of water, such as occurs slowly in alkaline permanganate solutions, may be disregarded, since in ethanolic media this would initiate the chain reduction of ferrate(VI) via OH and alcohol radicals, which is not observed during pulse-radiolysis experiments. In the more likely case that hydrogen peroxide is formed from oxide ligands of iron, the rate-limiting step would involve hydration of iron(V) followed by the reductive elimination of peroxide from cis oxide or hydroxide ligands as suggested in Scheme II.

Scheme II

$$FeO_4^{3-} + 2H_2O \xrightarrow{\text{slow}} Fe^V(OH)_4(O)_2^{3-} \xrightarrow{\text{fast}} [Fe^{III}(OH)_4(O_2^{2-})]^{3-} \quad (10)$$

The degree of hydrolysis for an octahedral iron(V) species is unknown, but it is probably extensive for the high oxidation state in alkaline solution. Cis oxide ligands are found, for instance, in the pentavalent vanadium ion, $VO_2(H_2O)_4^+$.[22d] The product, ferric-bound peroxide, could form directly, without dissociation of an Fe^VO ligand bond, if the peroxide moiety is bound in a side-on mode as it is in the $Fe^{III}EDTA(O_2^{2-})^{3-}$ complex.[28]

The chemistry of iron(V) is virtually unknown, but the present study suggests that its stability may be enhanced in aprotic and weakly coordinating solvents where both of its known decay modes are likely to be inhibited. Efforts are currently in progress to prepare iron(V) under conditions that will permit more detailed studies of its properties.

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Effect of Steric Crowding on the Rates of Reactions of a Nickel(I) Tetraaza Macrocycle with Organic Halides and Hydroperoxides

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The reactions of the sterically crowded decamethylcyclam complex of nickel(I), $Ni(dmc)^+$, with organic halides, hydrogen peroxide, and *tert*-butyl hydroperoxide occur some 10^4 times more slowly than the corresponding reactions of $Ni(tmc)^+$, a tetramethylcyclam complex. This supports the assignment of an inner-sphere mechanism in both cases, because reactions that necessarily adopt an outer-sphere mechanism (e.g., those of cobalt(III) amine complexes) differ no more in their relative rates than can easily be explained by the small difference in driving force.

Introduction

Significant progress has been made in recent years in understanding the chemistry of macrocyclic complexes of Ni(II) and Ni(I). The most extensively studied of these complexes are those containing the 1,4,8,11-tetraazacyclotetradecane (cyclam) ligand as well as the N-alkylated and C-alkylated derivatives.[2-5] Among these are tetramethylated (tmc) and decamethylated (dmc) macrocycles.

It has been established that these Ni(II) macrocycles can be reduced electrochemically[6] or photochemically[7] to generate reasonably stable Ni(I) complexes in aqueous solutions. This provides the opportunity for investigations of the reduction of alkyl halides by Ni(I) to be carried out.

The oxidation of two isomeric forms of Ni(tetramethylcyclam)$^+$, abbreviated $Ni(tmc)^+$, by alkyl halides and hydroperoxides has been investigated recently.[7-12] The reactions were proposed to occur in two steps:

$$Ni(tmc)^+ + RX \xrightarrow{\text{rds}} Ni(tmc)^{2+} + X^- + R^\bullet \quad (1)$$

$$Ni(tmc)^+ + R^\bullet \rightarrow RNi(tmc)^+ \quad (2)$$

Electron transfer in the rate-determining step can occur by either an inner-sphere (eq 3) or an outer-sphere mechanism (eq 4).

$$\begin{tikzcd} Ni(tmc)^+ + RX \arrow[r] & XNi(tmc)^+ + R^\bullet \arrow[d, shift left] & (3) \\ & X^- + Ni(tmc)^{2+} \arrow[u, shift left] & \end{tikzcd}$$

$$\begin{tikzcd} Ni(tmc)^+ + RX \arrow[r] & Ni(tmc)^{2+} + RX^{-\bullet} \arrow[d, shift left] & (4) \\ & X^- + R^\bullet \arrow[u, shift left] & \end{tikzcd}$$

A distinction between the two mechanisms is a difficult one to make owing to the lability of $Ni(tmc)^{2+}$ to axial substitution. The reactivity pattern for a series of alkyl halides, i.e. $CH_3 <$ primary < secondary < benzyl and $Cl^- < Br^- < I^-$, is similar to that observed in corresponding reactions of Co(II)[13] and Cr(II).[14] The latter reactions are known to proceed by an inner-sphere mechanism, and thus one might be tempted to conclude that the reactions of $Ni(tmc)^+$ adopt the same mechanism. This argument needs to be further substantiated by other evidence. It was against this background that we undertook the present study with the

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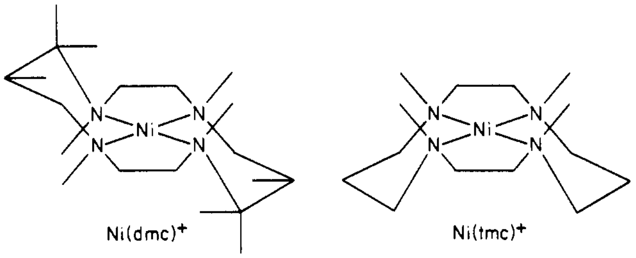

Figure 1. Structural formulas of (a) Ni(dmc) and (b) *R,R,S,S*-Ni(tmc).

Table I. Second-Order Rate Constants for the Reactions of $Ni(dmc)^+$ and $Ni(tmc)^+$ with Co(III) Complexes

complex	$k_{dmc}{}^a$/mol^{-1} dm^3 s^{-1}	$k_{tmc}{}^a$/mol^{-1} dm^3 s^{-1}	k_{tmc}/k_{dmc}
$Co(NH_3)_6{}^{3+}$	6.32×10^3 $1.7 \times 10^{4\,b}$	3.0×10^4 $8.0 \times 10^{5\,b}$	4.7
$Co(en)_3{}^{3+}$	2.37×10^3	9.0×10^3	3.8
$Co(sep)^{3+}$	9.59×10^3	7.2×10^4	7.5
$Co(NH_3)_5F^{2+}$	6.0×10^3		

[a] In aqueous solution at 25.0 °C, 0.1 M NaOH. [b] From ref 6.

((1*R*,4*R*,8*S*,11*S*)-*C-meso*-1,4,5,5,7,8,11,12,12,14-decamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I) complex ($Ni(dmc)^+$, Figure 1) and some alkyl halides and peroxides.

The reducing power of $Ni(dmc)^+$, $E° = -0.74$ V,[6] is similar to those of *R,R,S,S*-$Ni(tmc)^+$ (−0.91 V)[6] and *R,S,R,S*-$Ni(tmc)^+$ (−0.87 V).[11] The self-exchange rate constants are also comparable for the three complexes.[6,15] $Ni(dmc)^+$ is, however, considerably bulkier than either of the two tmc complexes. Inner-sphere reactions should thus strongly disfavor $Ni(dmc)^+$, whereas the reactivity of the three complexes in outer-sphere reactions should be comparable.

This paper reports our findings on the reactions of $Ni(dmc)^+$ with several inner-sphere and outer-sphere oxidants.

Experimental Section

Reagents. The *meso*-5,5,7,12,12,14-hexamethylcyclam ligand was prepared according to the published procedure.[16] $Ni(dmc)(ClO_4)_2$ was pepared according to the method of Wagner and Barefield.[3] The trifluoromethanesulfonate (triflate) salt was prepared in solution from the perchlorate by anion exchange (Amberlite IRA-400 or Dowex 2-X8). $Ni(dmc)^+$ was prepared by electrochemical reduction of aqueous $Ni(dmc)(CF_3SO_3)_2$ at −1.70 V vs SCE at a mercury-pool cathode. $Ni(dmc)^+$ was also obtained by reduction of $Ni(dmc)^{2+}$ with the photochemically generated $^{\bullet}C(CH_3)_2OH$.[7] *R,S,R,S*-$Ni(tmc)^+$ (hereafter $Ni(tmc)^+$) was prepared and used as described previously.[11]

Reaction Conditions. All experiments were performed under air-free conditions utilizing an argon atmosphere and syringe–septa methods. All reactions were carried out with limiting concentrations of $Ni(dmc)^+$ under pseudo-first-order conditions. The kinetics were monitored at an absorption maximum of $Ni(dmc)^+$ at 335 nm ($\epsilon = 3600$ M^{-1} cm^{-1}). Ionic strength was maintained with NaOH or Na_2SO_4, and temperature was controlled at 25.0 ± 0.1 °C by a constant-temperature bath.

Kinetics. Kinetic data were obtained by using either a Canterbury SF-3A stopped-flow or a Cary 219 spectrophotometer. The former is interfaced with an OLIS 3820 data acquisition and numerical analysis system.

Product Analysis. Organic products were identified by use of a Hewlett-Packard Model 5790 gas chromatograph. The retention times were checked with appropriate standards. Free bromide, produced in the reaction of $Ni(dmc)^+$ with $PhCH_2Br$, was determined by HPLC with a $-NR_3{}^+$ stationary phase. The yields were quantitative, confirming that the axial positions in $Ni(dmc)^{2+}$ are substitutionally labile.

Results and Discussion

Reactions with Cobalt(III) Complexes. $Ni(dmc)^+$ reduces $Co(NH_3)_6{}^{3+}$, $Co(en)_3{}^{3+}$, and $Co(sep)^{3+}$ in aqueous alkaline solutions. The pseudo-first-order rate constants for these reactions vary linearly with the concentration of the Co(III) complex as illustrated in Figure 2. Spectrophotometric titrations indicate a 1:1 stoichiometry, which supports the net reaction given in eq 5. This is consistent with a rate expression of the form (6). The

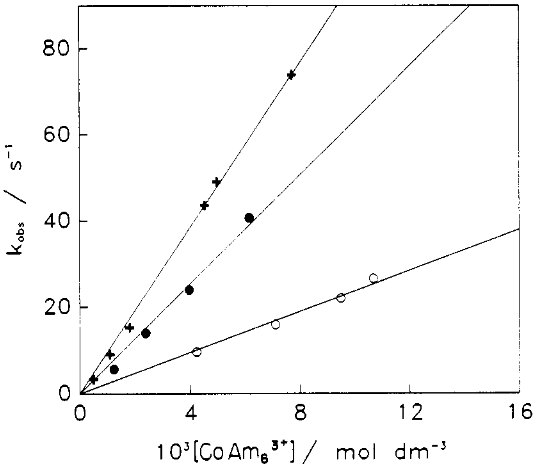

Figure 2. Kinetic data for reactions between the $Ni(dmc)^+$ and $Co(Am)_6{}^{3+}$ complexes. Data are shown for $Co(sep)^{3+}$ (crosses), $Co(en)_3{}^{3+}$ (open circles), and $Co(NH_3)_6{}^{3+}$ (filled circles).

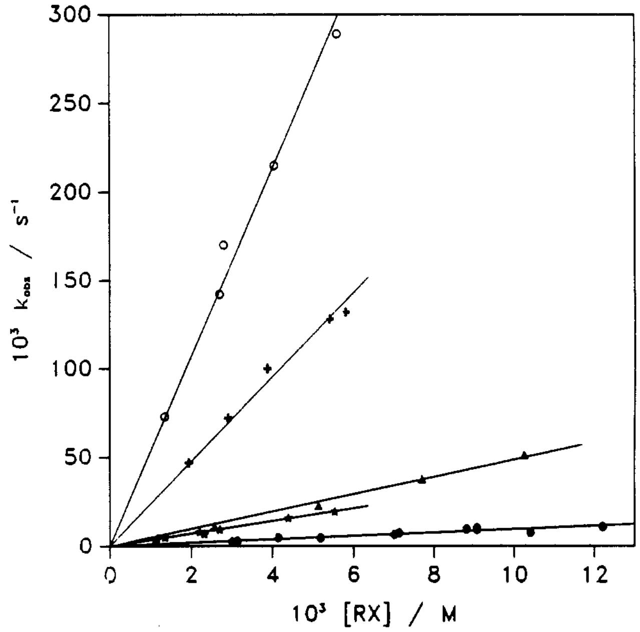

Figure 3. Kinetic data for reactions between $Ni(dmc)^+$ and some organic halides. Data are shown for benzyl bromide (open circles), allyl bromide (crosses), dibromomethane (triangles), benzyl chloride (stars), and dibromoethane (filled circles).

$$CoAm_6{}^{3+} + Ni(dmc)^+ \rightarrow CoAm_6{}^{2+} + Ni(dmc)^{2+} \quad (5)$$

$$-d[Ni(dmc)^+]/dt = k[Ni(dmc)^+][CoAm_6{}^{3+}] \quad (6)$$

values of k obtained for the Co(III) complexes studied are shown in Table I, along with results obtained for similar reactions with the $Ni(tmc)^+$ complex. From the results shown it is evident that the differences in reactivity between $Ni(tmc)^+$ and $Ni(dmc)^+$ are not very dramatic. $Ni(tmc)^+$ reacts more rapidly by a factor of only 4–8. This increase can be linked to the fact that the reduction potential of $Ni(tmc)^+$ is more negative than that of $Ni(dmc)^+$. The reduction of these Co(III) complexes by Ni(I) can proceed only by an outer-sphere mechanism. The rate constant we obtained for the reaction of $Co(NH_3)_6{}^{3+}$ and $Ni(dmc)^+$ is significantly lower than that obtained by pulse radiolysis by Jubran et al.[6] We have no explanation for this discrepancy.

Reactions with Organic Halides. The pseudo-first-order rate constants for these reactions vary linearly with the concentration of the excess reagent (Figure 3). Spectrophotometric titrations

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(15) The self-exchange rate constant for *R,S,R,S*-$Ni(tmc)^{2+/+}$ has not been reported, but it is reasonable to expect it to be similar to that of the *R,R,S,S* isomer.

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Table II. Second-Order Rate Constants for the Reaction of $Ni(dmc)^+$ with Alkyl Halides and Hydroperoxides

reactant	k_{dmc}/mol^{-1} dm^3 s^{-1} [a]	k_{tmc}[e]/mol^{-1} dm^3 s^{-1}	k_{tmc}/k_{dmc}
H_2O_2	5.1×10^2 [b]	1.6×10^7	3×10^4
$(CH_3)_3COOH$	27[b]	3.8×10^5	10^4
$Br(CH_2)_2Br$	0.48[c]	$>2 \times 10^5$	10^5
$C_6H_5CH_2Br$	52[d]	$>10^7$	10^5
$C_6H_5CH_2Cl$	3.6[c]	$\sim10^6$	10^5
$CH_2{=}CHCH_2Br$	12[c]	$\sim10^5$	10^3
Br_2CH_2	2.4[c]	$>10^5$	10^4

[a] The values listed for H_2O_2 and the dihaloalkanes are $k_{obsd}/2$ to account for the 2:1 stoichiometry; see text. All the other values are the measured rate constants, k_{obsd}. [b] In aqueous 0.035 M Na_2SO_4. [c] In aqueous acetone (3 M), with 2-propanol (1 M) and 0.1 M Na_2SO_4. [d] In aqueous CH_3CN (6 M), with 0.035 M Na_2SO_4. [e] From ref 6–10.

established a 1:1 stoichiometry for the reactions with benzyl bromide and allyl bromide. In these cases the observed organic products are bibenzyl and 1,5-hexadiene, respectively, formed by dimerization of the radicals (eq 7 and 8). Toluene, the predicted

$$Ni(dmc)^+ + RX \rightarrow Ni(dmc)^{2+} + R^\bullet + X^- \quad (7)$$

$$2R^\bullet \rightarrow R_2 \quad (8)$$

product of the reduction of benzyl radicals by $Ni(dmc)^+$, was not observed in the reaction with benzyl bromide. A small amount of propene, corresponding to the reduction of the allyl radical, was found in the reaction with allyl bromide. The values of k_7 are listed in Table II.

The reaction of $Ni(dmc)^+$ with dibromoethane produces only ethylene, as was the case for the reaction of $Ni(tmc)^+$.[10] Dibromomethane reacts to give CH_3Br as the major organic product, implying that the $^\bullet CH_2Br$ radical oxidizes $Ni(dmc)^+$ more rapidly than it dimerizes to $BrCH_2CH_2Br$ (eq 9 and 10). Thus, under the experimental conditions (excess Br_2CH_2), $k_{obsd} = 2k_9$.

$$Ni(dmc)^+ + Br_2CH_2 \rightarrow Ni(dmc)^{2+} + {}^\bullet CH_2Br + Br^- \quad (9)$$

$$Ni(dmc)^+ + {}^\bullet CH_2Br + H_2O \rightarrow Ni(dmc)^{2+} + CH_3Br + OH^- \quad (10)$$

Small amounts of methane, ethane, and ethylene were also observed. They seem to be formed in side reactions involving halogen transfer from the $BrCH_2^\bullet$ radical to $Ni(dmc)^+$ to form methylene, followed by reduction and dimerization steps. Similar chemistry has been proposed earlier in the reactions of Cr^{2+} with polyhalomethanes in dmf/H_2O,[17,18] although the involvement of dinuclear intermediates in that system cannot be ruled out.[19,20] In the present case we cannot completely exclude the possibility that CH_4 was formed by reduction of trace amounts of $BrCH_2Ni(dmc)^+$ by $Ni(dmc)^+$, although no spectral evidence was obtained for such an organonickel intermediate.

The reaction with hydrogen peroxide takes place with a 2:1 stoichiometry (eq 11) according to the rate law of eq 12, where

$$2Ni(dmc)^+ + H_2O_2 \rightarrow 2Ni(dmc)^{2+} + 2OH^- \quad (11)$$

$$-d[Ni(dmc)^+]/dt = k_{obsd}[Ni(dmc)^+][H_2O_2]_T \quad (12)$$

$[H_2O_2]_T$ represents the total concentration of hydrogen peroxide. The value of k_{obsd} is 1020 M^{-1} s^{-1} in the pH range 3–9[21] (Figure 4), but it decreases dramatically as the pH is raised above 11. Equation 13 describes the variation of k_{obsd} with $[H^+]$. The

$$k_{obsd} = \frac{k[H^+][H_2O_2]_T}{[H^+] + K_a} \quad (13)$$

reported value of K_a, the acid dissociation constant of H_2O_2, is 2.24×10^{-12} M.[22]

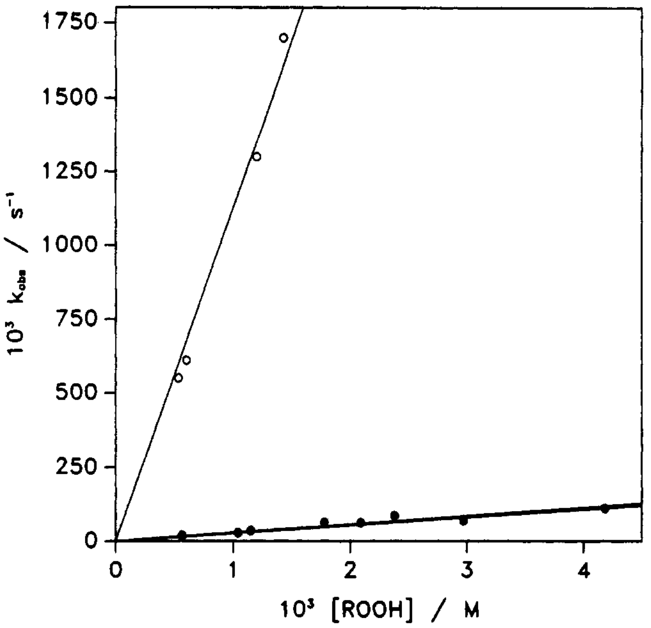

Figure 4. Kinetic data for reactions of $Ni(dmc)^+$ with hydrogen peroxide (open circles) and *tert*-butyl hydroperoxide (filled circles).

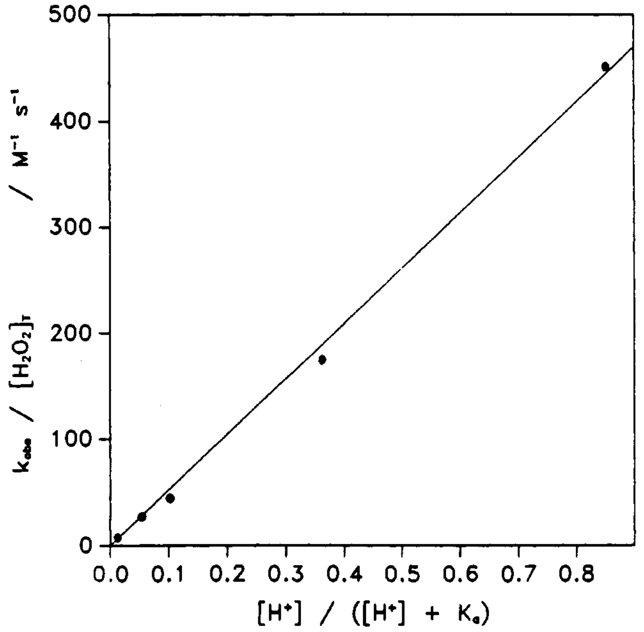

Figure 5. Dependence of the apparent second-order rate constant, $k_{obs}/[H_2O_2]_T$ on $[H^+]/(K_a + [H^+])$, suggested by eq 13.

Equation 13 indicates that H_2O_2 is the only reactive form of hydrogen peroxide. The same conclusion was reached earlier in the reactions with $Co(CN)_5^{3-}$,[23] $Cr(CN)_6^{4-}$,[24] and $Cr(CN)_5H_2O^{3-}$.[24] A plot suggested by eq 13 is shown in Figure 5 for the data obtained in alkaline solutions. The slope of the line is 520 M^{-1} s^{-1}. This value is within a factor of 2 of the rate constant obtained under the pH conditions where H_2O_2 is the dominant peroxide species present. Although not perfect, the agreement is considered satisfactory, given the wide pH range employed. It should be noted that $Ni(dmc)^+$ does not participate in any known acid–base equilibria.

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Kinetics experiments were also performed for the reaction of $Ni(tmc)^+$ with H_2O_2, values of k_{obsd} being determined as a function of $[H_2O_2]$ (0.15–0.60 mM) and $[OH^-]$ (0.035–0.11 M). The data also agree with eq 12 and 13 and yield the second-order rate constant for the reaction between $Ni(tmc)^+$ and H_2O_2 of $1.6 \times 10^7\ M^{-1}\ s^{-1}$.

Low-valent transition-metal complexes usually react with H_2O_2 in two one-electron steps. The sequence of reactions is shown for $Ni(dmc)^+$ in eq 14 and 15.[25] Irrespective of the nature of the reactive intermediate (hydroxyl radical or $Ni(dmc)H_2O_2^+$) formed in reaction 14, the rate constant k_{obsd}, obtained in the presence of an excess of H_2O_2, equals $2k_{14}$.

$$Ni(dmc)^+ + H_2O_2 \rightarrow Ni(dmc)OH^+ + OH^\bullet \text{ (or } Ni(dmc)H_2O_2^+) \quad (14)$$

$$Ni(dmc)^+ + OH^\bullet \rightarrow Ni(dmc)OH^+ \quad (15a)$$

$$Ni(dmc)H_2O_2^+ + Ni(dmc)^+ \rightarrow 2Ni(dmc)OH^+ \quad (15b)$$

In an attempt to distinguish between the two intermediates, a spectrophotometric titration of $Ni(dmc)^+$ with H_2O_2 was conducted in the presence of added 2-propanol and (in a separate experiment) HCOONa. Both of these solutes react rapidly with $OH^\bullet$[26] to give the strongly reducing radicals $C(CH_3)_2OH^\bullet/C(CH_3)_2O^{\bullet-}$ (pK_a 12.2)[27] and $CO_2^{\bullet-}$, respectively. The reduction of $Ni(dmc)^{2+}$ by $CO_2^{\bullet-}$ takes place with a rate constant of $4 \times 10^6\ M^{-1}\ s^{-1}$ (eq 16).[6] Thus, the addition of 2-propanol or sodium formate to the reaction solutions should change the stoichiometry from 2:1 to ≪2:1, since reaction 16 regenerates the $Ni(dmc)^+$ consumed in reaction 14. The exact stoichiometry is determined by the competition between reaction 16 and self-reactions of the radicals (eq 17). In the presence of an added excess of $Ni(dmc)^{2+}$, reaction 16 would dominate and no net consumption of $Ni(dmc)^+$ should take place. Instead, $Ni(dmc)^+$ would act as a catalyst for the reduction of H_2O_2 by the organic solute.

$$Ni(dmc)^{2+} + CO_2^{\bullet-} \rightarrow Ni(dmc)^+ + CO_2 \quad (16)$$

$$2C(CH_3)_2OH^\bullet \text{ (or } 2CO_2^{\bullet-}) \rightarrow \text{products} \quad (17)$$

The addition of 1 M 2-propanol or 1 M HCOONa to solutions of 2×10^{-4} M $Ni(dmc)^+$ had only a minor effect on the overall stoichiometry of the reaction with H_2O_2. At pH 7 a $[Ni(dmc)^+]/[H_2O_2]$ ratio of 1.3 was obtained for both scavengers. The addition of 7 mM $Ni(dmc)^{2+}$ had no additional effect. A titration at pH 12 in the presence of 1 M 2-propanol yielded a 1:1 stoichiometric ratio. If the free OH radicals were formed in reaction 14, one would expect ratios of 0.5 and 5×10^{-5} in the absence and presence of added $Ni(dmc)^{2+}$, respectively, in 1 M 2-PrOH at pH 7 and a ratio of 0.05 in 1 M HCOONa in the absence of added $Ni(dmc)^{2+}$. It thus seems safe to conclude that reaction 14 produces no free hydroxyl radicals.

***tert*-Butyl hydroperoxide** reacts with $Ni(dmc)^+$ much more slowly than H_2O_2 does, presumably because of unfavorable steric interactions. Organic products were identified as CH_4, C_2H_6, acetone, and *tert*-butyl alcohol. A spectrophotometric titration yielded a $[Ni(dmc)^+]/[ROOH]$ ratio of 1.2. Both the products and the fractional stoichiometry are consistent with the rate-determining formation of $(CH_3)_3CO^\bullet$, followed by β-scission (eq 18 and 19). The methyl radical then dimerizes to ethane (eq 20) or is reduced to methane by $Ni(dmc)^+$ (eq 21). *tert*-Butyl alcohol is probably formed by direct reduction of $(CH_3)_3CO^\bullet$ by $Ni(dmc)^+$.

$$Ni(dmc)^+ + (CH_3)_3COOH \rightarrow Ni(dmc)^{2+} + (CH_3)_3CO^\bullet + OH^- \quad (18)$$

$$(CH_3)_3CO^\bullet \rightarrow CH_3^\bullet + (CH_3)_2CO \quad (19)$$

$$2CH_3^\bullet \rightarrow C_2H_6 \quad (20)$$

$$Ni(dmc)^+ + CH_3^\bullet + H^+ \rightarrow Ni(dmc)^{2+} + CH_4 \quad (21)$$

The involvement of $(CH_3)_3CO^\bullet$ radicals was further confirmed by a spectrophotometric titration in the presence of 6 M 2-propanol. The high concentration of the alcohol was necessary to scavenge most of the $(CH_3)_3CO^\bullet$ before it underwent β-scission. The ratio obtained under these conditions at pH 7, $[Ni(dmc)^+]/[ROOH] = 0.6$, is quite close to the expected value of 0.5. An identical titration at pH 12 yielded a curved titration plot with the equivalence point approaching 0.2. This value seems reasonable, although the exact ratio cannot be calculated, since the rate constant for the reaction of $C(CH_3)_2O^{\bullet-}$ with $Ni(dmc)^{2+}$ has not been measured.

A summary of the rate constants for the reactions of $Ni(dmc)^+$ and $Ni(tmc)^+$ with the peroxides and the alkyl halides is given in Table II. Saturated alkyl halides react readily with $Ni(tmc)^+$,[7,11] but the corresponding $Ni(dmc)^+$ reactions are too slow to measure ($k < \sim 10^{-2}\ M^{-1}\ s^{-1}$), given the inherent slow loss of $Ni(dmc)^+$ over time. At the other end of the reactivity scale, the benzyl and allyl halides react measurably with $Ni(dmc)^+$, but with $Ni(tmc)^+$ the reactions occur too rapidly for other than order of magnitude estimates. Thus, relatively few precise reactivity ratios can be cited. It is quite apparent, however, that in each case $k_{tmc} \gg k_{dmc}$. The difference in reactivity between the two nickel complexes is quite striking. This is almost certainly linked to the bulkiness of the dmc ligand, which quite effectively blocks the metal center and drastically reduces the reactivity of the complex in inner-sphere reactions.

Conclusion. Co(III) amine complexes are reduced in aqueous solution by $Ni(dmc)^+$ in an outer-sphere electron-transfer reaction. The rate constants for these reactions do not vary greatly from those obtained with $Ni(tmc)^+$. The reduction of alkyl halides by $Ni(dmc)^+$ results in the formation of alkyl radicals that can react further with $Ni(dmc)^+$ or dimerize. These reactions are strongly disfavored for the $Ni(dmc)^+$ complex. The trend, shown in Table II, is very supportive of an inner-sphere electron-transfer mechanism for the reactions of alkyl halides and peroxides with both nickel(I) complexes.

Were reactions of both complexes occurring by an outer-sphere mechanism, the rate constants would be expected to be comparable as they are for the fully ligated cobalt complexes. We thus rule out that situation. We next consider the cases tmc(IS)–dmc(OS) and tmc(IS)–dmc(IS). Both are feasible, but we are less inclined to accept the former. Not only would a change in mechanism be entailed, but it would suggest an OS mechanism for H_2O_2 and *t*-BuOOH. Outer-sphere reduction of these peroxides is extremely rare, if not unknown entirely.[29] The fact that $Ni(dmc)^+$ reacts at all appears to us as strong evidence for an IS mechanism for its reactions with peroxides.

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Registry No. $Ni(dmc)^+$, 84026-55-1; $Ni(tmc)^+$, 103364-89-2; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(sep)^{3+}$, 63976-36-3; $Co(NH_3)_5F^{2+}$, 15392-06-0; H_2O_2, 7722-84-1; $(CH_3)_3COOH$, 75-91-2; $Br(CH_2)_2Br$, 106-93-4; $C_6H_5CH_2Br$, 100-39-0; $C_6H_5CH_2Cl$, 100-44-7; $CH_2{=}CHCH_2Br$, 106-95-6; Br_2CH_2, 74-95-3.

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