

## Hydrolysis of the Nickel-Carbon Bond of Organonickel Tetramethylcyclam Complexes

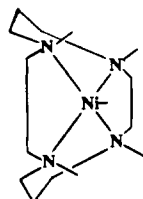
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Received May 8, 1986

The cationic organometallic complexes  $(1R,4S,8R,11S)\text{-RNi}(\text{tmc})^+$  (where  $\text{tmc} = 1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazacyclotetradecane}$ ) hydrolyze in alkaline, aqueous solutions to yield the alkane  $\text{RH}$  and  $\text{HONi}(\text{tmc})^+$ , the hydroxonickel(II) macrocycle. The rates of reaction are independent of pH (for  $9 < \text{pH} < 13$ ). Aside from a few special cases, the hydrolysis rate constants are rather insensitive to the variation of R in a series of 20 compounds that includes alkyls ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, i\text{-C}_3\text{H}_7, \text{sec-C}_4\text{H}_9, \text{CH}_2\text{C}_6\text{H}_5$ ), cyclopropyl, and substituted alkyls (e.g.,  $(\text{CH}_2)_n\text{X}$ , with  $\text{X} = \text{Br}, \text{Cl}, \text{OH}$ , and  $\text{OTs}$ ;  $n = 3\text{--}6$ ). These complexes, and also such bimetallic analogues as  $[\text{Ni}(\text{tmc})(\text{CH}_2)_3\text{Cr}(\text{[15]aneN}_4)^{3+}]$ , have  $k_{\text{hyd}}$  in the range  $(0.8\text{--}2.7) \times 10^{-2} \text{ s}^{-1}$  at  $25.0^\circ\text{C}$ . The activation parameters also span a narrow range, with  $\Delta H^\ddagger \sim 16 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger \sim -14 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The solvent deuterium kinetic isotope effect determined for several of these complexes is appreciable,  $k_{\text{H}}/k_{\text{D}} = 2.2\text{--}3.5$ , suggesting appreciable proton transfer from water to the incipient hydrocarbon in the transition state. Nucleophilic assistance by  $\text{OH}^-$ ,  $\text{OAc}^-$ , and  $\text{NH}_3$  was not observed. Exceptions to the general pattern were noted. The most striking cases are  $\text{R} = (\text{CH}_2)_3\text{OH}$ , where the enhanced rate of hydrolysis ( $k_{\text{hyd}} = 0.23 \text{ s}^{-1}$ ) suggests assistance from the pendant OH group in a cyclic transition state and cycloalkyls (other than cyclopropyl), where the enhanced rates (e.g., cyclobutyl  $\sim 0.2 \text{ s}^{-1}$  and cyclopentyl  $> 2 \text{ s}^{-1}$ ) suggest an acceleration by the strain of the nickel-carbon bond. In acidic solutions, the hydrolysis rate is enhanced because of direct protonolysis. The bimolecular reaction between  $\text{C}_2\text{H}_5\text{Ni}(\text{tmc})^+$  and  $\text{H}_3\text{O}^+$  has  $k = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

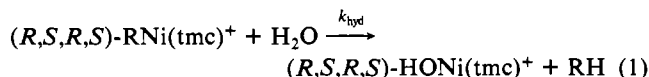
## Introduction

Two new series of organonickel macrocyclic complexes have recently been prepared and characterized.<sup>1-3</sup> These complexes contain one or another of the various isomers of  $\text{tmc}$ , the "tetramethylcyclam" ligand.<sup>4</sup> The organometallic complexes of interest in the present work are  $(R,S,R,S)\text{-[RNi}(\text{tmc})]^+$ , the

 $(R,S,R,S)\text{-[Ni}(\text{tmc})^{2+}]$ 

isomer substituted with a methyl group at each nitrogen to yield a complex with "four methyls up". The complex with  $\text{R} = \text{CH}_3$  can be prepared by a Grignard reaction,<sup>3</sup> as first described for  $(R,R,S,S)\text{-CH}_3\text{Ni}(\text{tmc})^+$ .<sup>5</sup>

A more general route, however, is the capture by the nickel(I) macrocycle of free radicals generated by reduction of alkyl halides or hydroperoxides.<sup>1,3</sup> This affords a good yield of the  $\text{RNi}(\text{tmc})^+$  complexes in alkaline aqueous solutions for a wide variety of alkyl, substituted alkyl, and aralkyl groups R. The organonickel complexes are recognized by a characteristic visible/UV absorption spectrum that features a maximum located generally about 390–410 nm. One of the reactions that has proved useful in characterizing the species prepared is its relatively slow hydrolysis. As shown in eq 1, this yields the stable nickel(II) macrocycle and the alkane or other hydrocarbon RH.



The preparation of the organonickel complexes and the observation that they slowly hydrolyze in aqueous solution provide an opportunity to determine the rates of bond protonolysis for a homologous series of complexes. Relatively little systematic work concerning the rates and mechanisms of such reactions have appeared, except in the case of the families of organochromium ions  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ ,<sup>6-11</sup>  $\text{Cr}(\text{[15]aneN}_4)\text{R}^{2+}$ ,<sup>12</sup> and related or-

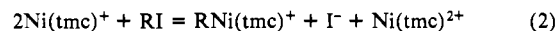
ganochromium complexes.<sup>13,14</sup> We thus viewed it as important to document for a different series of organometallic complexes the reaction kinetics, to detail further the mechanism of metal-carbon bond solvolysis. The relatively constant values of  $k_{\text{hyd}}$  over a wide variety of R groups in a substantial number of  $\text{RNi}(\text{tmc})^+$  complexes is one of the surprising features of the results that we have obtained.

## Experimental Section

The complex  $[(R,S,R,S)\text{-Ni}(\text{tmc})](\text{ClO}_4)_2$  was prepared by the literature procedure<sup>15</sup> with but minor modifications.<sup>3</sup> The nickel(I) complex was prepared in alkaline solutions, generally 0.02 M NaOH, by either electrochemical or photochemical methods.<sup>1,3</sup> The photochemical preparation of  $\text{Ni}(\text{tmc})^+$  utilizes reduction of  $\text{Ni}(\text{tmc})^{2+}$  by the radical  $\text{C}(\text{CH}_3)_2\text{O}^{\bullet}$ , generated by photolyzing acetone (typically 40 mM) in solutions containing 2-propanol (1.8 M). The electrochemical preparation, which was used in most of the experiments, consists of controlled potential reduction at a mercury-pool cathode. The standard reduction potential of  $\text{Ni}(\text{tmc})^{2+}$  is  $-0.87 \text{ V}$  vs. NHE.<sup>3</sup>

Solutions of  $\text{Ni}(\text{tmc})^+$  are quite air sensitive, as are the radical intermediates in the preparation of alkylnickel complexes and the latter complexes themselves. Thus rigorously air-free conditions were maintained throughout by the use of  $\text{Cr}^{2+}$ -scrubbed argon and careful syringe-septa techniques.

The reaction of  $\text{Ni}(\text{tmc})^+$  with alkyl iodides (eq 2) was used to prepare the organonickel complexes. They were detected by their characteristic UV/visible spectra,<sup>3</sup> and identified by the products of their reactions,



including the hydrocarbons formed by hydrolysis. The dimetallic complexes  $(\text{tmc})\text{Ni}(\text{CH}_2)_n\text{Cr}(\text{[15]aneN}_4)^{3+}$  were prepared from  $(\text{[15]aneN}_4)\text{Cr}(\text{CH}_2)_n\text{Br}$ <sup>12</sup> and  $\text{Ni}(\text{tmc})^+$ . The organic products were determined by gas chromatography on the solution or the gas phase above it. A Hewlett-Packard Model 5790 gas chromatograph with appropriate commercially available columns was used. The retention times and amounts were calibrated with known materials.

The methoxymethyl complex was prepared by a different procedure. A spectrophotometric cell containing NaOH (0.02 M),  $\text{LiClO}_4$  (0.08 M), dimethyl ether ( $\sim 0.3 \text{ M}$ ), acetone (2 M), and  $\text{Ni}(\text{tmc})^+$  ( $3.8 \times 10^{-4} \text{ M}$ ) was irradiated by medium-pressure mercury lamps in a Rayonet photochemical reactor for 10 min. The yellow color of  $\text{CH}_3\text{OCH}_2\text{Ni}(\text{tmc})^+$  was readily apparent. A similar experiment with diethyl ether did not yield an organonickel complex.

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- (3) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267.
- (4) The parent nickel(II) complex used here is  $(1R,4S,8R,11S)\text{-}(1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazacyclotetradecane})\text{nickel(II)}$ , which we abbreviate as  $(R,S,R,S)\text{-Ni}(\text{tmc})^{2+}$  or when not ambiguous simply as  $\text{Ni}(\text{tmc})^{2+}$ . This isomer has also been referred to in the literature as the *trans-I* isomer.
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**Table I.** Reaction Products and Rate Constants for the Hydrolysis of (*R,S,R,S*)-RNi(tmc)<sup>+</sup> in Alkaline Solution<sup>a</sup>

R	organic product <sup>b</sup>	$k_{\text{hyd}}/\text{s}^{-1}$
(a) Alkyls		
CH <sub>3</sub>	methane	$1.20 \times 10^{-2}$
C <sub>2</sub> H <sub>5</sub>	ethane	$1.10 \times 10^{-2}$
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	propane	$1.30 \times 10^{-2}$
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	propane	$1.47 \times 10^{-2}$
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	<i>c</i>	$1.5 \times 10^{-2}$
(b) Cycloalkyls		
<i>c</i> -C <sub>3</sub> H <sub>5</sub>	cyclopropane	$3.2 \times 10^{-2}$
<i>c</i> -C <sub>4</sub> H <sub>7</sub>	cyclobutane	~0.2
<i>c</i> -C <sub>5</sub> H <sub>9</sub>	cyclopentane	>2
(c) Substituted Alkyls		
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	toluene	$9.4 \times 10^{-3}$
CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> F(4-)	<i>c</i>	$6.1 \times 10^{-3}$
CH <sub>2</sub> OCH <sub>3</sub>	<i>c</i>	$<2 \times 10^{-3}$
(CH <sub>2</sub> ) <sub>4</sub> Cl	1-chlorobutane	$7 \times 10^{-3}$
(CH <sub>2</sub> ) <sub>4</sub> Br	1-bromobutane	$1.5 \times 10^{-2}$
(CH <sub>2</sub> ) <sub>4</sub> I	1-iodobutane	$2.7 \times 10^{-2}$
(CH <sub>2</sub> ) <sub>4</sub> OH	1-butanol	$8.1 \times 10^{-3}$
(CH <sub>2</sub> ) <sub>4</sub> OTs	<i>c</i>	$7 \times 10^{-3}$ <sup>d</sup>
(CH <sub>2</sub> ) <sub>3</sub> OH	1-propanol	0.23
(CH <sub>2</sub> ) <sub>5</sub> Br	1-bromopentane	$1.65 \times 10^{-2}$
(CH <sub>2</sub> ) <sub>6</sub> Br	1-bromohexane	$1.5 \times 10^{-2}$ <sup>d</sup>
(d) Alkenyls		
1-hexenyl	1-hexene and methylcyclopentane <sup>e</sup>	$1.1 \times 10^{-2}$
CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	1-butene	$1.5 \times 10^{-2}$
(e) Dimetallics		
(CH <sub>2</sub> ) <sub>4</sub> Cr([15]aneN <sub>4</sub> ) <sup>2+</sup>	<i>n</i> -butane <sup>f</sup>	$1.7 \times 10^{-2}$
(CH <sub>2</sub> ) <sub>5</sub> Cr([15]aneN <sub>4</sub> ) <sup>2+</sup>	<i>n</i> -pentane <sup>f</sup>	~ $1.5 \times 10^{-2}$

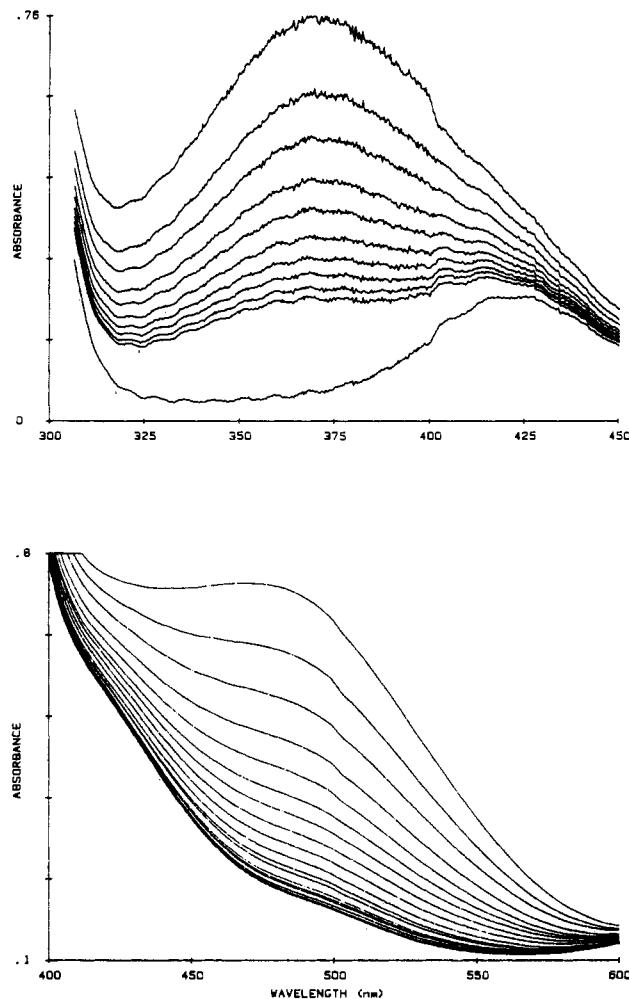
<sup>a</sup> At 25.0 °C, 0.020 M OH<sup>-</sup>,  $\mu = 0.10$  M (LiClO<sub>4</sub>). <sup>b</sup> Determined by GC on VZ-10, FFAP, and OV-101 columns. <sup>c</sup> Not determined. <sup>d</sup> In 1–2 M acetone. <sup>e</sup> Relative yield depends on the initial ratio of reactants (see ref 3). <sup>f</sup> After hydrolysis with H<sub>3</sub>O<sup>+</sup>; the initial product is identified as CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>Cr([15]aneN<sub>4</sub>)<sup>2+</sup>.

The rate constants for hydrolysis were determined by conventional spectrophotometry by the use of computer-interfaced Cary 219 or Cary 14 instruments. A fresh solution of RNi(tmc)<sup>+</sup> was made up for each determination. The kinetic data followed first-order kinetics to high precision. The rate constants were calculated from the absorbance–time data by nonlinear least-squares fitting to the equation ( $D = \text{absorbance}$ )  $D_t = D_\infty + (D_0 - D_\infty) \exp(-k_{\text{hyd}}t)$ . Duplicate determinations typically agreed to within 10%. The kinetic determinations were carried out at constant temperature (25.0 °C) and ionic strength (0.10 M, maintained with lithium perchlorate). Most reactions were studied at [OH<sup>-</sup>] = 0.020 M, but for the ethyl complex [OH<sup>-</sup>] was varied (without a perceptible effect on the rate constant) between 10<sup>-4</sup> and 0.10 M.

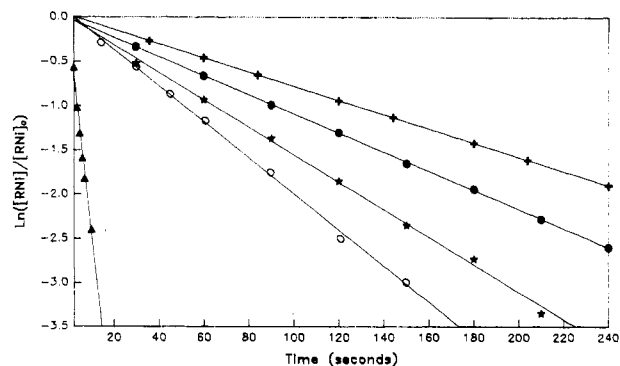
## Results

**Products.** The five-coordinate aquo and hydroxo Ni(II) complexes,  $pK_a$  10.82,<sup>16</sup> are in equilibrium with the diamagnetic, four-coordinate complex. Generally, we shall simply write Ni(tmc)<sup>2+</sup> to represent the equilibrium mixture. The thorough investigation of the coordination chemistry of the Ni(II) complex reveals that these species are equilibrated on the NMR time scale.<sup>17</sup> The inorganic product of hydrolysis of RNi(tmc)<sup>+</sup> was found to be Ni(tmc)<sup>2+</sup>.

The organic products are, as indicated in eq 1, the (substituted) hydrocarbon molecules, RH. The specific products determined are given in Table I. There is no indication of products from the dimerization or disproportionation of the free radicals R<sup>•</sup>, regardless of whether hydrolysis is carried out with RI<sup>18</sup> or Ni-



**Figure 1.** Intermittent scans of the UV/visible spectrum of RNi(tmc)<sup>+</sup>, showing the decrease in absorbance accompanying the hydrolysis. The reaction occurs without the intervention of intermediates that can be detected spectrophotometrically. Top: *c*-C<sub>3</sub>H<sub>5</sub>Ni(tmc)<sup>+</sup>, prepared from 1.0 mM Ni(tmc)<sup>+</sup> and 20 mM *c*-PrBr in 0.7 M acetone at 0.02 M NaOH. Spectral scans at 7.8-s intervals in a cell with a 1-cm optical path. Bottom: 4-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Ni(tmc)<sup>+</sup>, prepared from 1.0 mM Ni(tmc)<sup>+</sup> and 0.25 mM 4-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl. Spectral scans at 30-s intervals in a 2-cm cell.



**Figure 2.** Representative first-order kinetic plots for the hydrolysis of several organonickel complexes in aqueous solution at [OH<sup>-</sup>] = 0.0200 M, 25.0 °C, and 0.10 M ionic strength. Data are shown for RNi(tmc)<sup>+</sup> for R = (CH<sub>2</sub>)<sub>4</sub>OH (pluses), CH<sub>3</sub> (filled circles), *sec*-butyl (stars), (CH<sub>2</sub>)<sub>4</sub>Cr([15]aneN<sub>4</sub>)<sup>2+</sup> (open circles), and (CH<sub>2</sub>)<sub>3</sub>OH (triangles).

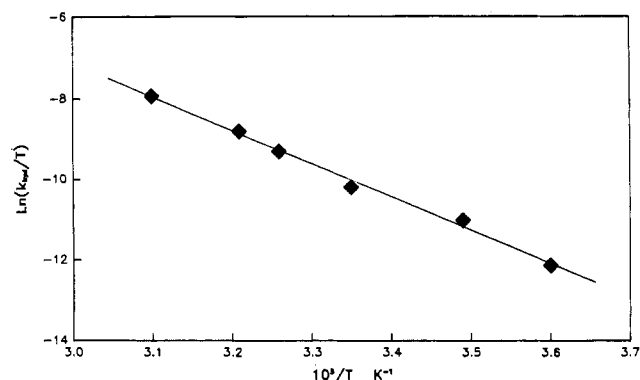
(tmc)<sup>+</sup> in excess. This is taken to imply that homolysis of the nickel–carbon bond is not important under any of the conditions used. Also, propene and butenes are not formed during the hydrolysis of *c*-C<sub>3</sub>H<sub>5</sub>Ni(tmc)<sup>+</sup> or *c*-C<sub>4</sub>H<sub>7</sub>Ni(tmc)<sup>+</sup>, respectively.

**Kinetics.** The hydrolysis reaction is accompanied by the steady decrease in the absorbance at the maximum of the organonickel

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(18) When RI is in large excess, there is a direct reaction between RI and RNi(tmc)<sup>+</sup>, as noted previously<sup>2</sup> for the (*R,R,S,S*)-Ni(tmc) isomer. That process leads to enhanced rates and to radical products, but it is a phenomenon quite different from the hydrolysis reactions and can safely be ignored in this context, since it does not contribute appreciably under the conditions employed for the hydrolysis.



**Figure 3.** Analysis of the temperature dependence of the rate constant for hydrolysis of  $(R,S,R,S)\text{-C}_2\text{H}_5\text{Ni}(\text{tmc})^+$  according to activated complex theory.

**Table II.** Activation Parameters for the Hydrolysis of Organonickel Complexes<sup>a,b</sup>

R	$\lambda_{\text{max}}/\text{nm}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$
CH <sub>3</sub>	355	16.0	-13.8
C <sub>2</sub> H <sub>5</sub>	406	16.5	-11.7
(CH <sub>2</sub> ) <sub>4</sub> Br	406	15.4	-15.1
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	498	15.9	-15
(CH <sub>2</sub> ) <sub>3</sub> OH	406	11.7	-21.9

<sup>a</sup>In H<sub>2</sub>O, with  $[\text{OH}^-] = 0.02 \text{ M}$ ,  $\mu = 0.10 \text{ M}$ . <sup>b</sup>Standard deviation in  $\Delta H^\ddagger = 0.8 \text{ kcal mol}^{-1}$  and in  $\Delta S^\ddagger = 2.9 \text{ cal mol}^{-1} \text{K}^{-1}$ .

complex, which is eventually replaced by the stable but much less intense spectrum of  $\text{Ni}(\text{tmc})^{2+}$ . Examples are shown in Figure 1. The plots of  $\log(D_t - D_\infty)$  vs. time are linear; several examples are shown in Figure 2. This establishes that the rate of reaction shows a simple first-order dependence on the concentration of the organonickel complex, as in eq 3. The values of  $k_{\text{hyd}}$  determined

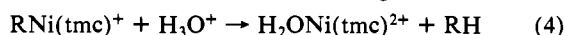
$$-d[\text{RNi}(\text{tmc})^+]/dt = k_{\text{hyd}}[\text{RNi}(\text{tmc})^+] \quad (3)$$

by the nonlinear least-squares fitting routine as described are given in Table I. The rate was not affected by addition of  $\text{Ni}(\text{tmc})^{2+}$  to  $10^{-2} \text{ M}$ . Variation of  $[\text{OH}^-]$  ( $10^{-4}$ – $10^{-1} \text{ M}$ ), or addition of nucleophiles such as  $\text{OAc}^-$ ,  $\text{N}_3^-$ , or  $\text{NH}_3$  ( $10^{-2} \text{ M}$ ), did not alter  $k_{\text{hyd}}$ .

**Activation Parameters.** The effect of variable temperature was determined for several complexes in the range 4–49 °C. The values adhered to the activated complex theory expression, as shown for the ethyl complex by the linear plot of  $\log(k_{\text{hyd}}/T)$  vs.  $1/T$  presented in Figure 3. A nonlinear least-squares analysis gives the activation parameters listed in Table II. The narrow range spanned by values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  should be noted, as this feature figures prominently in the assignment of a mechanism.

**Deuterium Isotope Effects.** The solvent deuterium isotope effect was determined by preparing a solution of the nickel complex and all other components in D<sub>2</sub>O/NaOD. The mole fraction of deuterium in the final reaction solution was >0.99. The value of  $k_{\text{hyd}}^{\text{D}}$  was determined at 25 °C and  $\mu = 0.10 \text{ M}$  for several complexes and used to calculate a value of the solvent isotope effect. The results summarized in Table III indicate that appreciable effects ( $k_{\text{H}}/k_{\text{D}} = 2.2$ – $3.5$ ) are observed.

**Reaction with H<sub>3</sub>O<sup>+</sup>.** All of the complexes are “instantaneously” decomposed upon acidification. Evidence was obtained for a direct electrophilic reaction with acid that is much faster than that with the solvent. In every case where the effect was examined, the products of the reaction with H<sup>+</sup> and H<sub>2</sub>O were the same, and so we formulate the former reaction as in eq 4. Quantitative



$$-d[\text{C}_2\text{H}_5\text{Ni}(\text{tmc})^+]/dt = k_{\text{H}}[\text{C}_2\text{H}_5\text{Ni}(\text{tmc})^+][\text{H}_3\text{O}^+] \quad (5)$$

determinations were made for  $\text{C}_2\text{H}_5\text{Ni}(\text{tmc})^+$ . These measurements yielded the second-order rate constant  $k_{\text{H}} = 5 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$  at 25 °C.

**Table III.** Solvent Kinetic Isotope Effects for the Hydrolysis of Several Organo(tetramethylcyclam)nickel Complexes<sup>a</sup>

R	$k_{\text{D}_2\text{O}}/\text{s}^{-1}$	$k_{\text{H}}/k_{\text{D}}$
CH <sub>3</sub>	$4.0 \times 10^{-3}$	3.0
C <sub>2</sub> H <sub>5</sub>	$3.1 \times 10^{-3}$	3.5
(CH <sub>2</sub> ) <sub>4</sub> Br	$6.9 \times 10^{-3}$	2.2
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	$3.9 \times 10^{-3}$	2.4
(CH <sub>2</sub> ) <sub>3</sub> OH	0.17	1.3 <sub>5</sub>

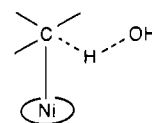
<sup>a</sup>Determined in water at  $[\text{OD}^-] = 0.02 \text{ M}$ ,  $\mu = 0.10 \text{ M}$ , with a mole fraction of deuterium >0.99.

It has been independently established that Ni(I) complexes themselves react very rapidly with  $\text{H}_3\text{O}^+$ . For example,  $\text{Ni}(\text{Me}_6[14]\text{aneN}_4)^+$  reacts with  $\text{H}_3\text{O}^+$ , HOAc, and  $\text{H}_2\text{PO}_4^-$  with rate constants  $>10^5 \text{ M}^{-1} \text{s}^{-1}$ .<sup>19</sup>

## Discussion

**Hydrolysis Mechanism.** The narrow spread found in the values of  $k_{\text{hyd}}$  is striking. A majority of the values lie in the range  $(1.1\text{--}1.6) \times 10^{-2} \text{ s}^{-1}$ , and 20 of the 23 rate constants lie within a factor of 6 ( $0.005\text{--}0.03 \text{ s}^{-1}$ ). Let us first deal with the reactions that appear “normal” in this respect. They are characterized by activation parameters that also span a narrow range, and thus one can be more confident that a common mechanism can be assigned.

The activation enthalpy for this group is about  $16 \text{ kcal mol}^{-1}$  (Table II). This value must clearly be smaller than the nickel–carbon bond strength, otherwise the complexes would decompose much more rapidly by a homolytic pathway. Clearly, then, the reaction proceeds by compensating bond-breaking (Ni–C, O–H) and bond-making (C–H) processes. Indeed, hydrolysis cannot be expected to proceed on the molecular level to yield  $\text{Ni}(\text{tmc})^{2+}$  and  $\text{R}^-$ , since the latter, with  $\text{pK}_a$ 's in the range 35–45,<sup>20</sup> is a species far too basic (i.e., with too high a free energy) to be formed, even as a transient intermediate in solution. This argues for the involvement of a solvent molecule in the activated complex, which we depict as follows.



This mechanism suggests the incipient formation of a C–H bond between the departing alkyl group and a proton from the solvent, by either a front-side or a back-side attack.<sup>21</sup> This provides an energetic compensation that lowers the activation enthalpy below the heterolytic bond strength of the nickel–carbon bond. The steric barrier posed by substituents of different sizes on the  $\alpha$ -carbon atom plays a minor role since the attacking group, a proton of a water molecule from the solvent, is very small.

In support of this mechanism, we note the substantial kinetic isotope effect, which amounts to a factor of 2.2–3.5 for these complexes (Table III). The isotope effects are, however, much lower than those reported for the hydrolysis of chromium–carbon bonds of  $(\text{D}_2\text{O})_5\text{CrR}^{2+}$  complexes, where values of 6–8 for  $k_{\text{H}}/k_{\text{D}}$  have been found.<sup>22–24</sup> Of course, in the latter a substantial part of the measured isotope effect can (and probably does<sup>23</sup>) arise from the secondary effects associated with deuteration of the coordinated water molecules. The analogous effects are absent in the organonickel complexes.

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The activation entropies are all substantially negative, lying in a relatively narrow range clustered about  $-14 \text{ cal mol}^{-1} \text{ K}^{-1}$ . These negative values also support the assigned mechanism, since they reflect the considerable organization that must accompany the utilization of a solvent molecule in the activation process.

**Nucleophilic Assistance?** We considered whether the mechanism can take advantage of certain structural (five-coordinated) and electronic (high-spin  $d^8$ ) features of these complexes.<sup>5</sup> That is, is hydrolysis assisted by attack of a solvent molecule at the vacant coordination site trans to the alkyl group? This issue is particularly pertinent, in that solvent exchange may well occur by an associative pathway with just such trans attack.<sup>17</sup> The rate of hydrolysis proved to be unaffected by variation of  $[\text{OH}^-]$  over a substantial concentration range, pH 9–13. Thus no kinetic assistance is provided by  $\text{OH}^-$ , a nucleophile even more potent than water. In addition, the nucleophiles  $\text{OAc}^-$ ,  $\text{N}_3^-$ , and  $\text{NH}_3$  were without effect on the hydrolysis rate. For that reason we are inclined to discard a mechanism in which nucleophilic displacement from the trans position assists the electrophilic cleavage mechanism. This situation differs from the hydrolysis of organochromium cations, where evidence for such nucleophilic assistance has been documented.<sup>25–27</sup>

**Accelerated Reactions.** We turn now to the cases that do not appear to fit the general pattern that governs almost all of the other complexes. The exceptional cases are the complexes  $\text{RNi}(\text{tmc})^+$  with  $\text{R} =$  cyclobutyl, cyclopentyl, 3-hydroxy-1-propyl, and benzyl, as follows.

**(a) Cycloalkyls.** The cyclobutyl complex was detected directly, although it is the fastest hydrolyzing of the complexes actually measured. The cyclopentyl complex hydrolyzes too rapidly for direct detection of its existence or measurement of its hydrolysis rate. Yet the product found clearly signals that it had been formed. Otherwise (as documented in other cases<sup>3</sup>), the products from dimerization and disproportionation of the free cyclopentyl radical would have been detected. The accelerated hydrolysis of the cycloalkylnickel complexes larger than cyclopropyl probably arises from repulsive nonbonded interactions with the ring *N*-methyl groups.

**(b) Hydroxyalkyls.** The data for the complexes  $\text{HO}(\text{CH}_2)_3\text{Ni}(\text{tmc})^+$  suggests that it adopts a special mechanism in which "attack" of the pendant OH group assists in the bond cleavage. This complex is unique in that it does not show the strong deuterium isotope effect demonstrated by  $\text{C}_2\text{H}_5\text{Ni}(\text{tmc})^+$  and other similar complexes. Furthermore, the activation enthalpy is much smaller, consistent with the additional bond making implied by the revised mechanism. The reaction is faster than the others, despite its being disfavored by an activation entropy that is substantially more negative than found for the others. The greater structural ordering implicit in this mechanism is believed to be responsible for the more negative value of  $\Delta S^\ddagger$ .

Related complexes such as  $\text{Br}(\text{CH}_2)_4\text{Ni}(\text{tmc})^+$  and  $\text{HO}(\text{CH}_2)_4\text{Ni}(\text{tmc})^+$  are characterized by a "normal" hydrolysis rate ( $(0.8\text{--}1.4) \times 10^{-2} \text{ s}^{-1}$ ) and a substantial kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 2.2$ , similar to that for ethyl). They are evidently unable to experience a kinetic acceleration from the analogous cyclic attack. The orientation of the OH group relative to the bond distances and angles within the complex is evidently sufficiently different, that the hydroxypropyl complex can react along a pathway that is not open to the hydroxybutyl complex. The five-membered cyclic transition state for the former undoubtedly provides a large kinetic advantage.

**(c) The benzyl complex** is perhaps the most difficult of the "unusual" cases to reconcile. It is one of the most hydrolytically stable of the complexes measured. This is particularly striking, in that the benzyl nickel complex of the other isomer,  $(R,R,S,S)\text{-PhCH}_2\text{Ni}(\text{tmc})^+$ , hydrolyzes so rapidly that it can be seen merely as a "flash of red color" when  $(R,R,S,S)\text{-Ni}(\text{tmc})^+$  and  $\text{PhCH}_2\text{Cl}$  are mixed. The nickel-carbon bond of the latter isomer hydrolyzes with  $t_{1/2} \sim 0.8 \text{ s}$  at  $25^\circ\text{C}$ , in contrast to the considerable kinetic stability of  $(R,S,R,S)\text{-PhCH}_2\text{Ni}(\text{tmc})^+$ . It is meaningful to compare the two, because all of the other alkylnickel complexes in the two tetramethylcyclam series react similarly (although quantitative rate constants for hydrolysis are being reported only for the one). At the present time, we offer no convincing rationale for the 100-fold difference between  $k_{\text{hyd}}$  for  $(R,S,R,S)\text{-PhCH}_2\text{Ni}(\text{tmc})^+$  ( $9.4 \times 10^{-3} \text{ s}^{-1}$ ) and the value for  $(R,R,S,S)\text{-PhCH}_2\text{Ni}(\text{tmc})^+$  ( $\sim 9 \times 10^{-1} \text{ s}^{-1}$ ).

**Acknowledgment.** This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

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