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Oxidation of a Macrocyclic Nickel(II) Complex by Alkyl Hydroperoxides

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Oxidation of NiL^{2+} (L = 1,4,8,11-tetraazacyclotetradecane) by alkyl hydroperoxides in acidic aqueous solutions produces NiL^{3+}. Kinetic measurements by the initial-rate method yielded rate constants that were ionic strength dependent. The yields of NiL^{3+} depend on the relative concentrations of the reactants and improve in the presence of oxygen. Possible causes for these observations are discussed. Bromide ions alter the stoichiometry and products of the reaction with *tert*-butyl hydroperoxide but have no effect on the reaction with *tert*-amyl hydroperoxide. This difference is rationalized in terms of the relative reactivities of the intermediate alkoxyl radicals toward β-scission versus bromide oxidation. The addition of alcohols containing α-hydrogens (CH_3OH and $(CH_3)_2CHOH$) decreases substantially the yield of NiL^{3+} for reactions with both hydroperoxides. Evidence is presented to attribute this effect to the reduction of NiL^{3+} by the α-hydroxyalkyl radicals formed in the reactions of alcohols with alkyl and alkoxyl radical intermediates.

Introduction

Nickel(II) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) and related macrocyclic ligands have long attracted attention, owing to their possible relevance to biological systems and their industrial importance. A number of investigations have characterized the conformations of nickel(II) macrocycles.[1-3] Studies of reactions involving radicals,[4,5] and metal complexes[6] as oxidizing agents have also been reported.

The reduction of peroxides by nickel(II) macrocycles may present challenging questions, but virtually no kinetic or mechanistic information is available for these reactions. We therefore investigated the reactions of alkyl hydroperoxides with NiL^{2+} (L = 1,4,8,11-tetraazacyclotetradecane).[7] The strategy has been to conduct kinetic measurements, to examine the reaction stoichiometry, and to determine the products formed, so that we can establish the reaction mechanism.

In the reaction with *tert*-butyl hydroperoxide (*t*-BuOOH), we searched for the possible intermediate, *t*-BuO•, by determining the stoichiometry under different conditions and by examining the effects of bromide ions and alcohols. We also studied the reaction with *tert*-amyl hydroperoxide (*t*-AmOOH) to learn whether the rate of β-scission of alkoxyl radicals has an effect on the kinetics and products. Experiments have been carried out under both aerobic and anaerobic conditions to establish the role of oxygen-sensitive intermediates in these reactions.

Experimental Section

Materials. The nickel(II) complex $NiL(ClO_4)_2$ was synthesized in solution by mixing stoichiometric amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ and ligand L (Strem Chemical Co.) as previously described.[8] The isolated solid was characterized by its UV–vis spectrum in 0.1 M $HClO_4$ (λ = 451 nm, ϵ = 47 M^{-1} cm^{-1}).[8] *tert*-Amyl hydroperoxide was prepared according to a literature method.[9] Cerium(IV) was obtained in solution form ($H_2Ce(ClO_4)_6$, ca. 0.5 M in 6 M $HClO_4$) from GFS Chemicals. 2-Propanol (Fisher) was further purified by distillation. Lithium perchlorate was prepared from lithium carbonate (Aldrich) and perchloric acid and was recrystallized three times prior to use. Other materials and solvents were of the highest grade commercially available and were used as received. *Caution! Perchlorate salts are potentially explosive and have to be handled with care.*

All solutions were prepared from distilled water further purified by a Milli-Q Millipore system. Samples were deaerated with a stream of water-saturated argon (99.99% pure, Air Products Corp.). For experiments designed to examine the oxygen effect, samples were prepared by purging with oxygen (Air Products Corp.).

Stock solutions of NiL^{2+} were prepared by dissolving solid $NiL(ClO_4)_2$ in dilute perchloric acid. NiL^{3+} was prepared in solution by oxidation of NiL^{2+} with a stoichiometric amount of Ce(IV). Alkyl hydroperoxides in dilute perchloric acid were stored in a refrigerator. Peroxide concentrations were determined spectrophotometrically by adding an aliquot into excess KI in 1 M H_2SO_4 and measuring the amount of I_3^- formed (ϵ_{355} = 26 000 M^{-1} cm^{-1}).[10] The concentrations of NiL^{3+} produced were determined spectrophotometrically at 308 nm (ϵ = 11 000 M^{-1} cm^{-1}) or 365 nm (ϵ = 7800 M^{-1} cm^{-1}).[11]

Instruments and Procedures. UV–vis electronic absorption spectra, spectrophotometric titrations, and kinetic measurements were performed by use of a Shimadzu UV-3101PC scanning spectrophotometer equipped with a thermostated cell holder. The temperature was controlled at 25.0 ± 0.2 °C, unless otherwise indicated.

Reaction rates were determined by the initial-rate method in order to avoid side reactions referred to later. Most of the measurements were made at 365 nm by monitoring the buildup of NiL^{3+}. The ionic strength of the solution was kept constant at 0.96 M with lithium perchlorate, except for those experiments designed to explore the ionic strength effect.

The organic products were identified by use of a Hewlett-Packard Model 5790 gas chromatograph with a 3390A integrator. Polar molecules such as acetone and *tert*-butyl alcohol were chromatographed with an OV-101 column at 30 °C by injection of liquid-phase samples; methane, ethane, ethylene, and butane were chromatographed with a VZ-10 column at 50 °C by injection of gas-phase samples. Electron impact ionization mass spectrometry was performed by use of a Kratos Model MS50 double-focusing mass spectrometer. Typical acceleration voltage was 8 kV.

Results

Kinetics. The reaction of *t*-BuOOH with NiL^{2+} yielded NiL^{3+} as a product. It has been shown previously[12] that NiL^{3+} slowly decomposes even at high [H^+]. In the present system, NiL^{3+} could also react with other chemical species in solution. To avoid

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(1) Barefield, E. K.; Bianchi, A.; Billo, E. J.; Connolly, P. J.; Paoletti, P.; Summers, J. S.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 4197.

(2) Billo, E. J. *Inorg. Chem.* **1984**, *23*, 236.

(3) Dei, A. *Inorg. Chem.* **1979**, *18*, 891.

(4) Kelley, D. G.; Marchaj, A.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 7583.

(5) Van Eldik, R.; Cohen, H.; Meshulam, A.; Meyerstein, D. *Inorg. Chem.* **1990**, *29*, 4156.

(6) Brodovitch, J. C.; McAuley, A. *Inorg. Chem.* **1981**, *20*, 1667.

(7) The formula NiL^{2+} is used here for the title complex which actually exists in two forms in acidic aqueous solution (eq 1). The water molecules are often omitted for simplicity. The formula NiL^{3+} is used for $NiL(H_2O)_2^{3+}$.

(8) Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1109.

(9) Milas, N. A.; Sugenor, D. M. *J. Am. Chem. Soc.* **1946**, *68*, 643.

(10) Awtry, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 5026.

(11) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.

(12) Barefield, E. K.; Mocella, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4238.

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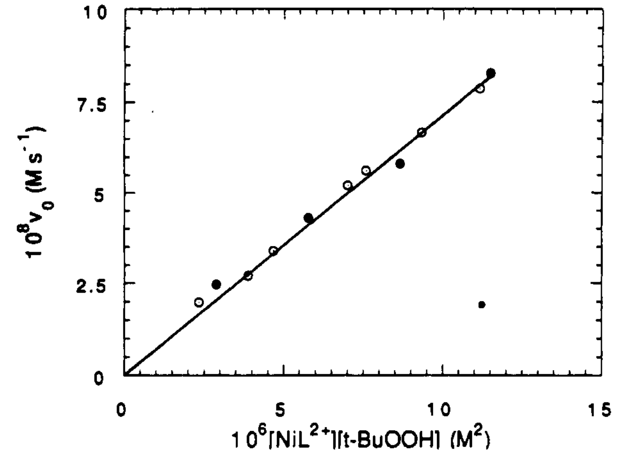

Figure 1. Plot of the initial rate v_0 versus [NiL^{2+}][*t*-BuOOH] ([NiL^{2+}] = (1.0–4.0) × 10^{-4} M, [*t*-BuOOH] = 0.020–0.105 M, [HClO$_4$] = 0.1 M (●) and 0.96 M (○), μ = 0.96 M) for argon-saturated solutions at 25 °C.

possible complications that came to light in preliminary experiments over the full time course of the reaction, we obtained the kinetic data by the initial-rate method. During the initial stage of the reaction (typically the first 20 s) the side reactions were insignificant because the products were present only at low concentrations. The reaction rate is first-order with respect to each reactant, as illustrated by the linearity of the plot of the initial rate (v_0) versus [NiL^{2+}][*t*-BuOOH]. All of the data at μ = 0.96 M are shown in Figure 1. The apparent second-order rate constant k_2 is given by the slope of the straight line. Experiments with variation of [*t*-BuOOH] (0.02–0.1 M) and [NiL^{2+}] ((1.0–4.0) 10^{-4} M) confirmed the first-order dependence on both reagents and yielded the rate constant k_2^{obs} = (6.8 ± 0.3) × 10^{-3} M^{-1} s^{-1} (μ = 0.96 M). No rate variation was observed over the [H$^+$] range 0.1–0.96 M at a constant ionic strength of 0.96 M or over the [H$^+$] range 0.1–2.0 M at a constant ionic strength of 2.0 M.

Experiments were then carried out to examine the ionic strength effect. The rate decreased with the increasing ionic strength, a somewhat surprising finding for a reaction involving an uncharged species. The kinetic results are summarized in Table I.

In order to gain further insight into the ionic strength dependence, the equilibrium relating the four- and six-coordinated forms of NiL^{2+} (eq 1) was studied over the ionic strength range

$$\mathrm{NiL^{2+} + 2H_2O \rightleftharpoons NiL(H_2O)_2^{2+}} \quad K \qquad (1)$$

0.1–2.0 M. The absorbance change was monitored at the absorption maximum of the square planar species (λ = 451 nm, ϵ = 64 M^{-1} cm^{-1}),[13] where the six-coordinated form does not absorb. The equilibrium constant K = [NiL(H$_2$O)$_2^{2+}$]/[NiL^{2+}] at different ionic strengths was then calculated (see Table I). Our result at μ = 0.1 M (K = 0.36) is in reasonable agreement with the literature value (K = 0.40).[13]

Kinetic measurements were also made in solutions saturated with oxygen. The values of k_2 were determined by the initial-rate method and found to be identical (within the experimental error) with those obtained under air-free conditions. For comparison, we also measured several rate constants by fitting complete kinetic curves. In this case, the rate constants obtained were generally larger than those derived by the initial-rate method under the same conditions owing to the decomposition of NiL^{3+} at longer times. At higher [H$^+$], however, the difference between these two sets of data became quite small (ca. 5%).

Stoichiometry and Products. Experiments were performed under different conditions to examine the yields of NiL^{3+} for a range of initial concentrations.

When NiL^{2+} (1.0 × 10^{-4} M) was allowed to react with excess *t*-BuOOH (0.02–0.1 M), only ca. 6 × 10^{-5} M NiL^{3+} was obtained even at high [H$^+$] (2.0 M), where it is most stable. Methane and ethane were produced in a 2:1 ratio. Experiments with *t*-AmOOH gave similar results. The yield of NiL^{3+} was only 44% in 0.1 M HClO$_4$, μ = 0.1 M. Ethane and ethylene were produced in comparable amounts. Small amounts of butane were also produced. In oxygen-saturated solutions, however, the yield of NiL^{3+} increased to >80% with *t*-BuOOH as the oxidant.

Experiments were also conducted with NiL^{2+} in excess over ROOH. Typical concentrations were [NiL^{2+}] = 0.05 M and [*t*-BuOOH] = 1.0 × 10^{-4} M. In this case, the ratio Δ[NiL^{3+}]:Δ[*t*-BuOOH] was 0.94:1. The ratio increased with the sulfate concentration (0.08–0.36 M) and reached a value of 1.7:1.

Analyses for the organic products were done for two sets of samples, both having NiL^{2+} in excess. The experiments were carried out at room temperature with [*t*-BuOOH] = 5 × 10^{-4} M, [H$^+$] = 0.1 M, and μ = 0.22 M. One sample contained 0.04 M NiL^{2+}, and the other, 1.0 × 10^{-3} M NiL^{2+}. Both solutions were allowed to stand for about 5 half-lives, and then the products were analyzed by GC. At the higher [NiL^{2+}], the only detectable product was *tert*-butyl alcohol (3.7 × 10^{-4} M). No methane or ethane was produced. At the lower [NiL^{2+}], small amounts of methane and ethane were detected in the gas phase. The solution contained both acetone (1.6 × 10^{-4} M) and *tert*-butyl alcohol (2.2 × 10^{-4} M).

Next, we studied the effect of added bromide ions. When 0.1 M Br$^-$ was added, the stoichiometry of the *t*-BuOOH reaction changed. The ratio Δ[NiL^{3+}]:Δ[NiL^{2+}] was 1:1 when *t*-BuOOH was in excess, and Δ[NiL^{3+}]:Δ[*t*-BuOOH] was 2:1 when NiL^{2+} was in excess. No methane or ethane was produced in these experiments. There was also no evidence for the formation of Br$_3^-$, which absorbs strongly at 266 nm (ϵ = 35 000 M^{-1} cm^{-1}).[14] In contrast, with *t*-AmOOH as the oxidant, Br$^-$ had no effect on the stoichiometry and products. The direct reaction of Br$^-$ with the hydroperoxides was negligible under the experimental conditions.

Experiments were also carried with alcohols added. Typical concentrations were [NiL^{2+}] = 1.0 × 10^{-4} M, [*t*-BuOOH] = 0.05 M, and [H$^+$] = 0.96 M. With [2-propanol] > 4 M, for example, the formation of NiL^{3+} was no longer observable as the reaction proceeded. The yield of ethane was much smaller, and that of methane, somewhat smaller than in the absence of 2-propanol. In one experiment (CD$_3$)$_2$CDOH was used. The reaction yielded CH$_3$D, which was identified by mass spectrometry. The amount of CH$_3$D increased with increasing [(CD$_3$)$_2$CDOH]. This result shows unequivocally that the deuterium in CH$_3$D in methane was derived from the alcohol. The effect of alcohols was much less prominent in solutions saturated with oxygen.

2-Propanol also affected the yields of NiL^{3+} and organic products in the *t*-AmOOH reaction, but to a much lesser extent than in the *t*-BuOOH case. Ethane was the main organic product in the *t*-AmOOH reaction in the presence of 2-propanol.

Discussion

In every known case, the reduction of peroxides by transition metal complexes occurs by an inner-sphere mechanism.[15-17] Some type of coordination of the peroxide to the metal center is a necessary step prior to reaction. Metal complexes with slow ligand substitution also react slowly with peroxides. Substitution is not

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(13) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta* **1977**, *24*, L21.

(14) Soulard, M.; Bloc, F. *J. Chem. Soc., Dalton Trans.* **1981**, *21*, 2300.

(15) Masarwa, M.; Cohen, H.; Meyerstein, D.; Hickman, D. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4293.

(16) Kim, H. P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1987**, *26*, 4090.

(17) Sadler, N.; Scott, S. L.; Bakac, A.; Espenson, J. H.; Ram, M. S. *Inorg. Chem.* **1989**, *28*, 3951.

Table I. Equilibrium Constants for $NiL^{2+} + 2H_2O \rightleftharpoons NiL(H_2O)_2^{2+}$ and Rate Constants for Reaction of Mixtures of $NiL^{2+}/NiL(H_2O)_2^{2+}$ with *t*-BuOOH in Aqueous Perchloric Acid at 25 °C

μ (M)	$K^a = [NiL(H_2O)_2^{2+}]/[NiL^{2+}]$	k_2^{obs} (M^{-1} s^{-1})^b	μ (M)	$K^a = [NiL(H_2O)_2^{2+}]/[NiL^{2+}]$	k_2^{obs} (M^{-1} s^{-1})^b
0.1	0.36	$(1.3 \pm 0.1) \times 10^{-2}$	0.77	0.18	$(8.1 \pm 0.2) \times 10^{-3}$
0.17	0.32	$(1.2 \pm 0.1) \times 10^{-2}$	0.96	0.15	$(6.8 \pm 0.3) \times 10^{-3}$
0.50	0.22	$(8.7 \pm 0.3) \times 10^{-3}$	2.0	0.10	$(5.8 \pm 0.3) \times 10^{-3}$

^{a} Calculated from the absorbance change at 451 nm ($\epsilon = 64$ M^{-1} cm^{-1} for the tetracoordinated form[13]). ^{b} Initial-rate method.

a problem for NiL^{2+}, because the exchange of coordinated water takes place rapidly.[18]

A straightforward mechanism that accommodates all the experimental evidence obtained in this work for the reduction of *t*-BuOOH by NiL^{2+} is a Fenton-type process as shown in eq 2. The reaction produces *tert*-butoxyl radicals, which undergo

$$NiL^{2+} + (CH_3)_3COOH \rightarrow LNiOH^{2+} + (CH_3)_3CO^\bullet \quad (2)$$

$$(CH_3)_3CO^\bullet \rightarrow {}^\bullet CH_3 + (CH_3)_2CO \quad (3)$$

β-scission to form acetone and methyl radicals (eq 3).[19] The final organic products are formed in subsequent rapid reactions of $^\bullet CH_3$ with itself, NiL^{2+}, NiL^{3+}, and possibly *t*-BuOOH. Under conditions of excess *t*-BuOOH, we have confirmed the formation of methane, ethane, and acetone. Ethane is produced in the self-reaction of methyl radicals. The source of CH_4 is probably the reaction between $^\bullet CH_3$ and excess *t*-BuOOH:

$${}^\bullet CH_3 + (CH_3)_3COOH \rightarrow CH_4 + {}^\bullet CH_2C(CH_3)_2OOH \quad (4)$$

More insight into the reaction may be gained from the product distribution in samples containing *t*-BuOOH as a limiting reagent with variation of $[NiL^{2+}]$. At a lower excess of $[NiL^{2+}]$ (1 mM), methane and ethane were still produced. Acetone and *tert*-butyl alcohol were also found in solution. At high $[NiL^{2+}]$, on the other hand, the only detectable product was *tert*-butyl alcohol, indicating that NiL^{2+} intercepted and reduced *t*-BuO$^\bullet$ (eq 5).

$$t\text{-BuO}^\bullet + NiL^{2+} \rightarrow t\text{-BuOH} + \text{Ni product} \quad (5)$$

However, the final spectrum yielded the ratio $\Delta[NiL^{3+}]:\Delta[t\text{-BuOOH}] = 0.94:1$. Not even with the largest excess of NiL^{2+} used (0.05 M, limited by solubility) did the stoichiometry change to 2:1. Thus NiL^{3+} was apparently not produced in reaction 5.

The stoichiometry did, however, change to 1.7:1 in the presence of sulfate. Coordination of sulfate to $[Ni(Me_6cyclam)]^{3+}$ and $Ni(cyclam)^{3+}$ is known[20] to increase the thermodynamic and kinetic stability of the Ni^{III} ion. The reduction potential of the ion-coordinated couple is substantially lower than that of the corresponding aqua couple.[21] This could perhaps explain why the second molecule of nickel(III) was produced in the reaction of NiL^{2+} with *t*-BuO$^\bullet$ in the presence of sulfate but not in its absence. If the nickel(II) sulfate complexes are involved, then it is possible that the reaction with *t*-BuO$^\bullet$ takes place by outer-sphere electron transfer.[22] As such, the reaction mechanism would differ from that in the perchlorate medium, where it appears more probable that *t*-BuO$^\bullet$ attacks the macrocyclic ligand. Subsequent self-reactions of ligand-centered radicals then yield the final (unidentified) nickel products.

A very noticeable difference between samples containing NiL^{2+} as a limiting reagent and samples with NiL^{2+} in excess is the increase of the ratio $\Delta[NiL^{3+}]:\Delta$[limiting reagent] from 0.6 to approximately 1. Control experiments have shown that the (somewhat) reduced stability of NiL^{3+} in the presence of excess peroxide cannot account for the change in observed stoichiometry. The results can be explained by the side reaction of eq 6, where

$$NiL^{3+} + R^\bullet \xrightarrow{H_2O} NiL^{2+} + ROH \text{ (or } R_{-H}) + H^+ \quad (6)$$

$R = CH_3$ or C_2H_5. The trapping of the alkyl radical by the d^7 NiL^{3+} ion is expected to be a rapid reaction possibly yielding a transient alkylnickel complex, whose decomposition would produce the final products of eq 6. When the reaction is conducted in the presence of excess NiL^{2+}, reaction 6 does not take place because NiL^{2+} either intercepts alkoxyl radicals or reacts with alkyl radicals, ultimately re-forming NiL^{2+} and the radical self-reaction products.[23]

Laser flash photolysis was employed in search of direct experimental evidence for reaction 6 ($R = CH_3$). Methyl radicals were produced by photohomolysis of $CH_3Co([14]aneN_4)^{2+}$,[24] and the loss of NiL^{3+} was monitored at 360 nm. The results were inconclusive, however, because the slow decomposition of NiL^{3+} yielded sufficient amounts of NiL^{2+} to interfere with the observations.

Indirect support for reaction 6 comes from experiments conducted in the presence of O_2, an efficient scavenger for alkyl radicals (eq 7).[25] Under these conditions, the yield of NiL^{3+}

$${}^\bullet CH_3 + O_2 \rightarrow CH_3O_2^\bullet \quad (7)$$

improved substantially (>80%), supporting the notion that the alkyl radicals were responsible for the reduction of NiL^{3+} in the absence of O_2.

Another conceivable side reaction that would also lower the observed yields of NiL^{3+} is that between the alkoxyl radicals and NiL^{3+}. This can be ruled out easily by the observation that the yields of NiL^{3+} were comparable in the experiments with *t*-BuOOH and *t*-AmOOH. The two peroxides have virtually identical reactivities toward NiL^{2+}, but the rates of the β-scission of the two alkoxyl radicals differ greatly.[19a] The rate constant for $(CH_3)_3CO^\bullet$ is 1.4×10^6 s^{-1}, and that for $(CH_3)_2(C_2H_5)CO^\bullet$ is $\sim 10^8$ s^{-1}. The latter radical is in fact too short-lived to be able to participate in bimolecular reactions with low-concentration species such as NiL^{3+}.

Ionic Strength Dependence. Generally speaking, the rate of reactions of *t*-BuOOH with metal complexes should be ionic strength independent since the peroxide is uncharged.[26] The reaction under investigation thus presents a special case. NiL^{2+} exists in solution as a mixture of the planar tetracoordinated and octahedral hexacoordinated forms (eq 1). The distribution between the two forms is ionic strength (or anion) dependent,[13] and we believe this to be the source of the ionic strength dependence

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[18] (a) Wilkins, R. G.; Yelin, R.; Margerum, D. W.; Weatherburn, D. C. *J. Am. Chem. Soc.* **1969**, *91*, 4326. (b) Pell, R. J.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1983**, *22*, 529.

[19] (a) Erben-Russ, M.; Michael, C.; Bors, W.; Saran, M. *J. Phys. Chem.* **1987**, *91*, 2362. (b) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593. (c) Walling, C.; McGuinness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053.

[20] Zeigerson, E.; Ginsburg, G.; Schwartz, N.; Luz, Z.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1979**, 241.

[21] (a) Zeigerson, E.; Ginzburg, G.; Kirschenbaum, L. J.; Meyerstein, D. *Electroanal. Chem. Interfacial Electrochem.* **1981**, *127*, 113. (b) Zeigerson, E.; Bar, I.; Bernstein, J.; Kirschenbaum, L. J.; Meyerstein, D. *Inorg. Chem.* **1982**, *21*, 73.

[22] We thank a reviewer for this suggestion.

[23] Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4578.

[24] Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 3901.

[25] Thomas, J. K. *J. Phys. Chem.* **1967**, *71*, 1919.

[26] Katakis, D.; Gordon, G. *Mechanisms of Inorganic Reactions*; John Wiley & Sons: New York, 1987; pp 33–34.

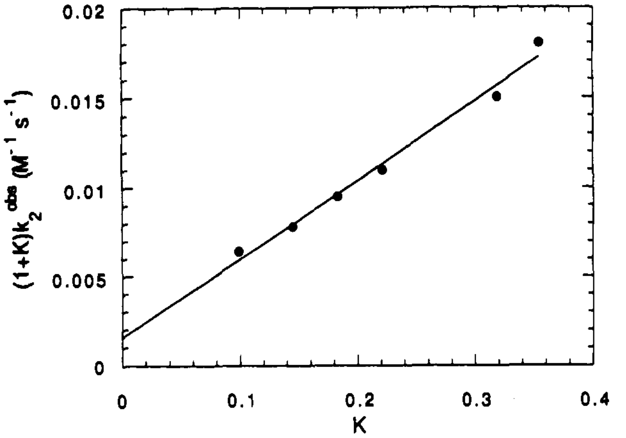

Figure 2. Plot of $(1 + K)k_2^{obs}$ as a function of K showing a linear relationship (T = 25 °C, μ = 0.1–2.0 M).

in the peroxide reactions. The equilibrium constant K was determined in this work as a function of ionic strength (Table I).

If the two forms have different reactivities toward the peroxides, then the rate law of eqs 8 and 9 applies, where $k_2(4)$ and $k_2(6)$

$$d[\mathrm{NiL}^{3+}]/dt = \frac{k_2(4) + k_2(6)\,K}{1+K}[\mathrm{NiL}^{2+}][t\text{-BuOOH}] \qquad (8)$$

$$k_2^{\mathrm{obs}} = \frac{k_2(4) + k_2(6)\,K}{1+K} \qquad (9)$$

represent the rate constants for the reactions of the four- and six-coordinate species, respectively. Thus, a plot of $(1 + K)k_2^{obs}$ vs K is expected to be linear with an intercept of $k_2(4)$ and a slope of $k_2(6)$. Figure 2 shows such a plot for the reaction of t-BuOOH with NiL^{2+} in the ionic strength range 0.1–2.0 M. The data yield $k_2(4) = (1.6 \pm 0.6) \times 10^{-3}$ M^{-1} s^{-1} and $k_2(6) = (4.4 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1}. The larger reactivity of the six-coordinate complex seems reasonable in view of the fact that the product NiL^{3+} is also a six-coordinate, octahedral species.

Experiments in the presence of Br^- provide additional support for the mechanism of eqs 2 and 3. *tert*-Butoxyl radicals are known to react efficiently with Br^- to form t-BuOH and Br_2 (eq 10).[27] Also, independent experiments showed that Br_2 rapidly oxidizes NiL^{2+} to NiL^{3+} (eq 11). Thus, if *tert*-butoxyl radicals are indeed

$$(\mathrm{CH_3})_3\mathrm{CO}^\bullet + \mathrm{Br}^- \rightarrow (\mathrm{CH_3})_3\mathrm{COH} + {}^1/_2\mathrm{Br_2} \qquad (10)$$

$${}^1/_2\mathrm{Br_2} + \mathrm{NiL}^{2+} \rightarrow \mathrm{Br}^- + \mathrm{NiL}^{3+} \qquad (11)$$

formed in the reaction of NiL^{2+} with t-BuOOH, the ratio $\Delta[NiL^{3+}]:\Delta$[limiting reagent] in the presence of Br^- should be 1:1 when NiL^{2+} is the limiting reagent and 2:1 when it is in excess. The experimental results were exactly as predicted. Also, consistent with the proposed scheme, no methane, ethane, or Br_3^- was produced.

As expected, bromide exhibited no effect on the stoichiometry or products in the reaction of *tert*-amyl hydroperoxide. This is again consistent with the rapid β-scission of *tert*-amyloxyl radicals, which renders the trapping with Br^- ineffective.

Effects of Alcohols. The decreased yield of NiL^{3+} in the presence of alcohols (methanol and 2-propanol) indicates that at least one reaction intermediate reacts with NiL^{3+}. We propose that this intermediate is the α-hydroxyalkyl radical derived from the alcohol. The following scheme can account for the observations:

$$\mathrm{R_2CHOH} + (\mathrm{CH_3})_3\mathrm{CO}^\bullet \rightarrow {}^\bullet\mathrm{CR_2OH} + (\mathrm{CH_3})_3\mathrm{COH} \qquad (12)$$

$$\mathrm{R_2CHOH} + {}^\bullet\mathrm{CH_3} \rightarrow {}^\bullet\mathrm{CR_2OH} + \mathrm{CH_4} \qquad (13)$$

$$\mathrm{NiL}^{3+} + {}^\bullet\mathrm{CR_2OH} \rightarrow \mathrm{NiL}^{2+} + \mathrm{R_2CO} + \mathrm{H}^+ \qquad (14)$$

Both t-BuO$^\bullet$ and $^\bullet CH_3$ are known[24,28] to react with alcohols by hydrogen atom abstraction (eqs 12 and 13). The reaction of eq 14 has not been studied directly, but it is almost certain that the strongly reducing α-hydroxyalkyl radicals will rapidly reduce NiL^{3+} as shown.

To distinguish between reactions 12 and 13 as the source of α-hydroxyalkyl radicals, experiments were performed with deuterated 2-propanol. They produced CH_3D, which clearly implicates methyl radicals, i.e. reaction 13, although this result does not rule out the participation of reaction 12 as well. Another result demonstrates that both reactions 12 and 13 take place. Ethane is almost completely eliminated as a product (no methyl radical self-reaction), and the yield of methane (CH_3D in the case of $(CD_3)_2CDOH$) is reduced compared to that in the experiments in the absence of alcohol. If reaction 12 were the only source of $^\bullet CR_2OH$, then both hydrocarbon products would have been eliminated and replaced by t-BuOH. The formation of some methane confirms that reaction 13 takes place, but the diminished yield indicates that some t-BuO$^\bullet$ was also scavenged, presumably in reaction 12. Finally, alcohols have a (limited) effect on the reaction of *tert*-amyl hydroperoxide as well. Considering again the rates of β-scission, one has to conclude that ethyl radicals are the main source of $^\bullet CR_2OH$, by a reaction analogous to eq 13. The fact that $^\bullet CH_3$ is responsible for the formation of some $^\bullet CR_2OH$ should not be surprising, despite the fact that alkyl radicals react with alcohols much more slowly than the alkoxy radicals do. The rapid competitive β-scission rules out most of the bimolecular reactions even for t-BuO$^\bullet$. The rate constant for the reaction of t-BuO$^\bullet$ with 2-propanol is ~5 × 10^6 M^{-1} s^{-1}.[29] Thus, even in 4 M 2-propanol, the reaction with the alcohol is not quantiative and some β-scission will take place. In deuterated solvents, the relative importance of β-scission will be even greater owing to the kinetic isotope effect on H-abstraction.

Reactions of NiL^{2+} with H_2O_2. A preliminary study using excess hydrogen peroxide showed that the reaction product was not the expected NiL^{3+}. Instead, a stable pink species was produced. In the sulfate medium, the nickel(III) complex was first formed, but it too decayed to yield the pink species. While our work was in progress, McAuley and co-workers identified this species as a binuclear complex of the highly oxidized macrocyclic ligand.[30]

Except for the difference in final products, many similarities exist between the reactions of NiL^{2+} with alkyl hydroperoxides and hydrogen peroxide. With NiL^{2+} in large excess, the reaction with H_2O_2 produced NiL^{3+} in a reaction with a 1:1 stoichiometry. The bromide effect was also observed. The ratio $\Delta[NiL^{3+}]:\Delta[NiL^{2+}]$ (excess H_2O_2) was 1:1, and $\Delta[NiL^{3+}]:\Delta[H_2O_2]$ (excess NiL^{2+}) was 2:1. With H_2O_2 in excess in the presence of 2-propanol, no NiL^{3+} or pink species was formed, consistent with reactions 15 and 16 taking place.

On the basis of observations, we propose that H_2O_2 also reacts with NiL^{2+} by a Fenton-type mechanism. The difference in products at high concentrations of peroxide may simply be a

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(27) Ma, R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1992**, *31*, 1925.

(28) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.

(29) Calculated for aqueous solutions from the value for β-scission in ref 18a ($k = 1.4 \times 10^6$ s^{-1}) and the relative rate ratios for β-scission and H-abstraction: Gilbert, B. C.; Marshall, P. D. R.; Norman, R. O. C.; Pineda, N.; Williams, P. S. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1392. The directly measured value in a 1:2 mixture of benzene and di-*tert*-butyl peroxide is 1.8 × 10^6 s^{-1}: Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

(30) McAuley, A.; Xu, C. Submitted for publication.

$$\mathrm{HC(CH_3)_2OH + {}^{\bullet}OH \rightarrow {}^{\bullet}C(CH_3)_2OH + H_2O} \quad (15)$$

$$\mathrm{{}^{\bullet}C(CH_3)_2OH + NiL^{3+} \rightarrow (CH_3)_2CO + NiL^{2+} + H^+} \quad (16)$$

result of $OH^{\bullet}$ being an extremely potent hydrogen atom abstracting reagent, which leads to the formation of a highly unsaturated (oxidized) product.

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