, to date, only a few reports in the literature regarding reactions of ·OH radical with nickel(II) macrocyclic complexes.[1-3] In those systems (Ni$^{II}$[Me$_6$[14]aneN$_4$], Ni$^{II}$[Me$_6$[14]-4,11-dieneN$_4$], Ni$^{II}$[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]) oxidation of the metal center leading to a Ni(III) intermediate was found to occur and no evidence for attack on the macrocyclic ring to generate Ni(II) ligand radicals was obtained.

We have now investigated reactions of ·OH radicals with a different series of closely related Ni(II) macrocyclic complexes (Ni$^{II}$(CR), Ni$^{III}$(CR+4H), and Ni$^{II}$(CR-2H))[5] and find that, by contrast with the earlier systems investigated, both Ni(III) species and ligand radical can be formed here.


CR+4H


CR


CR-2H

The choice of this present series of macrocylic ligands is attactive not only because of the variation in degree of ring unsaturation but also because solvent bonding at the sites axial to the planar tetradentate ligand differs among members of this group.[6] The complex Ni$^{II}$(CR) is reported to be fully aquated, namely Ni$^{II}$(CR)(H$_2$O)$_2$ in octahedral configuration; by coontrast the CR-2H ligand complex is known to be free of axial water and exists in a square-planar configuration. The

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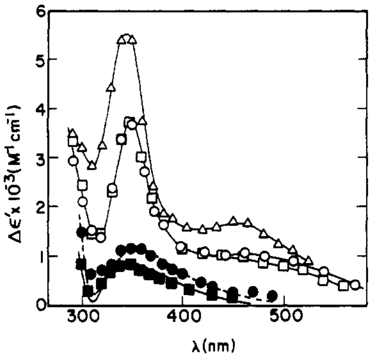

**Figure 1.** Transient spectra produced by ·OH reaction with $Ni^{II}(CR)(H_2O)_2$ in $N_2O$-saturated solutions. The spectra were recorded at various intervals after the pulse: (□) $t$ = 15 μs, pH 3.5; (○) $t$ = 13 μs, pH 6.7; (△) $t$ = 15 μs, pH 9.5; (●) $t$ = 8 ms, pH 9.5; (■) $t$ = 3 ms, pH 6.7. The two lower spectra (— and - - -) were recorded after γ irradiations at pH 6.7 and 9.5, respectively.

CR+4H system reveals both configurations and mixtures of $Ni^{II}(CR+4H)/Ni^{II}(CR+4H)(H_2O)_2$ in a ratio of about 1:1 are present in water at room temperature. These studies indicate strongly that both ring unsaturation and the axial bonding properties exert influence on the competing formation of Ni(III) and Ni(II) ligand radical species.

## Experimental Section

The techniques of pulse radiolysis have been previously described and the definition of $\Delta\epsilon'$ given.[4] Preparation of complexes and materials used were also previously described.[5] Because of the quantities of $H_3O^+$ produced by water radiolysis, phosphate buffers were used in the pH range 5–9. Solution pH outside this range was obtained with either perchloric acid or sodium hydroxide.

## Results and Discussion

**Formation of ·OH Radicals.** The radiolysis of water may be represented by reaction 1. In very dilute nitrogen saturated

$$H_2O \rightsquigarrow e_{aq}^-, \cdot OH, \cdot H, H_3O^+, H_2O_2, H_2 \qquad (1)$$

solutions the initial yield are $G_{e_{aq}^-} \approx G_{H_3O^+} \approx G_{\cdot OH} \approx 2.65$, $G_{\cdot H} \approx 0.6$, $G_{H_2} \approx 0.45$ and $G_{H_2O_2} \approx 0.75$, where $G$ is the number of species created per 100 eV of energy deposited in solution.[7] In the presence of nitrous oxide, hydrated electrons are converted into ·OH radicals with a rate constant $k_2 \approx 9 \times 10^9$ $M^{-1}$ $s^{-1}$ via reaction 2. The final yield of ·OH is then

$$e_{aq}^- + N_2O \xrightarrow{H_2O} \cdot OH + OH^- + N_2 \qquad (2)$$

equal to about 5.5, as $N_2O$ acts as a spur scavenger altering the interactions among primary water radicals.[8] In the range of these experiments, pH 3–11, formation of either hydrogen atoms via a reaction of $e_{aq}^-$ with protons or $O^-$ via deprotonation of $^-OH$ radicals is very inefficient. As hydrated electrons may react with the nickel(II) complexes ($k$ = $3.8 \times 10^{10}$, $4.5 \times 10^{10}$, and $5.2 \times 10^{10}$ $M^{-1}$ $s^{-1}$ where L = CR+4H, CR, and CR-2H, respectively), concentrations lower than $2 \times 10^{-4}$ M for the macrocyclic nickel(II) complexes must be used to avoid reduction by $e_{aq}^-$. Then under the conditions described, hydroxyl radicals are the predominant species able to react with these complexes ($[\cdot OH]/[\cdot H] \approx 10:1$).

**Reaction of ·OH Radical with $Ni^{II}(CR)(H_2O)_2$.** Reactions of ·OH radicals with the complex $Ni^{II}(CR)(H_2O)_2$ were investigated over the pH range 3.5–9.5. At each pH a pronounced transient growth in near-UV region is associated with the ·OH attack. The spectra recorded at the end of this reaction exhibit a large absorption band at 350 nm with a shoulder around 450 nm. These are given in Figure 1. As may be seen they are similar in structure for the various pHs even though stronger absorption is observed in basic solution. The course of this reaction was monitored by following the growth at 350 nm under pseudo-first-order conditions with various concentrations of $Ni^{II}(CR)(H_2O)_2$, leading to a rate constant $k_{\cdot OH+NiCR} = 4.5 \times 10^9$ $M^{-1}$ $s^{-1}$.

The spectrum of this first transient bears no resemblance to those observed when $Br_2^-$ or $(SCN)_2^-$ were the oxidizing agents and Ni(III) species were identified.[5] However, this initial spectrum may be compared to that of the first transient observed when ·H atoms react with the $Ni^{II}(CR)(H_2O)_2$ complex. In that system either a Ni(I) species or a Ni(II) ligand radical, formed by ·H atom addition to double bonds in the macrocycle ring, may be generated.[9] From these spectral similarities and the oxidative character of ·OH, one may suggest that this initial transient in the ·OH radical reaction is indeed a Ni(II) ligand radical. Hydroxyl addition to the pyridine ring, ·OH addition to the imino groups, or hydrogen abstraction are all possible mechanisms for the formation of the ligand radical species.[10] The variation of the intensity in the 350-nm band observed at high pH (pH 9.5) may be associated with modification of axial coordination ($H_2O$, $OH^-$). The fact that, unlike the earlier studies mentioned above, we did not observe any significant formation of Ni(III) species although the redox potential of ·OH radical is sufficient for oxidation of the metal center is itself of considerable interest. As may be seen in the members of this group of complexes, the inefficiency of the metal center oxidation pathway correlates with the presence of the axial water molecules in the $Ni^{II}(CR)(H_2O)_2$ system, making attack on the ligand more favorable. This would suggest that oxidation of the metal center by ·OH radicals arises from an inner-sphere mechanism and hence is largely unfavorable with octahedral Ni(II) complexes.

At longer times we observed a subsequent reaction which obeys second-order kinetics. Such decay is the expected pathway for a ligand radical species. We obtained rate constants equal to $2.8 \times 10^8$, $2.2 \times 10^8$, and $2.4 \times 10^8$ $M^{-1}$ $s^{-1}$ at pH 9.5, 6.7, and 3.4, respectively, by monitoring transient decay. The spectra recorded at the end of this second reaction at various pH values are identical with those recorded after γ irradiations (see Figure 1), demonstrating that this second decay is the last reaction in this system. However, the final products of reaction were not identified.

In the presence of oxygen, at concentrations low enough to avoid interference with reaction 2 ($[O_2] = (7–20) \times 10^{-5}$ M), the decay of the ligand radical was significantly enhanced and first-order kinetics were observed whose rate constants are proportional to $O_2$ concentrations. In acidic or neutral solutions an overall second-order rate constant of $3.1 \times 10^8$ $M^{-1}$ $s^{-1}$ was determined, which is in the right range for oxidation of large radical species by $O_2$[11] and far exceeds the rate constant found for oxygen reaction with Ni(III) species.[12,13] Taken in conjunction with the spectral data, the sensitivity of the transient species to oxygen lends considerable strength to the interpretation that ·OH radical reaction with the $Ni^{II}(CR)(H_2O)_2$ complex involves the macrocyclic ring rather than the metal center.

**Reaction of ·OH Radicals with $Ni^{II}$(CR-2H).** Because oxidation of the metal center by ·OH may occur via an inner-

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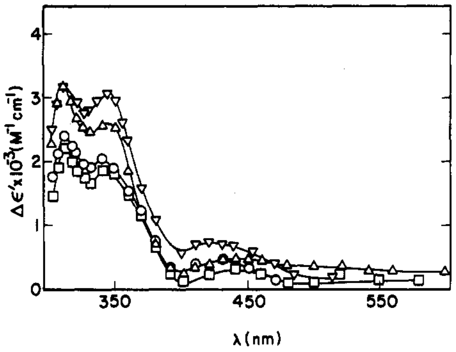

**Figure 2.** Transient spectra produced by •OH reaction with $Ni^{II}$(CR-2H) in $N_2O$-saturated solutions. The spectra were recorded at various intervals after the pulse: (△) $t$ = 25 μs, pH ~6 (unbuffered solutions); (▽) $t$ = 20 μs, pH 3.1; (□) $t$ = 1.5 ms, pH 6.7; (○) $t$ = 1.5 ms, pH 3.1.

sphere mechanism and because of the character of the ligand, either or both of the reactions 3 and 4 can be expected, where L• indicates, in general, a ligand radical.

$$Ni^{II}(CR\text{-}2H) + \cdot OH \xrightarrow{H_2O} Ni^{III}(CR\text{-}2H)(OH^-)(H_2O) \quad (3)$$

$$Ni^{II}(CR\text{-}2H) + \cdot OH \rightarrow Ni^{II}(L\cdot) \quad (4)$$

In neutral or acidic solutions we observed an initial reaction leading to spectra all of which are similar. These are reported in Figure 2. This reaction was monitored by following transient growth in the near-UV region and exhibits a rate constant of 6 × $10^9$ $M^{-1}$ $s^{-1}$. These spectra exhibit considerable similarity in band structure to the spectrum of the complex $Ni^{III}$(CR-2H)($OH^-$)($H_2O$) previously observed when $Br_2^-$ was used as the oxidizing agent.[5] However, these spectra are not absolutely identical with that of $Ni^{III}$(CR-2H)($OH^-$)($H_2O$), suggesting possible spectral contribution from both reactions 3 and 4.

In the pH range 3.3–8.7, a subsequent partial decay in the near-UV absorption was observed, substantiating the presence of more than one intermediate. This reaction obeys second-order (dose = 0.35–0.8 krd); and we obtained half-lives of 200, 250, and 375 μs at pH 3.3, 6.7, and 8.7, respectively, for doses of 0.5 krd. This second-order process is consistent with a bimolecular reaction involving a radical species, but as we cannot estimate the proportion of $Ni^{II}$ ligand radical initially produced by •OH attack, the absolute rate constants are not given. It is noteworthy, however, that the measured half-lives are in the right range for such processes. Again the small difference observed in the rate at various pHs may be due to different axial coordination in the radical species. In the presence of oxygen ($[O_2] \approx (1.3\text{–}2.9) \times 10^{-4}$ M), this partial second-order decay was again enhanced and exhibited pseudo-first-order kinetics with rate constants proportional to $O_2$ concentration; an overall constant, $k = 2.6 \times 10^8$ $M^{-1}$ $s^{-1}$, was obtained, once more in the range expected for radical behavior. At pH 7, following the disappearance of the spectral component assigned to the ligand radical, a separate decay in the near-UV was observed, which followed first-order kinetics with a rate constant equal to ~1.4 × $10^1$ $s^{-1}$. At pH 3.2 we were able to observe only the beginning of a decay in the time scale of 3 s, the time range limit of the detection system used. These slow processes may be attributed to decays of a Ni(III) intermediate formed as per reaction 3. However, because of overlap with product spectrum for ligand radical decay, we were not able to characterize reaction products and draw no further conclusion regarding this last step. In order to corroborate the evidence that this last decay involves a Ni(III) intermediate, we investigated electron transfer from ferrous ions at pH 3.2 where the natural decay is sufficiently slow. In the presence of $10^{-4}$ M $Fe(ClO_4)_2$, a concentration well below that at which a competing reaction of •OH radicals with iron(II) ions would interfer, the decay of the absorption at 350 nm was significantly enhanced. A pseudo-first-order rate constant of ~1 × $10^1$ $s^{-1}$ was determined, which is comparable to those previously reported for electron transfer from $Fe^{2+}$ to $Ni^{III}$ macrocyclic complexes.[3,4] Furthermore, the presence of 2 × $10^{-4}$ M $O_2$ did not affect the natural decay at pH 3.2, indicating a very low rate constant for oxygen sensitivity as expected for Ni(III) species.[12,13] All the data described above point strongly to competitive formation of a Ni(III) intermediate and a Ni(II) ligand radical as per reactions 3 and 4.

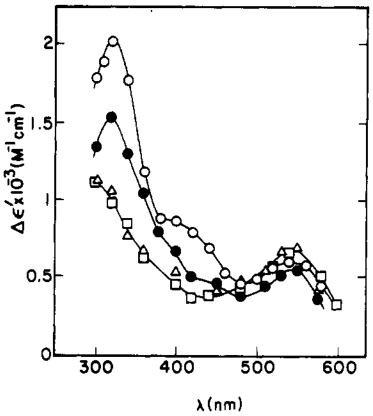

**Figure 3.** Transient spectra produced by •OH reaction with $Ni^{II}$(CR+4H) in $N_2O$-saturated solutions. The spectra were recorded at various intervals after the pulse: (○) $t$ = 13 μs, pH 4.7; (●) $t$ = 400 μs, pH 4.7; (□) $t$ = 7 ms, pH 4.7; (△) $t$ = 750 μs, pH ~6 (unbuffered solutions).

**Reactions of •OH Radicals with $Ni^{II}$(CR+4H).** The CR+4H system is reported to exist as a mixture of the aquated form, $Ni^{II}(CR+4H)(H_2O)_2$, and the square-planar form, $Ni^{II}$(CR+4H).[6] Hence it presents an excellent potential target for all three types of reactions, i.e., oxidation of the metal center, hydrogen abstraction from the ring, or addition to the pyridine ring. In neutral or acidic solutions, the first reaction observed between •OH radical and this complex leads to a transient spectrum which exhibits absorption in both the near-UV region ($\lambda_{max} \approx 320$ nm) and the visible region ($\lambda_{max} \approx 550$ nm). Over the pH range 4–9, this spectrum is unaffected by acid concentration and is reported in Figure 3. By following the growth at 320 nm the rate constant, $k_{\cdot OH+N2(CR+4H)} = 7.1 \times 10^9$ $M^{-1}$ $s^{-1}$, was determined, but the growth at 550 nm appears to be 10–20% slower. This data suggests that the initial reaction might involve overlapping rapid sequential processes. In basic solutions (pH >9) the first observed transient is slightly different, with a weaker absorption in the near-UV absorption and a small increase in the visible band (see Figure 4).

A previous study regarding the oxidation of $Ni^{II}[Me_6[14]\text{-}4,11\text{-}dieneN_4]$ and $Ni^{II}[Me_6[14]aneN_4]$ by •OH reported the formation of an asymmetrical Ni(III) complex absorbing in the visible region (λ ≈ 540 nm, Δε' ~$10^3$ $M^{-1}$ $cm^{-1}$).[1,13] The band was attributed to a d–d transition reflecting modification of the geometry of the nickel(III) complex. When $Ni^{II}$(CR+4H) was oxidized by $Br_2^-$ or $(SCN)_2^-$, formation of a transient absorbing at 550 nm was also observed in a step subsequent to the initial oxidation process.[4,5] In agreement with the earlier work, both kinetic and spectral data were interpreted to reflect the formation of a distorted complex, namely d-$Ni^{III}$(CR+4H)($OH^-$). From this information it appears reasonable to suggest that the absorption observed here in the visible region around 400 nm and at 550 nm is also due to the distorted species d-$Ni^{III}$(CR+4H)($OH^-$). By contrast with $Br_2^-$ or $(SCN)_2^-$ systems, however, this distortion occurs

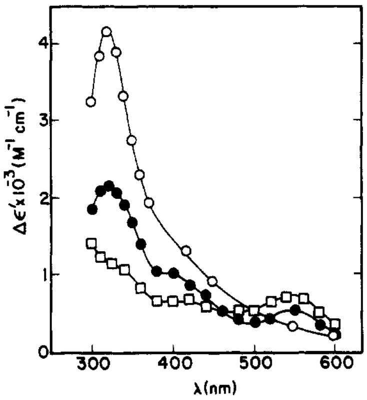

**Figure 4.** Transient spectra produced by ·OH reaction with $Ni^{II}$-(CR+4H) in $N_2O$-saturated solutions. The spectra were recorded at various intervals after the pulse: (●) $t$ = 30 μs, pH 3.1; (○) $t$ = 6 ms, pH 3.1; (□) $t$ = 10 μs, pH 9.6.

immediately after ·OH attack. One may suggest formation of a very short-lived five-coordinate species as per reaction 5.

$$Ni^{II}(CR{+}4H) + \cdot OH \rightarrow Ni^{III}(CR{+}4H)(OH^-) \quad (5)$$

In a very fast step this pentacoordinated species is distorted as per reaction 6, gives rise to the slight spectral changes

$$Ni^{III}(CR{+}4H)(OH^-) \rightarrow d\text{-}Ni^{III}(CR{+}4H)(OH^-) \quad (6)$$

overlapping the initial attack. This distortion process may be competing with reaction 7, leading to a symmetrical complex

$$Ni^{III}(CR{+}4H)(OH^-) + H_2O \rightarrow Ni^{III}(CR{+}4H)(H_2O)(OH^-) \quad (7)$$

which contributes to the near-UV absorption. This last may also be formed from reaction 8. According to an inner-sphere

$$Ni^{II}(CR{+}4H)(H_2O)_2 + \cdot OH \rightarrow Ni^{III}(CR{+}4H)(H_2O)(OH^-) + H_2O \quad (8)$$

mechanism and our observations with $Ni^{II}$(CR), the participation of this last reaction is expected to be very small. However, the spectral intensity of this first transient is not completely consistent with a simple mixture of distorted and undistorted complex alone. If indeed we assume from the visible absorption that about 40% of distorted complex is produced initially (3 < pH < 9), then the near-UV absorption would be expected to be much greater.[4] This indicates some fraction of ·OH reacting to produce a third transient with low absorption over the whole spectrum. One may again suggest the formation of a ligand radical species by either hydrogen abstraction or addition to the pyridine ring as per reaction 9.

$$Ni^{II}(CR{+}4H)(H_2O)_2 + \cdot OH \rightarrow Ni^{II}(CR{+}3H)(H_2O)_2 + H_2O \quad (9a)$$

$$\rightarrow Ni^{II}(CR{+}4H{+}OH)(H_2O)_2 \quad (9b)$$

At pH 4.7 a small decay at 320 nm followed the first reaction (see Figure 3). A dose dependence of the half-life indicates a second-order process ($\tau_{1/2}$ = 120–250 μs for dose ≈ 0.60–0.25 krd). As the pH increases, modifications were found in the kinetic behavior monitored at 320 nm. In the range 5 < pH < 9, a decay at 320 nm was measured which fits neither simple first- nor second-order behavior although dose dependence of the half-life was observed. At pH 9.5, a second reaction was again apparent involving a slight decay at 320 nm. This decay again essentially fits second-order kinetics with good dose dependence for the half-life ($\tau_{1/2}$ = 400 and 250 μs for dose ~0.35 and 0.55 krd). It is of interest to note that the half-lives for this decay are similar to those measured at pH 4.7. From this information it clearly appears that those second-order decays at pH 4.7 and 9.5, along with the complex decay in neutral solsution, are due to a radical species formed as per reaction 9. Again we investigated the oxygen sensitivity of this apparent transient to substantiate this assignment. At pH 9.6 in the presence of $O_2$ ($[O_2]$ = (1.3–2.2) × $10^{-4}$ M), the decay at 320 nm was significantly enhanced and became a first-order process with rate constants proportional to $O_2$ concentration. The resulting value, $k$ = 1.9 × $10^8$ $M^{-1}$ $s^{-1}$, as with the other systems, is the right range for $O_2$ oxidation of a large radical species.

At pH 4.7 in $O_2$ free solution, a third reaction, following decay of the radical, is observed involving a decay at 320 nm coupled to a slight growth at 550 nm. This reaction obeys first-order kinetics, and the spectrum recorded at the end is similar to that observed at the completion of the complex reaction at neutral pH. As observed earlier for the complex $Ni^{III}(CR{+}4H)(X^-)(H_2O)$, one may suggest that this step is associated with a base-catalyzed distortion of the complex $Ni^{III}(CR{+}4H)(H_2O)(OH^-)$(eq 10). If reaction 10 is clearly

$$Ni^{III}(CR{+}4H)(H_2O)(OH^-) \xrightarrow{OH^-} d\text{-}Ni^{III}(CR{+}4H)(OH^-) + H_2O \quad (10)$$

observed at pH 4.7, in neutral solution it is superimposed on the second-order decay of the ligand radical, leading to the undefined kinetic decay discussed above. At pH >9 reaction 10 becomes very fast and is, in fact, not observed; this gives an initial spectrum different than that at lower pH.

In order to establish that the assumed distorted complex $d\text{-}Ni^{III}(CR{+}4H)(OH^-)$ is effectively the same as that observed in $Br_2^-$ or $(SCN)_2^-$ oxidation, we investigated its decay in basic solutions (pH 9.5–10.5). First-order decays were observed with rate constants proportional to $OH^-$ concentration. The resulting value $k$ = 1.5 × $10^7$ $M^{-1}$ $s^{-1}$ is identical with that previously determined for $d\text{-}Ni^{III}(CR{+}4H)(OH^-)$ generated from $(SCN)_2^-$ or $Br_2^-$ oxidation.[4,5]

Following ·OH attack in acidic solution (pH ~3.1), there is a large growth in the near-UV region, with a decay of the visible absorption at 550 nm (see Figure 4). This behavior is exactly opposite to that observed at pH ≥4.7. At pH 3.1 the intermediate $Ni^{III}(CR{+}4H)(H_2O)(OH^-)$ may be protonated to give the complex $Ni^{III}(CR{+}4H)(H_2O)_2$.[4] This behavior is consistent with that observed for the complex $Ni^{III}(CR{+}4H)(H_2O)_2$ generated by $Br_2^-$ oxidation; we determined for that species an acid–base equilibrium with a $pK_a$ = 4 ± 0.8. The decay at 550 nm suggests that the distorted $d\text{-}Ni^{III}(CR{+}4H)(OH^-)$ is also protonated and coordinates a second water molecule to give the $Ni^{III}(CR{+}4H)(H_2O)_2$ complex.

Static irradiations with a $^{60}Co$ source were carried out to obtain information about the final products. Solutions of 2 × $10^{-4}$ M $Ni^{II}$(CR+4H) were irradiated at various pH to convert about 20–30% of the starting material, and differential spectra after irradiation were recorded with a Cary 219 spectrophotometer. Those spectra are reported in Figure 5. As may be seen, there are no important differences for the various acidities. These spectra are comparable to those obtained after $(SCN)_2^-$ or $Br_2^-$ oxidation, particularly in basic solutions. The band at 360 nm with the shoulder at 450 nm is characteristic of the more unsaturated $Ni^{II}$(CR+2H) complex.[14] The formation of this complex is not unexpected since we earlier demonstrated the possible pathway for $Ni^{II}$(CR+2H) formation (eq 10′). It is interesting to note that the data

$$2Ni^{III}(L) \rightarrow Ni^{II}(L) + Ni^{II}(L{-}2H) + 2H^+ \quad (10')$$

for $Ni^{II}$(CR+2H) in basic solution produces a yield of about 50% calculated from the known extinction coefficient of this

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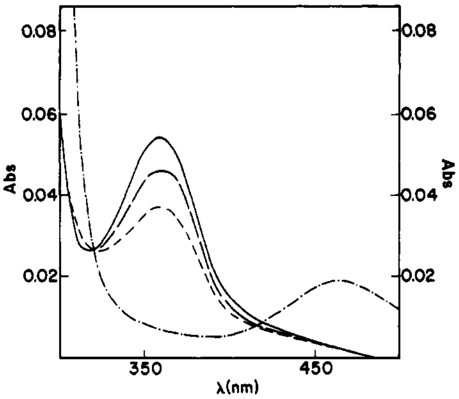

**Figure 5.** Differential spectra after γ-ray irradiations of $1.8 \times 10^{-4}$ M Ni$^{\mathrm{II}}$(CR+4H) and $N_2O$-saturated solutions at various pHs: (—) pH 10; (– –) pH 5.5; (- - -) pH 3.2; (–·–) spectrum of the starting material. Dosage = 8 krd; optical path = 1 cm.

complex at 360 nm and the absorption recorded after irradiation of $N_2O$-saturated solutions with a given dose. There must then be a contribution to this yield from both the ligand radical intermediate as well as the Ni(III) species. Addition of ·OH to the pyridine in reaction 4 provides no feasible pathway for generation of Ni$^{\mathrm{II}}$(CR+2H). It appears more likely then that hydrogen abstraction occurs essentially in position 2 or 12 (see Introduction); such ligand radicals could then disproportionate to give the Ni$^{\mathrm{II}}$(CR+2H) complex. At lower pH (neutral or acidic solution), the yield for Ni$^{\mathrm{II}}$-(CR+2H) is lower than that at pH 10. This loss may be attributable to competitive reactions: ligand degradation or demetalation, for example, when the formation of the ligand radical from the Ni$^{\mathrm{III}}$ species is decreased by the increasing acidity of the solution.[4]

## Conclusion

Both spectroscopic and kinetic data given here provide evidence that two types of initial intermediates, Ni(III) macrocyclics or Ni(II) ligand radicals, may be produced by ·OH attack on the group of CR complexes investigated. With use of differential reactivity toward oxygen it has been shown that, in the case of Ni$^{\mathrm{II}}$(CR-2H) and Ni$^{\mathrm{II}}$(CR+4H), ·OH attack can produce more than one type of intermediate in competing reactions. In the case of Ni$^{\mathrm{II}}$(CR+4H), product spectra suggest increased ring unsaturation best explained by formation of a ligand radical via hydrogen abstraction. The product spectra from ·OH reaction with Ni$^{\mathrm{II}}$(CR) do not suggest a similar pathway. The metal center oxidation is consistent with an inner-sphere mechanism, and the mode of attack on the complex appears to be influenced by the related parameters of ligand unsaturation and solvent binding in the axial positions.

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**Registry No.** Ni$^{\mathrm{II}}$(CR)$(H_2O)_2$, 36515-22-7; Ni$^{\mathrm{II}}$(CR–2H), 47023-96-1; Ni$^{\mathrm{II}}$(CR+4H), 53537-59-0; ·OH, 3352-57-6.

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# Chemical Kinetics of Nickel(III) Macrocyclic Complexes. Pulse Radiolysis Study of Ni$^{\mathrm{II}}$(CR+4H), Ni$^{\mathrm{II}}$(CR), and Ni$^{\mathrm{II}}$(CR-2H) in Aqueous Solutions of $Br^-$ and $CNS^-$

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Oxidation of three closely related nickel(II) macrocyclic complexes Ni$^{\mathrm{II}}$(CR-2H), Ni$^{\mathrm{II}}$(CR), and Ni$^{\mathrm{II}}$(CR+4H) via anion radical reaction has been investigated by pulse radiolysis methods. While the initial oxidation products follow the form Ni$^{\mathrm{III}}$(L)$(X^-)(H_2O)$, in agreement with previous studies (L = macrocyclic ligand; $X^-$ = $Br^-$, $SCN^-$), pH- and anion-concentration-dependent behavior provides evidence indicating subsequent formation of several other complexes Ni$^{\mathrm{III}}$(L)$(X^-)_2$, Ni$^{\mathrm{III}}$(L)$(OH^-)(H_2O)$, Ni$^{\mathrm{III}}$(L)$(OH^-)$, and Ni$^{\mathrm{III}}$(L)$(OH^-)_2$. The kinetics for interconversion among these species have been measured and are found in several cases to exhibit reversible behavior. In those cases the associated equilibrium constants have been determined. The formation of Ni$^{\mathrm{III}}$(L)$(X^-)_2$ may be seen to depend on the degree of macrocyclic unsaturation and character of the anion. With the exception of the fully unsaturated CR-2H ligand, Ni$^{\mathrm{III}}$(L)$(OH^-)$ and Ni$^{\mathrm{III}}$(L)$(OH^-)(H_2O)$ and Ni$^{\mathrm{III}}$(L)$(OH^-)_2$ decay via ligand radical formation at neutral pH and higher. Steady-state radiolysis results indicate introduction of an additional double bond into the ligand. At low pH, anion-substituted Ni(III) species return almost quantitatively to their parent Ni(II) complexes.

## Introduction

There are now several papers in the literature which report the oxidation of Ni(II) complexes by anion radicals, principally $Br^-_2$.[1-4] Such work has, to a degree, been motivated by increased interest in the chemistry of complexes exhibiting unstable oxidation states;[5] certain catalytic reactions as well as some biological processes are thought to involve intermediates with highly oxidized metal centers.[6]

The mechanism initiated by such oxidation has been shown to be complicated by the interaction of anion and central metal which extends well beyond the initial electron-transfer step. For example, in a recent report from our laboratory[4] con-

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