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Formation and Homolysis of Organonickel(III) Complexes

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Abstract: The reactions of Ni(1,4,8,11-tetraazacyclotetradecane)$^{2+}$ with alkyl radicals were studied. Data were collected for the *R,R,S,S* (or β) and *R,R,R,R* (or α) isomers. The reactions form σ-bonded organometallic cations, as in the equation $NiL^{2+} + R^\bullet + H_2O \rightleftarrows RNiL(H_2O)^{2+}$. The values of the rate constants for the forward (colligation) and reverse (homolysis) reactions were measured separately by laser flash photolysis techniques with a kinetic probe. The values of k_{col} lie in the order $CH_3 \gg$ primary $\gg$ secondary, and just the reverse order applies to k_{hom}. Thus the equilibrium constants for formation of $RNiL(H_2O)^{2+}$, given by k_{col}/k_{hom}, are most favorable for methyl and least favorable for secondary alkyls. These nickel–alkyl bonds are much weaker than those in corresponding cobalt and chromium complexes. For that reason, values of k_{col} vary widely with the nature of $R^\bullet$. Values of k_{col} are considerably higher for α-Ni(cyclam)$^{2+}$ than for the β isomer, and the reverse order applies to k_{hom}. Also, the α isomer has the highest equilibrium constant for the formation equilibrium. The kinetic and thermodynamic trends can be rationalized by structural effects.

Introduction

Organonickel intermediates of the nickel-containing N_4 macrocycle factor F430 may be involved during the reduction of carbon dioxide to methane. The occurrence of organonickel complexes of simple, synthetic N_4 macrocycles has been little studied, however, and so we undertook studies to prepare a family of such complexes and examine their reactivity.

Studies of the formation and dissociation rates of σ-bonded metal alkyl complexes in solution have largely been limited to the relatively stable cobalt(III) and chromium(III) complexes such as $RCo^{III}(N_4\ macrocycle)^{n+}$ (including vitamin B_{12} derivatives) and $(H_2O)_5Cr^{III}{-}R^{2+}$. Attempts to describe the analogous chemistry in other systems have been hampered because the organometallic species are less stable thermodynamically and more labile kinetically.

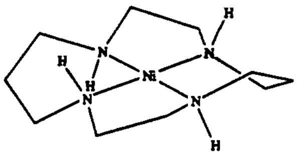
This was the case with alkylnickel complexes until the recent discovery that the formation (colligation[1]) and decomposition (homolysis) rates of $CH_3Ni(cyclam)(H_2O)^{2+}$ (cyclam = [14]-aneN_4 = 1,4,8,11-tetraazacyclotetradecane) could be measured by pulse radiolysis.[2] This method is largely limited to R = CH_3, since most other alkyl radicals cannot readily be generated pulse radiolytically.

We have now found that Ni(cyclam)$^{2+}$ reacts with a number of alkyl radicals in a similarly reversible equilibrium. We thus undertook studies that used laser flash photolysis techniques to evaluate the rate law and kinetic constants. The reactions occurring are represented by the equation

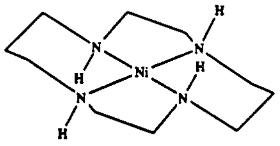
$$R^\bullet + Ni(cyclam)^{2+} + H_2O \rightleftarrows RNi(cyclam)(H_2O)^{2+} \quad k_{col}, k_{hom} \quad (1)$$

Our goal was to measure the rate constants for the forward (colligation) and reverse (homolysis) reactions and to evaluate the equilibrium constant K_1 ($=k_{col}/k_{hom}$). In particular, we wished to understand any change or trend in these values with the nature of the R group. It should be noted that this is the first series of nickel complexes for which such kinetic and thermodynamic data are available. Also, no cobalt or chromium series is as complete, in that homolysis rates of the primary alkyl complexes of these metals have usually been too small for evaluation.

Two isomeric forms of planar Ni(cyclam)$^{2+}$ were used in the investigation. They are the *R,R,S,S* and *R,R,R,R* isomers, also known as trans-III and trans-V, or β and α isomers, respectively. We anticipated chemistry that is qualitatively the same, although we did expect quantitative differences in kinetics and thermodynamics. Indeed, an additional goal of this research was to evaluate such differences and to account for them in a fundamental way.



α-Ni(cyclam)$^{2+}$



β-Ni(cyclam)$^{2+}$

Experimental Section

Reagents. The following compounds were prepared by literature methods: $[RCo(dmgH)_2(py)]$[3] ($dmgH^-$ is the monoanion of butanedione dioxime), $[RCo(cyclam)(H_2O)](ClO_4)_2$[4] (cyclam = 1,4,8,11-tetraazacyclotetradecane), *R,R,S,S*- (or β-) $[Ni(cyclam)](ClO_4)_2$,[5] and *cis*-$[Ni(cyclam)(en)](ClO_4)_2$.[6] To remove any unconverted β-Ni(cyclam)$^{2+}$ from the last complex, the precipitate was washed several times with an ice-cold 2% aqueous solution of ethylenediamine and then with ether. The product was dried in a vacuum desiccator. Stock solutions of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ were prepared by dissolving the salt in aqueous perchloric or sulfuric acid at pH 2–3, where the cis–trans isomerization is the slowest.[6] These solutions remain unchanged for several days at 0 °C. The absorption spectra of *cis*-Ni(cyclam)(en)$^{2+}$ and *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ agreed with the values reported.[6] The planar isomer α-Ni(cyclam)$^{2+}$ was obtained from *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ by increasing the perchlorate concentration to 6.0 M (5.9 M $NaClO_4$, 0.1 M $HClO_4$). In this medium, 20.2% of the nickel complex exists as the α isomer and the balance as *cis*-Ni(cyclam)$(H_2O)_2^{2+}$, as calculated from the molar absorptivities, $\epsilon_\alpha = 100$ L mol^{-1} cm^{-1} and $\epsilon_{cis} = 0.7$ L cm^{-1} at 450 nm.[7]

The salt $(NH_4)_2ABTS$ was used as purchased from Sigma, where $ABTS^{2-}$ is 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate). Stock solutions of $ABTS^{\bullet -}$ were prepared by mixing aqueous solutions of Br_2 and $ABTS^{2-}$.[8] The resulting solutions were thoroughly purged with argon to remove excess bromine. The $ABTS^{\bullet -}$ solutions are stable for several weeks and are an intense blue-green. Solutions of MV^{2+} (=methyl viologen = 1,1,′-dimethyl-4,4′-bipyridinium ion) in 5 mM $HClO_4$ were reduced over zinc amalgam for about 40 s to yield $MV^{\bullet +}$. The resulting deep blue solutions were stored in a gastight syringe. These two species, $ABTS^{\bullet -}$ (usually) and $MV^{\bullet +}$ (rarely), were used as kinetic probes.

Reagent solutions were prepared from distilled water purified by passage through a Milli-Q Millipore system. The concentrations of the reagents were determined spectrophotometrically: $MV^{\bullet +}$, $\epsilon_{600} = 1.37 \times 10^4$ L mol^{-1} cm^{-1};[9] Ni(cyclam)$^{2+}$, $\epsilon_{448} = 45$ L mol^{-1} cm^{-1}; $ABTS^{\bullet -}$, $\epsilon_{650} = 1.2 \times 10^4$ L mol^{-1} cm^{-1}.[10] Typical initial concentrations of $ABTS^{\bullet -}$

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(1) Colligation is the term coined for bond formation between two odd-electron species: Ingold C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 4–7.

(2) Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988,** *27,* 4578.

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and $MV^{\bullet +}$ were (2–6) × 10^{-5} M in the absence and 2.5 × 10^{-5} M in the presence of $Ni(cyclam)^{2+}$. The concentration of $Ni(cyclam)^{2+}$ ranged from 2 × 10^{-5} to 1 × 10^{-2} M, and that of alkylcobalt complexes was held at 1 × 10^{-4} M.

Kinetics. The laser flash photolysis system used to conduct the experiments has been described previously.[11,12] The dyes used were Coumarin 460 and LD 490, which emit light matching the absorptions of the alkylcobalt complexes, 450–500 nm. Both $MV^{\bullet +}$ and $ABTS^{\bullet -}$ are relatively transparent in this region. In a typical experiment, a deaerated sample solution was prepared in a 1-cm, square fluorescence cuvette and then flashed with a 0.6-μs laser pulse. The analyzing beam was positioned at a right angle to the laser beam. The photomultiplier tube voltage was acquired and digitized with a Nicolet 2090-3A digitizing oscilloscope. The temperature was controlled at 25.0 ± 0.5 °C.

The digitized transmittance–time data were converted to absorbance (D) and then analyzed by a nonlinear least-squares program according to a first-order equation: $D_t = D_\infty + (D_0 - D_\infty) \exp(-k_\psi t)$. Actually, each kinetic trace consists of sequential exponential losses of absorbance. The two parts are well separated in time, and so each was analyzed as a separate exponential.

Products. Reaction products were determined with a Hewlett-Packard Model 5790 gas chromatograph and a Model 3390 integrator. Hydrocarbons were determined on a column packed with VZ10.

Results

Reactions of Alkyl Radicals with the $ABTS^{\bullet -}$ Radical. Because this is the probe reaction by which the nickel–radical colligation reactions are monitored, it will be considered first. When a free radical is generated by the laser flash dissociation of an alkylcobalt complex (eq 2), two other reactions may ensue. One is the second-order self-reactions (dimerization and disproportionation) in eq 3. The other is the combination reaction wherein the radical adds to a ring position of $ABTS^{\bullet -}$, as in eq 4 (actually ~30% of eq 4 yields an alkene, R_{-H}, suggesting parallel outer-sphere electron transfer; these experiments were done at high $[ABTS^{\bullet -}]$ to minimize eq 3).

$$RCo^{III}L_n \xrightarrow{h\nu} R^\bullet + Co^{II}L_n \qquad (2)$$

$$2R^\bullet \rightarrow (RH + R_{-H}) + RR \quad k_d \qquad (3)$$

$$R^\bullet + ABTS^{\bullet -} \rightarrow \text{adduct} \quad k_A \qquad (4)$$

According to this scheme, the rate of disappearance of $R^\bullet$ is given by

$$-d[R^\bullet]/dt = 2k_d[R^\bullet]^2 + k_A[R^\bullet][ABTS^{\bullet -}] \qquad (5)$$

Because the first term cannot be entirely ignored, the reaction really follows mixed second- and first-order kinetics. The second-order term contributes very little, always <10%, because $[R^\bullet]$ is small, ~10^{-6} M. If we take $[R^\bullet]$ as the average value during the run, then the data are approximated by first-order kinetics with a rate constant given by

$$k_\psi = 2k_d[R^\bullet]_{av} + k_A[ABTS^{\bullet -}] \qquad (6)$$

The value of $[R^\bullet]_{av}$ can be obtained from the loss of absorbance of $ABTS^{\bullet -}$ in each experiment with due allowance for the percent of $R^\bullet$ reacting in eq 4. Since $[ABTS^{\bullet -}]_0 > 10[R^\bullet]_0$, the expression is[13]

$$[R^\bullet]_{av} = \frac{k_\psi \Delta[ABTS^{\bullet -}]}{2k_A[ABTS^{\bullet -}]_{av}} \qquad (7)$$

This requires an iterative procedure. First, k_a is estimated at high $[ABTS^{\bullet -}]$ from eq 5 and is then used in eq 7. The resulting $[R^\bullet]$ is used to refine the value of k_A. The process converges rapidly, and a single expression explains how k_A is obtained as the slope of k_{corr} vs $[ABTS^{\bullet -}]$, with the calculation being done iteratively, if necessary, to obtain a constant value:

Table I. Rate Constants for the Reaction of Alkyl Radicals with the $ABTS^{\bullet -}$ Radical at 25 °C

	$k_A/10^9$ L mol^{-1} s^{-1}			$k_A/10^9$ L mol^{-1} s^{-1}	
$R^\bullet$	1.0 M $HClO_4$	6.0 M ClO_4^-	$R^\bullet$	1.0 M $HClO_4$	6.0 M ClO_4^-
CH_3	1.2	1.2	$ClCH_2$	1.2	1.18
C_2H_5	1.1	1.06	$BrCH_2$	2.0	2.3
1-C_3H_7	1.2	1.03	$CH_2CH(CH_3)_2$	1.1	0.87
1-C_4H_9	1.3	0.84	$CH_2C(CH_3)_3$		0.74
1-C_5H_{11}	1.2		CH_2Ph	1.2	1.10
1-C_6H_{13}	1.1		2-C_3H_7	1.4	0.90
1-C_7H_{15}	1.2		2-C_4H_9		1.14
1-C_8H_{17}	1.3	1.13	c-C_5H_9	1.2	0.91
CH_3OCH_2	1.8	1.19	2-C_8H_{17}		1.02

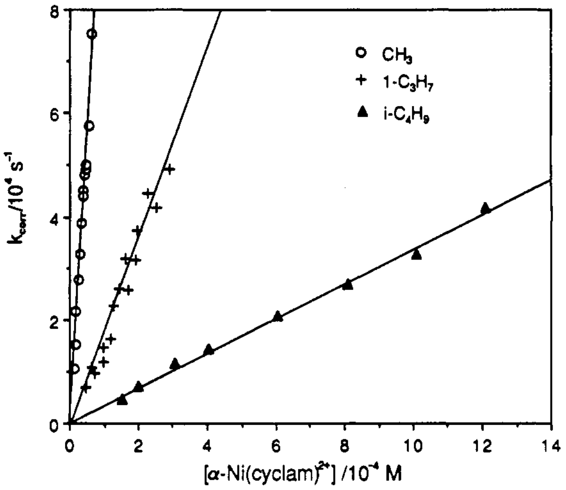

Figure 1. Plots of kinetic data for the colligation reactions between alkyl radicals and α-$Ni(cyclam)^{2+}$. The data are shown as a plot of k_{corr} vs [α-$Ni(cyclam)^{2+}$] in accordance with eq 9.

$$k_{corr} = k_\psi - 2k_d \frac{k_\psi \Delta[ABTS^{\bullet -}]}{2k_A[ABTS^{\bullet -}]_{av}} = k_A[ABTS^{\bullet -}]_{av} \qquad (8)$$

Values of k_A are summarized in Table I. The accuracy of this procedure was verified by simulating sets of kinetic data with the program KINSIM.[14] These data, treated as in eq 8, yielded the same value of k_A as was used to construct the simulation.

Reactions between Alkyl Radicals and the $Ni(cyclam)^{2+}$ Isomers. The reactions are as before, eq 2–4, except that the step in eq 1 involving $Ni(cyclam)^{2+}$ is added. This results in the terms $k_{col}[Ni(cyclam)^{2+}] + k_{hom}$ (added because eq 1 follows reversible first-order kinetics). The applicable equation is therefore

$$\begin{aligned} k_{corr} &= k_\psi - 2k_d \frac{k_\psi \Delta[ABTS^{\bullet -}]}{2k_A[ABTS^{\bullet -}]_{av}} - k_A[ABTS^{\bullet -}]_{av} \\ &= k_{col}[Ni(cyclam)^{2+}] + k_{hom} \end{aligned} \qquad (9)$$

The concentration of $Ni(cyclam)^{2+}$ in the above expression represents the actual concentration of the reactive isomer. Thus, in the case of the α isomer, the total concentration of the nickel complex was multiplied by 0.202. Independent experiments have shown that *cis*-$Ni(cyclam)(H_2O)_2{}^{2+}$ does not react with radicals. In the case of the β isomer, there was no observable dependence of k_{corr} on ionic strength in the range 0.1–6.0 M, despite the fact

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(11) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4104.

(12) Hoselton, M. A.; Lin, C.-T.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383. The energy of the laser pulse is 250 mJ.

(13) Equation 7 derives from the distribution of the amounts of $R^\bullet$ consumed in reactions 3 and 4:

$$\frac{\Delta[ABTS^\bullet]}{[R^\bullet]_{tot}} = \frac{k_A[ABTS^{\bullet -}]_{av}}{k_A[ABTS^{\bullet -}] + 2k_d[R^\bullet]_{av}} = \frac{k_A[ABTS^{\bullet -}]_{av}}{k_\psi}$$

$$[R^\bullet]_{av} = \frac{[R^\bullet]_{tot}}{2} = \frac{k_\psi \Delta[ABTS^{\bullet -}]}{2k_A[ABTS^{\bullet -}]_{av}}$$

(14) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 130.

Table II. Rate Constants for Colligation Reactions between Alkyl Radicals and Two Configurational Isomers of the Ni(cyclam)$^{2+}$ Complex at 25 °C

	$k_{col}/10^7$ L mol^{-1} s^{-1}			$k_{col}/10^7$ L mol^{-1} s^{-1}	
R$^\bullet$	α-Ni(cyclam)$^{2+\,a}$	β-Ni(cyclam)$^{2+\,b}$	R$^\bullet$	α-Ni(cyclam)$^{2+\,a}$	β-Ni(cyclam)$^{2+\,b}$
CH_3	107 (3)	73 (2)	$ClCH_2$	21.1 (7)	1.9 (5)
C_2H_5	23.4 (5)	1.3 (1)	$BrCH_2$	37.4 (10)	4.8 (4)
1-C_3H_7	16.8 (3)	1.0 (1)	$CH_2CH(CH_3)_2$	3.40 (6)	<0.02
1-C_4H_9	22.7 (6)	1.0 (1)	$CH_2C(CH_3)_3$	0.80 (4)	
1-C_5H_{11}		0.86 (9)	CH_2Ph	0.47 (3)	<0.02
1-C_6H_{13}		0.90 (10)	2-C_3H_7	0.62 (3)	<0.02
1-C_7H_{15}		0.78 (13)	2-C_4H_9	0.65 (6)	
1-C_8H_{17}	16.3 (4)	0.81 (11)	c-C_5H_9	1.04 (7)	<0.02
CH_3OCH_2	23.9 (5)	1.5 (1)	2-C_8H_{17}	1.00 (13)	

[a] The data refer to μ = 6.0 M (ClO_4^-) (5.9 M $NaClO_4$, 1.0 M $HClO_4$). [b] The data refer to 1.0 M $HClO_4$, with no correction for the planar/octahedral equilibration; see text.

Table III. Rate Constants for the Homolysis of RNi(cyclam)(H_2O)$^{2+}$ Complexes at 25 °C

	k_{hom}/s^{-1}			k_{hom}/s^{-1}	
R$^\bullet$	α-Ni(cyclam)$^{2+\,a}$	β-Ni(cyclam)$^{2+\,b}$	R$^\bullet$	α-Ni(cyclam)$^{2+\,a}$	β-Ni(cyclam)$^{2+\,b}$
CH_3	1.16 (26)	80 (20)	$ClCH_2$	83 (5)	2.7 (4) × 10^4
C_2H_5	112 (8)	6.8 (2) × 10^3	$BrCH_2$	7.1 (16)	3.9 (6) × 10^4
1-C_3H_7	99 (3)	5.3 (3) × 10^3	$CH_2CH(CH_3)_2$	89 (6)	
1-C_4H_9	106 (6)	1.00 (3) × 10^4	$CH_2C(CH_3)_3$	7.9 (13) × 10^2	
1-C_5H_{11}		5.8 (3) × 10^3	2-C_3H_7	2.0 (4) × 10^3	
1-C_6H_{13}		7.0 (3) × 10^3	2-C_4H_9	2.8 (19) × 10^3	
1-C_7H_{15}		8.5 (4) × 10^3	c-C_5H_9	4.4 (15) × 10^3	
1-C_8H_{17}	104 (12)	1.2 (1) × 10^4	2-C_8H_{17}	4.1 (3) × 10^3	
CH_3OCH_2	36 (2)	2.5 (1) × 10^3			

[a] μ = 6.0 M. [b] 1.0 M $HClO_4$.

that the proportion of the planar form increases from 70% to nearly 100% under those conditions. This result can be explained by assuming either that the two β forms, planar and octahedral, have similar rate constants or that the planar form is much more reactive, but the rate constant decreases somewhat (30–40%) as the ionic strength increases in the range given. Since we cannot distinguish between these possibilities, we have used the total concentration of Ni(cyclam)$^{2+}$ in the calculations involving the β isomer.

Typical plots of k_{corr} vs [Ni(cyclam)$^{2+}$] are shown in Figure 1. The slopes of these lines provide the values of k_{col}, which are given in Table II. The branched and secondary radicals react with β-Ni(cyclam)$^{2+}$ too slowly to provide the value of k_{col}. For these, a lower limit of $k < 10^5$ L mol^{-1} s^{-1} is given. The intercepts give values for k_{hom}. Owing to the subtractions involved, this value of k_{hom} is not particularly accurate. A much better method for the evaluation of k_{hom} is explained in the next section.

Kinetics of Homolysis of Alkylnickel Macrocycles. The absorbance of $ABTS^{\bullet-}$ undergoes a second and slower decrease, derived from the reaction of $ABTS^{\bullet-}$ with the R$^\bullet$ that results from Ni–C scission. The kinetic scheme consists of only two reactions, the reverse of eq 1 and eq 4.

$$R^\bullet + ABTS^{\bullet-} \rightarrow RABTS^- \quad k_A \tag{4}$$

Because the alkyl radical is now produced at a slow rate and not in a flash, the R$^\bullet$ + R$^\bullet$ reaction can be ignored. With the steady-state approximation for [R$^\bullet$], the rate constant is given by

$$k_\psi = \frac{k_{hom}}{1 + \dfrac{k_{col}[\mathrm{Ni(cyclam)}^{2+}]}{k_A[\mathrm{ABTS}^{\bullet-}]}} \tag{10}$$

This expression can be rearranged into a linearized form, eq 11.

$$\frac{1}{k_\psi} = \frac{1}{k_{hom}} + \left(\frac{k_{col}}{k_{hom}k_A}\right)\left(\frac{[\mathrm{Ni(cyclam)}^{2+}]}{[\mathrm{ABTS}^{\bullet-}]}\right) \tag{11}$$

Figure 2 displays this dependence graphically for several complexes. Numerical values of k_{hom} were calculated from eq 10 by a nonlinear least-squares program, treating values as known from the direct determinations. Values of k_{hom} are given in Table III.

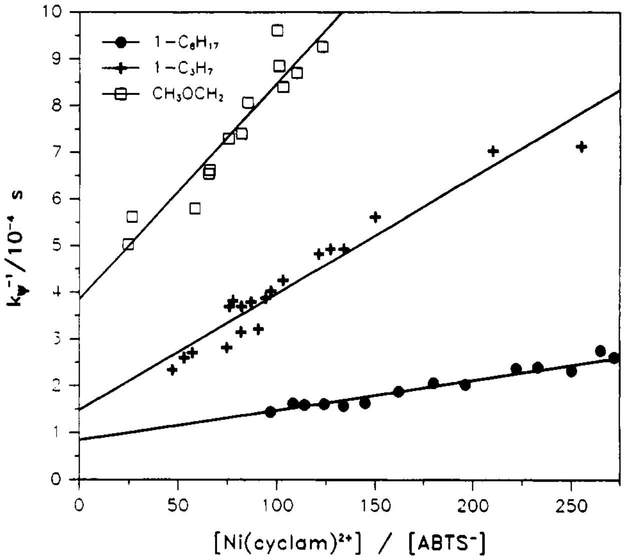
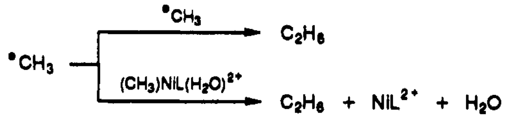


Figure 2. Plots of $1/k_\psi$ vs [Ni(cyclam)$^{2+}$]/[$ABTS^{\bullet-}$] for the reactions of β-Ni(cyclam)$^{2+}$. A linear relation is found, as in eq 11.

Activation Parameters. The effect of temperature on the homolysis of β-(C_2H_5)Ni(cyclam)(H_2O)$^{2+}$ was explored over a temperature range of 10–36 °C. A nonlinear least-squares fit to the Eyring equation gave the values $\Delta H^\ddagger_{hom}$ = 74 kJ mol^{-1} and $\Delta S^\ddagger$ = 80 J mol^{-1} K^{-1}.

Product Analysis. The hydrocarbon products were determined in the absence of $ABTS^{\bullet-}$ under conditions where colligation is the predominant reaction: 1 × 10^{-2} M β-Ni(cyclam)$^{2+}$, 5 × 10^{-4} M RCo(dmgH)$_2$(OH$_2$) (R = CH_3, C_2H_5). As before,[2] with R = CH_3, only ethane is observed, consistent with the equations



(12a)

(12b)

Table IV. Equilibrium Constants for the Formation of $RNi(cyclam)(H_2O)^{2+}$ Complexes at 25 °C

$$R^{\bullet} + Ni(cyclam)^{2+} + H_2O \rightleftharpoons RNi(cyclam)(H_2O)^{2+}$$

R	K_{eq}/L mol^{-1}		R	K_{eq}/L mol^{-1}	
	α-Ni(cyclam)$^{2+a}$	β-Ni(cyclam)$^{2+b}$		α-Ni(cyclam)$^{2+a}$	β-Ni(cyclam)$^{2+b}$
CH_3	9.2×10^8	9.1×10^6	$ClCH_2$	2.5×10^6	7.0×10^2
C_2H_5	2.1×10^6	1.9×10^3	$BrCH_2$	5.3×10^7	1.2×10^3
1-C_3H_7	1.7×10^6	1.9×10^3	$CH_2CH(CH_3)_2$	3.8×10^5	
1-C_4H_9	2.1×10^6	1.0×10^3	$CH_2C(CH_3)_3$	1.0×10^4	
1-C_5H_{11}		1.5×10^3	2-C_3H_7	3.1×10^3	
1-C_6H_{13}		1.3×10^3	2-C_4H_9	2.3×10^3	
1-C_7H_{15}		9.2×10^2	c-C_5H_9	2.4×10^3	
1-C_8H_{17}	1.6×10^6	6.8×10^2	2-C_8H_{17}	2.4×10^3	
CH_3OCH_2	6.6×10^6	6.0×10^3			

[a] In 6.0 M ClO_4^- (Na^+, H^+). [b] In 1.0 M $HClO_4$.

With R = C_2H_5, the products are butane, ethylene, and ethane in yields consistent with the known ratios[15] for self-reactions of ethyl radicals, $k_d/k_c = 0.35 \pm 0.04$. The data suggest that radicals other than methyl do not react as in eq 12b but are instead lost in self-reactions.

Ni(tmc) Complexes. The tetramethylcyclam ligand has been incorporated previously into organonickel complexes, $RNi(tmc)^+$. These are Ni(II) complexes and differ by one electron from the macrocyclic complexes reported here. We explored whether the $RNi(tmc)^{2+}$ complexes might form but were unable to detect formation of *R,R,S,S*-$Ni(tmc)CH_3^{2+}$ ($k_{col} < 10^5$ L mol^{-1} s^{-1}). This may not be unexpected in view of the steric hindrance and the oxidation potential of NiL^{2+} being much higher for tmc than for cyclam. A more favorable case might be *R,S,R,S*-$Ni(tmc)^{2+}$; these experiments were more difficult owing to its low stability in acid and a more intense visible spectrum, but its reaction with $^{\bullet}CH_3$ was still not appreciable.

Discussion

It is evident from the observed changes in [$ABTS^{\bullet-}$] that this radical is consumed in two stages, separated in time from one another. The disappearance of $ABTS^{\bullet-}$ always signals consumption of $R^{\bullet}$, since $ABTS^{\bullet-}$ reacts only with it and not with any of the metal complexes. The first of the decreases in [$ABTS^{\bullet-}$] is attributed to the reaction with $R^{\bullet}$ occurring in competition with colligation between $R^{\bullet}$ and $Ni(cyclam)^{2+}$. In support of this, the (corrected) first-order rate constant varies linearly with nickel concentration. The second reaction begins after colligation is complete. It, too, is a reaction between $R^{\bullet}$ and $ABTS^{\bullet-}$, which now accompanies nickel–carbon bond homolysis. This stage shows kinetic retardation by $Ni(cyclam)^{2+}$. From the first stage, it is possible to extract k_{col} and k_{hom}, although the latter value is somewhat imprecise. The second stage affords an accurate value of k_{hom} and also verifies the value of k_{col} determined in the first stage.

Colligation Reactions. For both series of complexes, the reactivity lies in the order CH_3 > primary > secondary. This is apparent for α-$Ni(cyclam)^{2+}$, where all three values were measured, as in the series CH_3 (1.07×10^9 L mol^{-1} s^{-1}) > C_2H_5 (2.34×10^8 L mol^{-1} s^{-1}) > 2-C_3H_7 (6.2×10^6 L mol^{-1} s^{-1}). The trend is even sharper in the β-$Ni(cyclam)^{2+}$ series where the secondary radicals react too slowly for measurement: CH_3 (7.3×10^8 L mol^{-1} s^{-1}) > C_2H_5 (1.3×10^7 L mol^{-1} s^{-1}) > 2-C_3H_7 ($< 2 \times 10^5$ L mol^{-1} s^{-1}). These data lead us to suggest that the rate constants for the reaction between β-$Ni(cyclam)^{2+}$ and the secondary radicals are probably not too much below the lower experimental limit.

It is noteworthy that all primary, nonbranched radicals react at about the same rate with a given complex. For α-$Ni(cyclam)^{2+}$, the four values lie in the narrow range $(1.68–2.34) \times 10^8$ L mol^{-1} s^{-1}; for β-$Ni(cyclam)^{2+}$, the range of seven values is $(0.81–1.3) \times 10^7$ L mol^{-1} s^{-1}. Again, for the secondary alkyl radicals, all four values for α-$Ni(cyclam)^{2+}$ fall in the range $(0.62–1.04) \times 10^7$ L mol^{-1} s^{-1}; the heavily branched neopentyl radical reacts comparably to the secondary radicals.

In every case, the α complex binds radicals with a higher kinetic efficiency than the β does. The reason for this does not appear to be steric. On the basis of the reported crystal structures,[16,17] we conclude that a radical, approaching one of the axial positions at the metal, would experience similar steric hindrance from the macrocyclic ligand atoms of either isomer. If anything, the steric crowding is somewhat greater in the case of the α isomer. One would thus expect a smaller k_{col} and a larger k_{hom} for this isomer, exactly opposite from the experimental observations.

The differences in the observed stability order of the two series of organonickel products may be related to the large difference in the average Ni–N bond lengths for the two Ni(II) complexes, 2.058 Å for the β isomer[16] and 1.916 Å for the α.[17] The formation of a (formally) organonickel(III) complex might be more favorable for a complex with a shorter Ni–N bond. The effect of the nickel–ligand bond lengths on the reduction potentials of macrocyclic nickel complexes has been observed and discussed previously.[18]

Homolysis Rates. The trends in the values of k_{hom} reflect those found for k_{col}, although the effect is of course in the opposite direction. It is apparent from the values obtained that the homolysis rates are lower for the α series than for the β, often by factors of 10^2 or more. Also, within each family of $RNi(cyclam)(H_2O)^{2+}$ complexes, there is a marked trend in reactivity, CH_3 < primary < secondary. The values of k_{hom} for the β isomer cannot be measured for *sec*-alkyl complexes which have values of k_{col} so small that these species do not form to any appreciable extent. With each isomer, k_{hom} values are essentially constant for the group of nonbranched primary ($k_{hom} = (1.0–1.1) \times 10^2$ s^{-1} for the α isomer and $(5.3–12) \times 10^3$ s^{-1} for the β) and secondary alkyls ($(2.0–4.4) \times 10^3$ s^{-1} for α).

The activation parameters for the homolysis of the β isomer of $(C_2H_5)Ni(cyclam)(H_2O)^{2+}$ were determined. To a first approximation, the value of $\Delta H^{\ddagger}_{hom}$, 74 kJ mol^{-1}, can be taken as an estimate of the Ni–C bond dissociation enthalpy (BDE). Actually, allowing for $\Delta H^{\ddagger}_{col}$, which might be some 10–12 kJ/mol from solvent viscosity (note that $k_{col} = 1 \times 10^7$ L mol^{-1} s^{-1}, which is not diffusion controlled), a more realistic estimate of the BDE is $\sim 60 \pm 5$ kJ mol^{-1}. This value is much lower than values recorded for $RCoL_n$ and $RCrL_n$ complexes, which are much more stable and do not, by and large, undergo ready homolysis. In other words, the weakness of the Ni–C bond arises primarily from the high rate of homolysis, although the low colligation rates for R = secondary alkyls also contribute to the effect.

The value of $\Delta S^{\ddagger}$, 80 J mol^{-1} K^{-1}, is consistent with the dissociation of the nickel–ethyl bond into two fragments, one of which is a hydrophobic group that can disrupt the hydrogen-bonded structure of the solvent. The homolysis reaction is not an interchange process as it appears to be for 6-coordinate cobalt and chromium, in which a water molecule must begin to form a bond

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Table V. Rate Constants for Colligation Reactions between Selected Alkyl Radicals and Divalent Metal Complexes in Aqueous Solution

	$k_{col}/10^7$ L mol^{-1} s^{-1}				
R$^\bullet$	α-Ni(cyclam)$^{2+}$	β-Ni(cyclam)$^{2+}$	$Cr(H_2O)_6{}^{2+}$ [a]	$(H_2O)_2Co(cyclam)^{2+}$ [b]	B_{12r} [c]
CH_3	107	73	22	1.6	44
C_2H_5	23	1.3	19	1.1	51
1-C_3H_7	17	1.0	22		61
2-C_3H_7	0.62	<0.02			25
c-C_5H_9	1.04	<0.02	8		

[a] Reference 19. [b] References 19d and 20. [c] Reference 20.

to the metal synchronously as the alkyl moiety departs. With nickel, on the other hand, the product formed from (C_2H_5)Ni(cyclam)$(H_2O)^{2+}$ is the 4-coordinate Ni(cyclam)$^{2+}$ complex. Thus $\Delta S^\ddagger$ is a large, positive value, in keeping with what appears to be a purely dissociative process.

Equilibrium Constants. The quotient k_{col}/k_{hom} is equal to the equilibrium constant for the reaction of any given R group. The values obtained are listed in Table IV. These constitute the largest such body of data known for any group of metal alkyls, including the list of values for $(H_2O)_5CrR^{2+}$ complexes, which is much shorter.[19] Because of the opposing effects that the variation of R has on the values of k_{col} and k_{hom}, the trend in K_{eq} is a function of the identity of R. In the α series, for instance, K varies from 9×10^8 for CH_3 to 2×10^3 L mol^{-1} for secondary alkyls. A similar variation, 9×10^6 to <1 L mol^{-1}, is seen for the β isomer. Roughly speaking, there is a factor of 10^3 favoring the stability of any given member of the α series over its counterpart for the β isomer. Once again, the higher thermodynamic stability of the nickel–carbon bond in the α series probably reflects the relative stabilization of the higher oxidation state for the isomer with shorter Ni–N bonds.

Comparisons to Other Systems. The only comparison we can legitimately make is among values of k_{col}, since series of k_{hom} and K values are not available in other systems. The comparison organometallic complexes we consider are $(H_2O)_5CrR^{2+}$,[19] RCo(cyclam)$(H_2O)^{2+}$,[19d,20] and RB_{12}.[20] Values of k_{col} are summarized in Table V. For metals other than nickel, the steric effect along the series of R groups is quite small. That is, in the sequence CH_3, primary, and secondary, the trend for Co and Cr spans at most a factor of 3. Compared to this, the Ni(cyclam)$^{2+}$ rates vary by factors of 10^2 (α) and $>3.6 \times 10^3$ (β).

There are two major differences between the nickel macrocycles studied in this work and the chromium and cobalt complexes. First, there is no axial H_2O ligand on Ni(cyclam)$^{2+}$ (on the prevailing form of the β isomer), and thus colligation is simply an addition reaction. In contrast, the 6-coordinate species $Cr(H_2O)_6{}^{2+}$ and $(H_2O)_2Co(cyclam)^{2+}$ lose an axial water molecule synchronously with the addition of R.

Another major difference between RNi(cyclam)$(H_2O)^{2+}$ and the other alkylmetal complexes is that the alkylnickel complexes show relatively low thermodynamic stability toward homolytic dissociation (Table IV) in comparison to the very stable RCo and RCr complexes.[21] As the value of K_{eq} decreases toward unity, the rate constants k_{col} and k_{hom} (or at least one of them) must change to reflect the growing instability. This may be enough to cause the variation of k_{col} with R for Ni(cyclam)$^{2+}$.

In all of these series, there is a similar trend in k_{hom}. For example, $(H_2O)_5CrCH(CH_3)_2{}^{2+}$ homolyzes readily[19b] but similar complexes with R = C_2H_5 and CH_3 do not. Likewise, $(CH_3)_2CHCo(cyclam)(H_2O)^{2+}$ is too unstable for isolation, whereas crystalline samples of the derivatives with R = C_2H_5 and CH_3 are easily obtained. In each case, even the pentaaquachromium series, one can reasonably invoke a repulsion between R and the equatorial ligand(s) that grows larger with increasing substitution on R.

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(21) Relatively few values of K_{eq} have been determined for RCr^{2+} and $RCoL_n$ complexes. The complex $(H_2O)_5CrCH(CH_3)_2{}^{2+}$ has $K_{eq} \sim 10^{12}$ L mol^{-1}.[19a,b] Similar complexes with R = CH_3 and C_2H_5 have much larger values, because k_{col} is about the same as that for $CH(CH_3)_2$ and because these complexes show no evidence for homolytic decomposition. Similar trends would be found in the series $CrCH_2OH^{2+}$, $CrCH(CH_3)OH^{2+}$, and $CrC(CH_3)_2OH^{2+}$ for which values of $-\log K_{eq}$ are 12.64, 10.96, and 8.6. Similar qualitative arguments apply to cobalt complexes, but few quantitative values are known.