$$Cr^{III}\text{–}OOH + Fe^{II} \rightarrow Fe^{III}\text{–}OH + Cr^{III}\text{–}O^{\bullet} \quad (10)$$

$$Cr^{III}\text{–}O^{\bullet} \xrightarrow{H^+} Cr^{IV}\text{–}OH \xrightarrow{OAc^-} Cr^{IV}\text{–}OAc \quad (11)$$

$$Cr^{IV}\text{–}OAc + Cr^{III}\text{–}OOH \rightarrow Cr^{III}\text{–}OAc + Cr^{III}\text{–}O_2^{\bullet} + H^+ \quad (12)$$

$$Cr^{III}\text{–}O_2^{\bullet} + Fe^{III}\text{–}OH \rightarrow Cr^{III} + O_2 + Fe^{II} + OH^- \quad (13)$$

lyzed decomposition of H_2O_2.[28] Here the Fe(II)-induced homolysis of Cr(III)-bound peroxide (eq 10) is taken to yield a $Cr^{III}\text{–}O^{\bullet}$ fragment, which is rapidly converted (eq 11) via internal electron transfer and protonation to a Cr^{IV}–OH complex, derived from an oxidation state known to be substitution-labile.[29] Ligand substitution at this center should yield an acetato derivative of Cr(IV), which would undergo reduction by bound peroxide in the subsequent step (eq 12). At high acetate concentrations, partial conversion to diacetato species would be expected.

Finally, it may be asked why iron and (to a much lesser extent) copper are active catalysts for the Cr(IV)–NH_3OH^+ reaction whereas other transition metal ions fail. The suggested sequence (5)–(9) implies that the catalytic metal must exist in two accessible oxidation state differing by a single unit and that the higher must coordinate effectively with the hydroxylammonium cation. Moreover, the reduction potential of the upper state should be sufficiently positive to allow the electron transfer in step 9 to proceed, a requirement that excludes the poorly oxidizing Ti(IV).[30]

Catalysis by the Co(II,III) pair is probably disfavored by the multiplicity gap separating high-spin Co(II) from low-spin Co(III) (the predominant states in the more usual ligand environments). Beyond this, it is desirable that ligand substitution at the upper of the two catalytic metal states be rapid. Thus, the catalytic action of Fe(III) is eliminated in the presence of excess EDTA, and the systems $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, and $IrCl_6^{2-/3-}$ are found to be inactive, although each features a formal potential that should allow recycling between states in the system at hand.[31]

Acknowledgment. We thank Arla White for technical assistance.

(28) See, for example: Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. I, p 628.
(29) (a) Ogard, A. E.; Taube, H. *J. Phys. Chem.* **1958**, *62*, 357. (b) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.
(30) The formal potential for Ti(III,IV) is recorded as +0.056 V at 1 M H^+. This value drops sharply as pH is increased. See, for example: Latimer, W. M. *Oxidation Potentials*; 2nd ed.; Prentice-Hall, Englewood Cliffs, NJ, 1952; p 368.

(31) A reviewer suggests an alternate sequence, (14)–(17), in which Fe(II) attacks a peroxide ligand, forming a Cr(IV) bound hydroxyl species, II,

$$\underset{\text{I}}{Cr^{IV}(O_2)_2} + Fe^{II} \xrightarrow{H_2O} \underset{\text{II}}{(O_2)Cr^{IV}(OH^{\bullet})} + FeOH^{2+} \quad (14)$$

$$\underset{\text{II}}{(O_2)Cr^{IV}(OH^{\bullet})} \rightarrow \underset{\text{III}}{(O_2^-)Cr^{IV}(OH)} \quad (15)$$

$$\underset{\text{III}}{(O_2^-)Cr^{IV}(OH)} \rightarrow O_2 + \underset{\text{IV}}{Cr^{III}(OH)} \quad (16)$$

$$Cr^{III}(OH) + OAc^- \rightarrow Cr^{III}(OH)(OAc) \quad (17)$$

followed by internal conversion to a superoxo complex, III, which, in turn, yields O_2 and a coordinatively unsaturated Cr(III) intermediate, IV. Acetate then enters the coordination sphere of the latter. This scheme, in which the role of NH_3OH^+ is to maintain an adequate concentration of catalytic Fe(II), accommodates the observed stoichiometry and the intrusion of carboxylate from the medium. It does not appear, however, to be consistent with rate law 2, because the Fe(III)–NH_3OH^+ redox reaction is known to be slow. The Cr(IV) complex would function as a scavenger for Fe(II), and the kinetic dependence on [Cr^{IV}] would disappear. In addition, this scheme suggests that the incorporation of acetate is dependent on the extrusion of O_2, whereas our earlier experiments with the Cr(IV)–Ti(III) system[3d] show that acetate intrudes even when all bound peroxide is reduced to water.

Contribution from Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Reactions of Disubstituted Alkanes with a Nickel(I) Macrocycle

M. S. Ram, Andreja Bakac,* and James H. Espenson*

Received April 27, 1988

The reactions of disubstituted alkanes, $X(CH_2)_nY$ (X, Y = Cl, Br, I, OH, OTs), with the cationic macrocyclic ion (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), abbreviated Ni(tmc)$^+$, are characterized by kinetic accelerations compared to the rates for the monohalides, most noticeably for the smaller molecules, n = 2, 3. No transient organonickel species is detected for any vicinal disubstituted alkane, and the alkene is formed quantitatively. This is attributed to a "reductive elimination" reaction between Ni(tmc)$^+$ and the radical $^{\bullet}CH_2CH_2OH$, known to result from the very rapid unimolecular solvolysis of the initially formed $^{\bullet}CH_2CH_2Y$. Although $Br(CH_2)_3OH$ yields 1-propanol from the hydrolysis of the observed species (tmc)Ni$(CH_2)_3OH^+$, 1,3-disubstituted propanes (X, Y = Br, Cl, OTs) form cyclopropane exclusively. A rapid, unimolecular reaction of (tmc)Ni$(CH_2)_3Y^+$ appears responsible. The 1,4-disubstituted alkanes yield (tmc)Ni$(CH_2)_4Y^+$ with deficient Ni(tmc)$^+$, but ethylene is formed rapidly and quantitatively in the presence of even a catalytic concentration of Ni(tmc)$^+$ (with Y = Br, I and to some extent Y = Cl). Similarly, (tmc)NiCH$(CH_3)(CH_2)_3Y^+$ forms a 1:1 mixture of ethylene and propene (Y = Br, I) when Ni(tmc)$^+$ is present and otherwise hydrolyzes to 1-Y-pentane. Alkene formation from 1,4-disubstituted alkanes is attributed to the reaction of (tmc)Ni$(CH_2)_4Y^+$ with Ni(tmc)$^+$, producing a species (tmc)Ni$(CH_2)_4^{\bullet+}$ that yields ethylene and regenerates Ni(tmc)$^+$. The formation of cyclopentane as the exclusive product from the reaction of 1,5-dibromopentane with excess Ni(tmc)$^+$ is attributed to a unimolecular reaction of (tmc)Ni$(CH_2)_5^{\bullet+}$.

Introduction

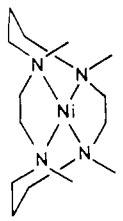
Some results concerning the nickel alkyls of the tetraaza macrocycle known as tmc[1] have already been reported.[2-5] These include the characterization of the mechanism by which nickel–carbon bonds are formed[3,4] and some of the reactions they undergo.[6,7]

(1) The complex depicted is (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), which we abbreviate as (*R*,*S*,*R*,*S*)-Ni(tmc)$^+$ or, when it is not confusing, simply as Ni(tmc)$^+$. Convenient electrochemical, photochemical, and chemical methods have been reported[2-4] for the preparation of the highly unstable and air-sensitive solutions of the nickel(I) reagent from the nickel(II) salt, which is very stable and is readily prepared.[5]

(2) Jubran, N.; Ginzburg, G.; Cohen, H.; Koresh, Y.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251.
(3) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713.
(4) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, 3267.
(5) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(6) Ram, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4115.
(7) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 5353.

0020-1669/88/1327-4231$01.50/0 © 1988 American Chemical Society

We have now devoted some effort to the reactions of disubstituted alkanes with $Ni(tmc)^+$. It has already been communicated that 1,4-dihaloalkanes and 1,5-dihaloalkanes yield exclusively ethylene and cyclopentane, respectively.[8,9]



(*R,S,R,S*)-$Ni(tmc)^+$

Reactions of $Ni(tmc)^+$ with a considerable number of disubstituted alkanes, $X(CH_2)_nY$ (n = 2–6; X, Y = Cl, Br, I, OH, OTs), are considered here. The literature reports some earlier kinetic data for reactions of dihaloalkanes with other metal complexes, including those of chromium(II),[10-14] cobalt(II),[15-18] iron(II),[19] and rhodium(I).[20] We are particularly interested in evaluating kinetic accelerations relative to the rates for monohalides, which are often quite substantial, particularly for the smaller molecules, n = 2, 3. It is also important to establish whether organonickel complexes are formed, either as kinetically stable species or as transient intermediates.

Experimental Section

The complex (*R,S,R,S*)-$[Ni(tmc)](ClO_4)_2$[4,5] was reduced electrochemically to $Ni(tmc)^+$ in aqueous 0.02 M NaOH–0.08 M $LiClO_4$ immediately prior to use.[3,4] The solutions of the nickel(I) complex are extremely air-sensitive and were handled by careful syringe–septum techniques. Organic halides were distilled before use.

Kinetic data for the reactions of Ni(I) were obtained spectrophotometrically by using a Cary 219 or Cary 14 spectrophotometer for the slower reactions and a Canterbury SF3A stopped-flow spectrophotometer for the more rapid ones. Data collection and analysis for the last two instruments were performed with the OLIS 3820 kinetic data system. The precision of the kinetic data is about 8%.

The absorption maximum of nickel(I) at 352 nm (ϵ 4.0 × 10^3 M^{-1} cm^{-1}) was used to follow the progress of the main reaction. If an organonickel derivative was formed, its subsequent decomposition was monitored at the absorption maximum near 405 nm, where the molar absorptivity is typically 2 × 10^3 M^{-1} cm^{-1}. The characteristic UV–visible spectrum is sufficient to recognize the organometallic species $(tmc)NiR^+$, which have previously been more fully characterized.[3,4,6,7] The organic products of the main reaction or of hydrolysis reactions were hydrocarbons or substituted hydrocarbons. They were identified by VPC, using commercial columns in a Hewlett-Packard Model 5790 gas chromatograph. The retention times and peak areas were calibrated with known materials.

Results and Interpretation

1,2-Disubstituted Alkanes. Ethylene was formed in the reactions of $Ni(tmc)^+$ with $Br(CH_2)_2Br$, $Cl(CH_2)_2Cl$, $Br(CH_2)_2OH$, and $Br(CH_2)_2OTs$. Propene was the only organic product from the reactions of $BrCH_2CH(OH)CH_3$ and $ClCH_2CH(OH)CH_3$. The reaction of dl-$CH_3CH(Cl)CH(Cl)CH_3$ with $Ni(tmc)^+$ gave 72% *trans*-2-butene and 28% *cis*-2-butene. The chemical equation describing these reactions can be written as

$$X(CHR)_2Y + 2Ni(tmc)^+ \rightarrow H(R)C{=}C(R)H + 2Ni(tmc)^{2+} + X^- + Y^- \quad (1)$$

$$R = H, CH_3$$

The reaction rates follow the previously noted[3,4] second-order rate law, with the rate constant defined as in eq 2. Kinetic data

$$-d[Ni(tmc)^+]/2dt = -d[X(CH_2)_nY]/dt = k_2[Ni(tmc)^+][X(CH_2)_nY] \quad (2)$$

are given in Table I. The reactions occur very rapidly in comparison with those of the monohalo analogues. For example, $k(C_2H_4Br_2) > 2 \times 10^5$ M^{-1} s^{-1} versus $k(C_2H_5Br) = 9.5 \times 10^2$ M^{-1} s^{-1} and $k(C_2H_4Cl_2) = 2.6 \times 10^2$ M^{-1} s^{-1} versus $k(C_2H_5Cl) \cong 2$ M^{-1} s^{-1}. No organonickel complex was evident in any of the reactions with 1,2-disubstituted alkanes. By that statement we mean that there was no indication in the UV–vis range for the spectrum characteristic of $(tmc)NiR^+$, with a typical hydrolysis rate constant of ~0.01 s^{-1}.[6]

Table I. Kinetics and Products of Reaction of $Ni(tmc)^+$ with 1,2-Disubstituted Alkanes[a]

compd	range of [RX]/mM	k_2/M^{-1} s^{-1}	organic product
$Br(CH_2)_2Br$	0.5	$>2 \times 10^5$	ethylene
$Cl(CH_2)_2Cl$	0.5–12	2.6×10^2	ethylene
$Br(CH_2)_2OH$	1.0–8.0	3×10^3	ethylene
$Br(CH_2)_2OTs$			ethylene
$BrCH_2CH(OH)CH_3$			propene
$ClCH_2CH(Cl)CH_3$			propene
dl-$CH_3CH(Cl)CH(Cl)CH_3$			2-butenes[b]

[a] At 25 °C in 0.02 M NaOH–0.08 M $LiClO_4$. [b] 72% trans, 28% cis.

1,3-Disubstituted Alkanes. The 1,3-dibromo- and 1,3-dichloropropanes gave only cyclopropane as product, as did $Br(CH_2)_3OTs$. On the other hand, the reaction of $Br(CH_2)_3OH$ yielded a detectable organonickel complex, $(tmc)Ni(CH_2)_3OH^+$. As expected from earlier work[3] on the hydrolysis reactions, 1-propanol was the product of its decomposition.

Kinetic determinations were limited to a single compound; $Cl(CH_2)_3Cl$ reacted with $Ni(tmc)^+$ according to second-order kinetics (eq 2) with k_2 = 19.1 M^{-1} s^{-1}, compared to 2.2 M^{-1} s^{-1} for 1-chloropropane.

1,4-Disubstituted Alkanes. More so than in the previously described reactions, the phenomena observed depend on the identities of groups X and Y in the particular $X(CH_2)_4Y$ molecule and on the reaction conditions. The compounds $Br(CH_2)_4Cl$, $Br(CH_2)_4OH$, and $Br(CH_2)_4OTs$ behaved like conventional monohalides. That is, each reaction was accompanied by the formation of an organonickel complex, a bright yellow species with an absorption maximum near 405 nm. In each of these cases, the nickel alkyl hydrolyzes slowly, with a half-life near 1 min, which is the behavior characteristic[9] of virtually all of the simple alkyl complexes $RNi(tmc)^+$. Consistent with hydrolysis, the first two compounds produced 1-chlorobutane and 1-butanol, respectively; presumably the third gave butyl tosylate, but that was not confirmed. In these instances the net reactions occurring were simply those represented by eq 3, followed by hydrolysis (eq 4).

$$Br(CH_2)_4Y + 2Ni(tmc)^+ \rightarrow (tmc)NiBr^+ + (tmc)Ni(CH_2)_4Y^+ \quad (3)$$

$$(tmc)Ni(CH_2)_4Y^+ + H_2O \rightarrow (tmc)NiOH^+ + Y(CH_2)_3CH_3 \quad (4)$$

These reactions are "ordinary" not only as regards the formation of the alkylnickel complexes and the hydrolysis products but also in the rates of the bromine atom abstraction step that begins the sequence summarized in eq 3. The reaction of $Br(CH_2)_4OH$ with $Ni(tmc)^+$ has $k_2 = 3.6 \times 10^5$ M^{-1} s^{-1}, very much like that for 1-bromobutane, 1.5 × 10^5 M^{-1} s^{-1}.

(8) Espenson, J. H.; Ram, M. S.; Bakac, A. *J. Am. Chem. Soc.* **1987**, *109*, 6892.
(9) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 2011.
(10) Castro, C. E.; Kray, W. C., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 2768.
(11) Stephan, D.; Gorgues, A.; LeCoq, A. *Tetrahedron Lett.* **1984**, *25*, 5649.
(12) Kray, W. C., Jr.; Castro, C. E. *J. Am. Chem. Soc.* **1964**, *86*, 4603.
(13) Singleton, D. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 6547.
(14) Kochi, J. K.; Singleton, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1582.
(15) Smith, E. L.; Mervyn, L.; Muggleton, P. W.; Johnson, A. W.; Shaw, N. *Ann. N.Y. Acad. Sci.* **1964**, *112*, 565.
(16) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738.
(17) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582.
(18) Espenson, J. H.; Chao, T.-H. *Inorg. Chem.* **1977**, *16*, 2553.
(19) Eberhardt, M. K. *J. Org. Chem.* **1984**, *49*, 3720.
(20) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 218.

Table II. Rate Constants for the Hydrolysis of Organonickel Complexes of Substituted Alkyls[a]

complex	$k_{hyd}/10^2$ s^{-1}
$Br(CH_2)_4Ni(tmc)^+$	1.3
$I(CH_2)_4Ni(tmc)^+$	2.7
$HO(CH_2)_4Ni(tmc)^+$	0.8
$TsO(CH_2)_4Ni(tmc)^+$	0.7
$Cl(CH_2)_4Ni(tmc)^+$	0.7
$Br(CH_2)_5Ni(tmc)^+$	1.6
$Br(CH_2)_6Ni(tmc)^+$	1.1

[a] At 25 °C in 0.020 M NaOH–0.080 M $LiClO_4$.

With other 1,4-disubstituted compounds, however, the behavior was more complex. Consider the case of $Br(CH_2)_4Br$. Only when $Ni(tmc)^+$ was present in stoichiometrically deficient quantity was the chemistry similar to that described above. Under such conditions, a seemingly ordinary organonickel complex was formed. It was identified as $(tmc)Ni(CH_2)_4Br^+$ on the basis of its hydrolysis to 1-bromobutane with the rate constant of 1.3×10^{-2} s^{-1}. The hydrolysis rate constants of other $(tmc)Ni(CH_2)_nY^+$ complexes lie in the same narrow range, as summarized in Table II.

When 1,4-dibromobutane was present in stoichiometric or deficient quantity, the situation changed dramatically. The reaction occurred in two stages, a rapid phase with 1–4-s half-time, which typically accounted for 80% of the absorbance change, followed by the balance of the absorbance change, which occurred at the hydrolysis rate, $t_{1/2} \approx 1$ min. The major product was ethylene. Some butyl bromide was also produced in these reactions, but its yield depended on the proportion of the slow reaction phase. Acidification immediately after the mixing of $Ni(tmc)^+$ and $Br(CH_2)_4Br$ increased the proportion of butyl bromide, but even then substantial amounts of ethylene were found. Some butane was also found, but the yields (<25%) were always much smaller than the ethylene yields. The stoichiometry, even with $Ni(tmc)^+$ in excess, never approached the 4:1 ratio expected if each bromine atom reacted independently.

These results can be presented in terms of three independent chemical equations of stoichiometric but not mechanistic significance:

$$2Ni(tmc)^+ + Br(CH_2)_4Br + H_2O \rightarrow 2Ni(tmc)^{2+} + n\text{-}BuBr + Br^- + OH^- \quad (5)$$

$$4Ni(tmc)^+ + Br(CH_2)_4Br + 2H_2O \rightarrow 4Ni(tmc)^{2+} + n\text{-}C_4H_{10} + 2Br^- + 2OH^- \quad (6)$$

$$2Ni(tmc)^+ + Br(CH_2)_4Br \rightarrow 2Ni(tmc)^{2+} + 2C_2H_4 + 2Br^- \quad (7)$$

The first of these is the reaction that predominates when $Ni(tmc)^+$ is not present in excess. It gives rise to the organonickel intermediate $(tmc)Ni(CH_2)_4Br^+$, which releases butyl bromide by hydrolysis. This complex has the composition shown and is not, for example, the dimetallic complex $(tmc)Ni(CH_2)_4Ni(tmc)^{2+}$. This claim is supported by the stoichiometry, the hydrolysis product found, and the formation of independently identified $Co(dmgH)_2(CH_2)_4Br$ upon reaction with $Co^{II}(dmgH)_2$. Since to some extent the formation and hydrolysis reactions overlap in time, the butyl bromide product can react with still-present $Ni(tmc)^+$ to yield butane as a minor side product. The net effect is represented by eq 6. When $Ni(tmc)^+$ is present in ≥2:1 excess over the dibromide, the reaction is represented by eq 7. This results from the formation of $(tmc)Ni(CH_2)_4Br^+$ (eq 3) followed by a catalytic reaction between the organonickel complex and $Ni(tmc)^+$ (eq 8). This process also occurs when $Ni(tmc)^+$ is added to a

$$Br(CH_2)_4Ni(tmc)^+ \xrightarrow{Ni(tmc)^+} Ni(tmc)^{2+} + 2C_2H_4 + Br^- \quad (8)$$

sample of the organonickel complex previously prepared in situ.

Similar results were obtained with 1,4-diiodobutane. Ethylene was again the sole product when $Ni(tmc)^+$ was present in excess. The products from 1,4-dibromopentane were the analogous alkenes, ethylene and propene, formed in equal amounts. In effect the (4-bromobutyl)- and (4-iodobutyl)nickel complexes react as in eq 8, whereas analogous complexes with Cl, OH, or OTs groups on C4 undergo hydrolysis to yield 1-substituted butanes.

Table III. Kinetic Data[a] for the Reactions of Various 1,4-Disubstituted Butanes with $Ni(tmc)^+$

reactant	$k_2/10^{-3}$ M^{-1} s^{-1}	organic products
$Br(CH_2)_4Ni(tmc)^+$		ethylene
$Br(CH_2)_4H$	1.5	butane
$Br(CH_2)_4Br$	4.5[b]	ethylene[c]
$Br(CH_2)_4Cl$	3.6	1-chlorobutane
$Br(CH_2)_4OH$	3.6	1-butanol
$Br(CH_2)_4OTs$	1.5	(butyl tosylate)[d]
$CH_3CH(Br)(CH_2)_3Br$	8.5[e]	ethylene + propene (1:1)[c]
$BrCH_2CH{=}CHCH_2Br$	>200	1,3-butadiene
$Br(CH_2)_5Br$	4.2[b]	cyclopentane
$Br(CH_2)_6Br$	~0.8[b]	mixture[c,f]

[a] At 25 °C in aqueous 0.020 M NaOH–0.080 M $LiClO_4$ solution. [b] Divided by a statistical factor of 2 to facilitate comparison. [c] When excess $Ni(tmc)^+$ is used. [d] Presumed. [e] Compare to the rate for a secondary alkyl bromide; e.g., for 2-bromopropane, $k = 2.8 \times 10^3$ M^{-1} s^{-1}. [f] With excess $Ni(tmc)^+$, the vapor phase contains 1-hexene (40%), cyclohexane (40%), and *n*-hexane (20%); the liquid phase also contains a small amount of 1-bromohexane.

Further quantitative results bearing on these systems were possible, with kinetic data obtained for reactions of $Br(CH_2)_4Y$ with $Ni(tmc)^+$. Indeed, the comparison for the cases Y = (a) $Ni(tmc)^+$, (b) H, (c) Br or I, and (d) Cl, OH, or OTs are instructive. The kinetic and product data are given in Table III. The rate constants vary little among these four categories. This suggests that in every case the kinetics reflect the rate of bromine atom abstraction from RBr by $Ni(tmc)^+$.

In the reaction of *trans*-1,4-dibromo-2-butene with $Ni(tmc)^+$, 1,3-butadiene was formed. This occurs very rapidly ($k_2 > 2 \times 10^5$ M^{-1} s^{-1}), without the formation of an observable organonickel intermediate.

1,5- and 1,6-Disubstituted Alkanes. The reaction of $Ni(tmc)^+$ with $Br(CH_2)_5Br$ resembled that with 1,4-dibromobutane in many ways. The reaction produced cyclopentane and 1-bromopentane in proportions that depended on the concentrations of the two reactants. With deficient $Ni(tmc)^+$, the expected organonickel intermediate was seen; it subsequently yielded 1-bromopentane. With an excess of $[Ni(tmc)^+]$ as small as 10^{-4} M, the intermediate was formed but transiently and cyclopentane predominated. Even with a 4:1 excess of $Ni(tmc)^+$, the yield of *n*-pentane is less than 25% of that for cyclopentane.

The reaction of excess $Ni(tmc)^+$ with 1,6-dibromohexane produced 1-hexene, cyclohexane, and *n*-hexane; some 1-bromohexane was found in the liquid phase. A typical organonickel intermediate was detected, which hydrolyzed normally ($t_{1/2} \approx 60$ s). This reaction was not studied in great detail because of the low solubility of the 1,6-dibromide.

Discussion

The issues to be considered are (1) the kinetic accelerations, most noticeably for the 1,2-disubstituted alkanes, (2) product formation without the detectable intervention of $(tmc)Ni(CH_2)_nY^+$ complexes for $n = 2, 3$, (3) the formation of ethylene and other alkenes in the reactions of 1,4-disubstituted alkanes with excess $Ni(tmc)^+$, and (4) the formation of cyclopentane from 1,5-dibromopentane in analogous circumstances.

The well-characterized initial step in the reaction of monobromo- and monoiodoalkanes with $Ni(tmc)^+$ is the (presumably inner-sphere) reduction of RX (eq 9).[3,4]

$$Ni(tmc)^+ + RX \rightarrow XNi(tmc)^+ + R^\bullet \quad (9)$$

There is every reason to believe that all of the disubstituted organic bromides and iodides react with $Ni(tmc)^+$ analogously. The principal issues are to understand the kinetic accelerations and the fates of the free radicals so produced.

Kinetic Accelerations. The rates of the dihalides are substantially enhanced relative to those of their monohalo analogues, the

more so the fewer the number of intervening methylene units. The trivial case is that of dichloromethane ($k/2 = 3.4 \times 10^3$ M^{-1} s^{-1}); the dibromo and diiodo analogues react too rapidly ($k > 10^5$ M^{-1} s^{-1}) for stopped-flow detection. We estimate that CH_2Cl_2 is accelerated relative to CH_3Cl by a factor of about 3000. (The rate constant for methyl chloride is estimated very roughly as 1 M^{-1} s^{-1} from the rate constants[4] available for methyl iodide (1.7×10^3 M^{-1} s^{-1}), 1-propyl chloride (2.2 M^{-1} s^{-1}), and 1-propyl iodide (3.3×10^3 M^{-1} s^{-1}).)

Rate constants for $Br(CH_2)_2Br$ ($k > 10^5$ M^{-1} s^{-1}) and $Cl(CH_2)_2Cl$ ($k/2 = 1.3 \times 10^2$ M^{-1} s^{-1}) are substantially enhanced relative to those for the respective standards C_2H_5Br (9.5×10^2 M^{-1} s^{-1})[4] and C_3H_7Cl (2.2 M^{-1} s^{-1}).[4]

Other reactions known to proceed by abstraction of a halogen atom are similarly accelerated. For example, (a) $Co(CN)_5^{3-}$ reacts 1100 times more rapidly with $I(CH_2)_2I$ than it does with C_2H_5I,[17] (b) *trans*-1,2-dibromocyclohexane reacts with Cr^{2+} in ethanol 3000 times more rapidly than bromocyclohexane does, whereas the cis isomer is affected to a much smaller extent,[13] and (c) Cr^{2+} in aqueous dimethylformamide reacts 4600 times more rapidly with $Br(CH_2)_2Br$ than with *n*-propyl bromide.[12] The rate acceleration caused by a β-halo substituent was first recognized by Kray and Castro,[12] who attributed it to the ability of the neighboring halogen to stabilize a halogen-bridged bromoethyl radical. The validity of this suggestion was strengthened by the large difference in rates of reaction of *cis*- and *trans*-1,2-dibromocyclohexane by chromium(II)[13] and by the stereospecificity attending other eliminations of vicinal dihalides.[14] Others suggest that the accelerations are caused by inductive effects or "through-bond" interactions involving orbital mechanisms.[21] The general situation regarding bridged haloalkyl radicals has been reviewed.[22]

These accelerations appear limited to reactions occurring by atom abstraction mechanisms, as is the case for all the examples cited above. On the other hand, the reactions of a rhodium(I) macrocycle, which occur by two-electron, S_N2-like mechanisms, are not significantly accelerated for vicinal dihalides as compared to monohaloalkanes.[20] For example, $Br(CH_2)_2Br$ ($k/2 = 2.3 \times 10^{-2}$ M^{-1} s^{-1}) reacts comparably to 1-bromobutane (1.7×10^{-2} M^{-1} s^{-1}).

The 1,3-disubstituted alkanes are also accelerated in their reactions with $Ni(tmc)^+$. Thus, $Cl(CH_2)_3Cl$ ($k/2 = 9.6$ M^{-1} s^{-1}) reacts a factor of 4.4 more rapidly than C_3H_7Cl (2.2 M^{-1} s^{-1}),[4] an effect comparable to those found[17] in the reactions of $Co(CN)_5^{3-}$ with $I(CH_2)_3I$ ($k/2 = 0.50$ M^{-1} s^{-1}) and $I(CH_2)_3Br$ ($k = 0.68$ M^{-1} s^{-1}) relative to 1-iodopropane ($k = 0.043$ M^{-1} s^{-1}).

Still more modest effects are found for 1,4- and 1,5-disubstituted alkanes. Thus, $Br(CH_2)_4Br$ ($k/2 = 4.5 \times 10^3$ M^{-1} s^{-1}), $Br(CH_2)_4Cl$ ($k = 3.6 \times 10^3$ M^{-1} s^{-1}), and $Br(CH_2)_5Br$ ($k/2 = 4.3 \times 10^3$ M^{-1} s^{-1}) react with $Ni(tmc)^+$ only about 3 times more rapidly than 1-bromobutane ($k = 1.5 \times 10^3$ M^{-1} s^{-1})[4] does. The 1,4-dibromo compound that would react initially at the secondary halogen, $CH_3CH(Br)(CH_2)_3Br$ ($k = 8.5 \times 10^3$ M^{-1} s^{-1}), is also only 3 times more reactive than 2-bromopropane ($k = 2.8 \times 10^3$ M^{-1} s^{-1}).[4]

Alkene Formation from 1,2-Disubstituted Alkanes. We can illustrate numerous possibilities by considering conceivable alternative fates of the radical $^{\bullet}CH_2CH_2Br$, the species initially formed in the reaction of 1,2-dibromoethane. They are as shown in the seven options

(i) homolytic β-cleavage

$$^{\bullet}CH_2CH_2Br \rightarrow CH_2{=}CH_2 + Br^{\bullet}$$

(ii) hydrolysis

$$^{\bullet}CH_2CH_2Br + H_2O \rightarrow {}^{\bullet}CH_2CH_2OH + Br^- + H^+$$

(iii) reduction by $Ni(tmc)^+$

$$^{\bullet}CH_2CH_2Br + Ni(tmc)^+ \rightarrow {}^{-}CH_2CH_2Br + Ni(tmc)^{2+}$$

(iv) capture by $Ni(tmc)^+$

$$^{\bullet}CH_2CH_2Br + Ni(tmc)^+ \rightarrow Ni(tmc)CH_2CH_2Br^+$$

(v) hydrolysis followed by reduction

$$^{\bullet}CH_2CH_2OH + Ni(tmc)^+ \rightarrow {}^{-}CH_2CH_2OH + Ni(tmc)^{2+}$$

(vi) hydrolysis followed by capture

$$^{\bullet}CH_2CH_2OH + Ni(tmc)^+ \rightarrow Ni(tmc)CH_2CH_2OH^+$$

(vii) "reductive elimination", which may or may not be preceded by hydrolysis

$$^{\bullet}CH_2CH_2Br + Ni(tmc)^+ \rightarrow Ni(tmc)^{2+} + CH_2{=}CH_2 + Br^-$$

$$^{\bullet}CH_2CH_2OH + Ni(tmc)^+ \rightarrow Ni(tmc)^{2+} + CH_2{=}CH_2 + OH^-$$

Of these options, pathway vii is preferred, both because there are precedents[19] for this type of reaction and because the other pathways can be ruled out on the basis of other experimental results. We recognize the possibility that the organonickel complexes $(tmc)NiCH_2CH_2Br^+$ (pathway iv) and $(tmc)NiCH_2CH_2OH^+$ (pathway vi) are formed as intermediates in pathway vii.

Although homolytic β cleavage of carbon–bromine bonds as in pathway i is known,[23,24] it has been shown[25] by pulse radiolysis that in aqueous solution a more rapid reaction of β-bromoalkyl radicals produced is hydrolysis as in pathway ii, unless the bromo radical is first intercepted by another reaction.

A mechanism in which a radical is reduced to an anion, e.g., pathway iii or v, may be discounted for the following reasons. Such a carbanion would be immediately converted in a protic medium to the respective alkyl derivative, bromoethane or ethanol, respectively. Neither of these would give ethylene under these circumstances; C_2H_5Br would yield ethane via a detectable ethylnickel complex, and the alcohol shows no reaction with $Ni(tmc)^+$.

For the β-bromoethyl radical to be captured by $Ni(tmc)^+$ (pathway iv), prior to its solvolysis pathway ii), requires $k_{iv}[Ni(tmc)^+] \gg k_{ii}$. With k_{ii} about 10^4 s^{-1}, a value estimated from determinations[25] on closely related systems, this requires $k_{iv} \gg 10^8$ M^{-1} s^{-1} with $[Ni(tmc)]^+ \approx 10^{-4}$ M. This appears inconsistent with the value of $\sim 10^{7.4}$ determined[4] for the capture of primary radicals by $Ni(tmc)^+$. The values of the rate constants are, however, not so different as to permit a decisive conclusion. The failure to observe $(tmc)NiCH_2CH_2Br^+$ in this system does not rule out its transient existence. The β-elimination from such a complex is expected to be very fast,[13] and it would yield the observed products. Similar arguments could be applied to $(tmc)NiCH_2CH_2OH^+$, although the rate constant for β-elimination from this complex in alkaline solutions would be expected to be significantly smaller than for the bromoethyl derivative.

It has been reported[19] that ethylene is formed from the reaction of $^{\bullet}CH_2CH_2OH$ with the powerful reducing reagent $Fe^{II}(edta)$ and from the reaction of $^{\bullet}CH_2CH_2Br$ with the mildly reducing $Fe^{2+}(aq)$.[26] These precedents suggest that the most likely processes for ethylene formation in this system are either or both of the reactions shown in pathway vii.

Cyclopropane Formation from 1,3-Disubstituted Alkanes. Cyclopropane is formed from the reactions of $Br(CH_2)_3Br$, Cl-

(21) Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3329.
(22) Kaplan, L. *Bridged Free Radicals*; Marcel Dekker: New York, 1972; pp 302–303.
(23) Barker, R.; Maccol, A. *J. Chem. Soc.* **1963**, 2839.
(24) Nonhebel, D. C., Walton, J. C., Eds. *Free Radical Chemistry*; Cambridge University Press: Cambridge, England, 1974; pp 472–475.
(25) Koltzenburg, G.; Behrens, G.; Schulte-Frohlinde, D. *J. Am. Chem. Soc.* **1982**, *104*, 7311.
(26) These are perfectly reasonable reactions for the pair of iron(II) reagents.[19] It is not clear, however, why the reaction between Fe^{2+} and $^{\bullet}CH_2CH_2Br$ occurs more rapidly than hydrolysis of the radical, whereas $Fe^{II}(edta)$ reacts only after hydrolysis, given that reduction of $^{\bullet}CH_2CH_2Br$ by $Fe^{II}(edta)$ has a much greater driving force than reduction by Fe^{2+}.

$(CH_2)_3Cl$, and $Br(CH_2)_3OTs$ with $Ni(tmc)^+$, whereas $Br(CH_2)_3OH$ yields only 1-propanol. The first three give no detectable organometallic intermediate, whereas the fourth proceeds via the independently known $(tmc)Ni(CH_2)_3OH^+$. The formation of cyclopropane by the reactions of 1,3-dihalopropanes has been reported for $Co(CN)_5^{3-}$,[17,27] Cr(II),[28] and $Co(dmgH)_2$.[16]

If the reactions of $Ni(tmc)^+$ yielding cyclopropane proceed via organometallic intermediates, they must readily undergo the reaction

$$(tmc)Ni(CH_2)_3X^+ \rightarrow Ni(tmc)^{2+} + c\text{-}C_3H_6 + X^- \quad (10)$$

It seems perfectly reasonable to suggest that this, in fact, is responsible for the results obtained, since the better leaving groups (X = Br, Cl, OTs) readily react as shown, whereas the poorer one (X = OH) exists in a complex that hydrolyzes as in eq 4.

Alkene Formation from 1,4-Disubstituted Alkanes. The reactions of $Br(CH_2)_4Br$ and analogues (Table III) proceed via a distinct organometallic intermediate, $(tmc)Ni(CH_2)_4X^+$, a species that can be observed directly and that hydrolyzes to 1-X-butane in a spontaneous manner or by addition of H_3O^+. The fact that this complex yields ethylene only in the presence of a catalytic concentration of $Ni(tmc)^+$ rules out any direct pathway to this product. This is unlike the case for $Br(CH_2)_4Li$, for which a Grob-type rearrangement has been suggested for ethylene formation (eq 11).[29]

$$Li\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}Br \rightarrow Li^+ + 2C_2H_4 + Br^- \quad (11)$$

It is also unlike the results for the reactions of $Br(CH_2)_4Br$ with Cr^{2+} [10] and with $Co(CN)_5^{3-}$.[17] In these cases the product is butane, the usual product of successive single-electron reductions. The intermediacy of a tetramethylene diradical in the $Ni(tmc)^+$ case can also be discounted, since the diradical is known[30] to undergo competitive cyclization and fragmentation, yet no cyclobutane was found here.

On the basis of the relative reaction rates of $(tmc)Ni(CH_2)_4Br^+$ and 1-bromobutane, and similar comparisons (Table III), we suggest that the initial step is an electron-transfer reaction between the haloalkyl complex and $Ni(tmc)^+$:

$$(tmc)Ni(CH_2)_4X^+ + Ni(tmc)^+ \rightarrow XNi(tmc)^+ + (tmc)Ni(CH_2)_3CH_2^{\bullet+} \quad (12)$$

The reaction occurs readily for the iodide and bromide, slowly for the chloride, and not at all for X = OH or OTs. This trend supports the assignment of the initial reaction as the indicated inner-sphere electron-transfer reaction. In addition, when the 1,4-disubstituted compounds $BrCH(CH_3)(CH_2)_3X$ are used, the products with excess $Ni(tmc)^+$ are ethylene and propene (1:1) for X = Br, I, yet the product is 1-X-pentane for X = Cl, OH, and OTs. This again reflects simply the relative rates of inner-sphere electron-transfer reactions and hydrolyses of the organonickel intermediates.

In keeping with the effect of $Ni(tmc)^+$ on the 4-halobutyl complex being a catalytic and not a stoichiometric one, the fate of the nickel-bearing radical formed in eq 12 may be alkene formation with Ni(I) release. This may perhaps proceed via a metallacycle, for which some precedents can be cited.[31-33] This is represented by

$$(tmc)Ni(CH_2)_3CH_2^{\bullet+} \rightarrow c\text{-}\{(tmc)Ni(CH_2)_4^+\} \rightarrow Ni(tmc)^+ + 2C_2H_4 \quad (13)$$

The nonbonded interactions in the metallacycle intermediate, given the planar macrocycle and especially the pendant $N\text{-}CH_3$ groups in the vicinity of the nickel–carbon bond, may disfavor the macrocyclic intermediate suggested in eq 13. Instead, one can also consider internal electron transfer with concerted C=C bond formation and Ni—C bond breakage. This alternative avoids the metallacyclic intermediate. The subtle distinction between these possibilities requires the use of 1,4-dihalides that are structurally more rigid than the ones used.

Cycloalkane Formation from 1,5-Disubstituted Alkanes. Here, too, there is observed directly an intermediate organonickel complex, shown to be $(tmc)Ni(CH_2)_5X^+$ by its hydrolysis to 1-bromopentane in the absence of excess $Ni(tmc)^+$. The further reaction of this complex with $Ni(tmc)^+$, in the cases of X = Br, I, is the process that leads to cyclopentane. The data suggest that these reactions also start by a halogen atom abstraction between $Ni(tmc)^+$ and the (haloalkyl)nickel complex, analogous to eq 12. The kinetic comparisons and stoichiometric data strongly support such an assignment.

Cyclopentane formation is quantitative when even a trace quantity of $Ni(tmc)^+$ is added to the organonickel species or when $Ni(tmc)^+$ is used initially in stoichiometric excess (>2:1) over 1,5-dibromopentane. Cyclization of the radical intermediate so generated is responsible for the product observed. The rate constant for eq 14 must exceed 10^5 s^{-1}, or else formation of a

$$(tmc)Ni(CH_2)_4CH_2^{\bullet+} \rightarrow c\text{-}\{(tmc)Ni(C_2H_5)^+\} \rightarrow Ni(tmc)^+ + c\text{-}C_5H_{10} \quad (14)$$

dimetallic complex would have occurred, given the rate constants at which primary carbon-centered radicals react with $Ni(tmc)^+$.

Precedents for *quantitative* cyclopentane formation are rare. Radical-induced reactions of 1,5-diiodopentane with peroxides form cyclopentane, but in yields of only 4–8%,[34] and the reaction of $Co(CN)_5^{3-}$ with the same compounds yields 1-pentene (94%) and *cis*-2-pentene (6%).[17] Excellent yields of cyclopentane are formed in reactions of 1,5-dihaloalkanes with sodium naphthalenide[35] and with *tert*-butyllithium.[36]

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

(27) Kwiatek, J. *Catal. Rev.* **1967**, *1*, 37.
(28) Kochi, J. *Rec. Chem. Prog.* **1966**, *27*, 307.
(29) Grubbs, R. H.; Brunck, T. K. *J. Am. Chem. Soc.* **1972**, *94*, 2538.
(30) (a) P. B. Dervan, as cited by: Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155. (b) Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863.
(31) Grubbs, R. H.; Brunck, T. K. *J. Am. Chem. Soc.* **1972**, *94*, 2538.
(32) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porzio, W.; Zocchi, M. *J. Chem. Soc., Dalton Trans.* **1983**, 967.
(33) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1977**, 52.
(34) Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 4059.
(35) Garst, J. H.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3329.
(36) Gailey, W. F.; Gagnier, R. P.; Particia, J. J. *J. Org. Chem.* **1984**, *49*, 2098.