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Ion Cyclotron Resonance Investigations of Alkylation of $(\eta^5\text{-}C_5H_5)Ni^+$ and $(\eta^5\text{-}C_5H_5)Fe^+$ by Methyl Halides in the Gas Phase

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A detailed study of the sequential alkylation of $(\eta^5\text{-}C_5H_5)Ni^+$ and $(\eta^5\text{-}C_5H_5)Fe^+$ by methyl bromide in the gas phase using the techniques of ion cyclotron resonance (ICR) spectroscopy is reported. A reaction mechanism for the alkylation process is proposed through the use of both ICR double resonance techniques and deuterium-labeled methyl bromide. The reactions of $CpNi^+$ with C_2H_5Br and of $CpNi^+$ and $CpFe^+$ with CH_3X (X = F, Cl, I) are briefly discussed.

Introduction

Ion cyclotron resonance spectroscopy (ICR) is proving to be a valuable tool for investigating the reactions,[1-3] thermochemistry,[3] and photochemistry[4] of metal ions in the gas phase. In the condensed phase, solvation effects may obscure the intrinsic reactivity of chemical species,[5] and complicating rapid equilibria between different reaction intermediates are common.[6] ICR methods, however, facilitate the study of single bimolecular ion–molecule encounters; reaction intermediates which may be similar to those hypothesized to occur in solution can be observed and reaction mechanisms proposed. The present work describes an ICR study of the sequential alkylation of the $CpNi^+$ and $CpFe^+$ cations[7] by repeated ion–molecule reaction with CD_3Br. The results are discussed in terms of a proposed mechanism for the alkylation process.

Experimental Section

The theory and instrumentation of ICR mass spectrometry have been previously described.[8-10] This work employed an instrument constructed at Caltech equipped with a 15-in electromagnet capable of a maximum field strength of 23.4 kG.

Both cyclopentadienylnickel nitrosyl (Strem Chemicals, Inc., Danvers, Mass.) and methyl-d_3 bromide (EM Laboratories Inc., Elmsford, N.Y.) were obtained commercially and used without further purification; no impurities were observed in their ICR mass spectra. Because of the high vapor pressure of CpNiNO at 25 °C (mp −41 °C, bp 47–48 °C (15 mm)), the sample was kept in an ice–water bath during use to prevent it from condensing in the ICR spectrometer inlet. Cyclopentadiene was prepared immediately before use by thermally cracking dicyclopentadiene[11] and was kept in a dry ice–acetone bath (−78 °C) during use to inhibit the rapid dimerization which occurs at room temperature.[11] All other chemicals used in this study were readily available from commercial sources. Before use, each sample was degassed by repeated freeze–pump–thaw cycles.

Pressures were measured with a Schulz-Phelps type ion gauge calibrated against a MKS Baratron Model 90H1-E capacitance manometer in a manner previously described.[12] The estimated uncertainty in absolute pressures, and thus in all rate constants reported, is ±10%. All experiments were performed at ambient temperature (20–25 °C).

Table I. Ion–Molecule Reactions and Rate Constants for the Reactions of $CpNi^+$ with CD_3Br and C_2H_5Br

Reaction	k^a
$CpNi^+ + CD_3Br \rightarrow (CD_3)C_5H_4Ni^+ + HBr$	2.8
$(CD_3)C_5H_4Ni^+ + CD_3Br \rightarrow (CD_3)_2C_5H_3Ni^+ + HBr$	1.5
$(CD_3)_2C_5H_3Ni^+ + CD_3Br \rightarrow (CD_3)_3C_5H_2Ni^+ + HBr$	1.5
$(CD_3)_3C_5H_2Ni^+ + CD_3Br \rightarrow (CD_3)_4C_5HNi^+ + HBr$	1.5
$CpNi^+ + C_2H_5Br \rightarrow \begin{cases} CpNi(HBr)^+ + C_2H_4 \\ CpNi(C_2H_4)^+ + HBr \end{cases}$	5.0

[a] Total rate constants in units of 10^{-10} cm³ molecule⁻¹ s⁻¹ measured for the disappearance of the reactant ion.

Results

When a mixture of CpNiNO and CD_3Br is examined using trapped ion ICR techniques,[9] the series of reactions 1–4 are initiated by $CpNi^+$. The temporal variation of relative ion

$$C_5H_5Ni^+ + CD_3Br \rightarrow (CD_3)C_5H_4Ni^+ + HBr \tag{1}$$

$$(CD_3)C_5H_4Ni^+ + CD_3Br \rightarrow (CD_3)_2C_5H_3Ni^+ + HBr \tag{2}$$

$$(CD_3)_2C_5H_3Ni^+ + CD_3Br \rightarrow (CD_3)_3C_5H_2Ni^+ + HBr \tag{3}$$

$$(CD_3)_3C_5H_2Ni^+ + CD_3Br \rightarrow (CD_3)_4C_5HNi^+ + HBr \tag{4}$$

abundance in a 1:3 mixture of CpNiNO and CD_3Br following a 20-eV, 10-ms electron beam pulse is illustrated in Figure 1 (exclusive of ions from CpNiNO[13] or CD_3Br[14] alone);[15] rates for these processes are given in Table I. Reactions 1–4 suggest the sequential alkylation of the cyclopentadienyl ring of $CpNi^+$ by CD_3Br. The four alkylation steps (eq 1–4) proceed rapidly in accordance with the generalized scheme of reaction 5, with

$$(CD_3)_nC_5H_{5-n}Ni^+ + CD_3Br \rightarrow (CD_3)_{n+1}C_5H_{4-n}Ni^+ + HBr \qquad n = 0\text{–}3 \tag{5}$$

each step involving CD_3 addition to the ring and subsequent loss of H in the form of HBr. Double resonance experiments[8,10] clearly demonstrate the sequential nature of process 5, with each product ion exhibiting double resonance signals[8] from each of its precursor ions. The rate of addition of a fifth CD_3 group (eq 6) is so slow that the process, if it

$$(CD_3)_4C_5HNi^+ + CD_3Br \rightarrow (CD_3)_5C_5Ni^+ + HBr \tag{6}$$

occurs at all, is not observed in these experiments.

For reasons which are not understood, the sequential alkylation of $CpNi^+$ by CH_3Br is somewhat unique. Under otherwise identical conditions, the yields of alkylation products with CH_3F, CH_3Cl, and CH_3I are less than 2% of those observed with CD_3Br, making the process difficult to fully characterize for these species.

In contrast to CD_3Br, $CpNi^+$ reacts with C_2H_5Br to give only two products, $CpNi(HBr)^+$ and $CpNi(C_2H_4)^+$ (eq 7 and 8). Reactions 7 and 8 represent two different product

$$CpNi^+ + C_2H_5Br \begin{cases} \xrightarrow{87\%} CpNi(HBr)^+ + C_2H_4 & (7) \\ \xrightarrow{13\%} CpNi(C_2H_4)^+ + HBr & (8) \end{cases}$$

channels for the $CpNi^+$-induced dehydrohalogenation of ethyl bromide.[13] Both HBr in $CpNi(HBr)^+$ and C_2H_4 in $CpNi(C_2H_4)^+$ are weakly bound labile species which are rapidly displaced by C_2H_5Br in the ligand transfer reactions 9 and 10.

$$CpNi(HBr)^+ + C_2H_5Br \rightarrow CpNi(C_2H_5Br)^+ + HBr \tag{9}$$

$$CpNi(C_2H_4)^+ + C_2H_5Br \rightarrow CpNi(C_2H_5Br)^+ + C_2H_4 \tag{10}$$

Reaction of $CpFe^+$ with CH_3X (X = F, Cl, Br, I) leads to the four alkylations of the Cp ring (eq 11). The abundance

$$(CH_3)_nC_5H_{5-n}Fe^+ + CH_3X \rightarrow (CH_3)_{n+1}C_5H_{4-n}Fe^+ + HX \qquad X = F, Cl, Br, I;\ n = 0\text{–}3 \tag{11}$$

of any product ions formed as the result of a fifth alkylation

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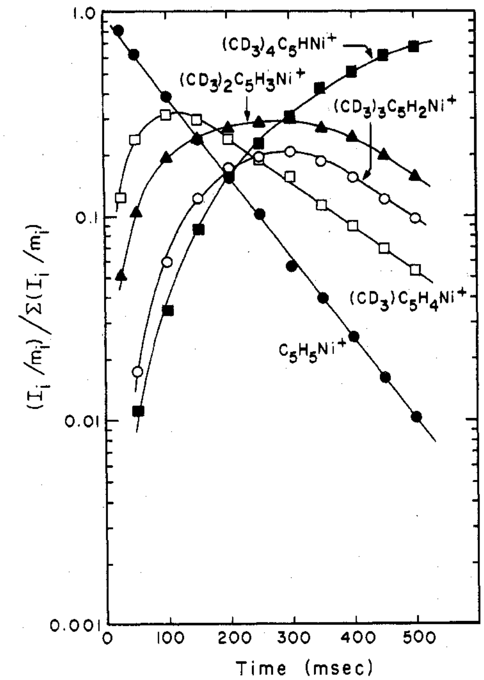
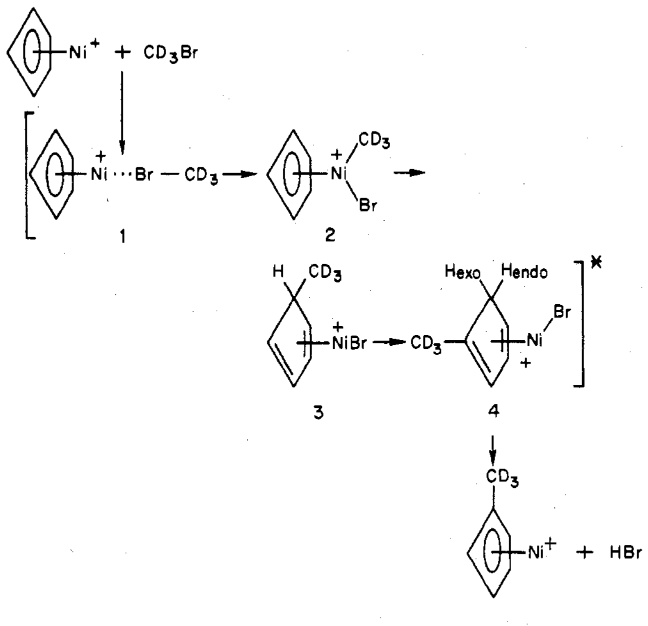


Figure 1. Temporal abundances of the variously alkylated $CpNi^+$ ions observed in a mixture of CpNiNO (3.2×10^{-7} Torr) and CD_3Br (1.0×10^{-6} Torr) following a 20-eV 10-ms electron beam pulse. Other ions present not included in the normalization are CD_3Br^+ and $CpNiNO^+$ and their various product and fragment ions.

Scheme I



step was so low as to be undetectable in these experiments. As with $CpNi^+$, significant product yields are obtained only in the case of CH_3Br.

Sequential alkylation reactions are not observed for the $C_5H_5^+$, $C_5H_6^+$, and $C_5H_5^-$ ions from cyclopentadiene nor for the $C_6H_5^+$ and $C_6H_7^+$ ions from benzene.

Discussion

The combination of ion cyclotron double resonance techniques[8,10] and the use of deuterium-labeled methyl bromide provide considerable information about the mechanism of the sequential alkylation reactions 1–4. Scheme I illustrates a proposed mechanism for the first step in the sequential alkylation of $CpNi^+$ by CD_3Br (reaction 1) in the gas phase at low (10^{-6} Torr) pressures. Initially the coordinatively unsaturated $CpNi^+$ cation interacts with CD_3Br to form the activated complex **1**, which has an internal energy equal to $D(CD_3Br\text{–}CpNi^+) \simeq 40$ kcal/mol.[16] The internal energy of **1** is sufficient to allow for oxidative addition of nickel to the carbon–bromine bond, yielding **2**.[17,18] CD_3 migrates to the cyclopentadienyl ring, giving **3**, the (methyl-d_3-cyclopentadiene)nickel bromide cation. Species **3** rapidly rearranges to **4** via a [1,5] sigmatropic shift (thermally allowed in the ground state[19]), which is known to occur rapidly at room temperature in methylcyclopentadiene.[20] Finally, HBr elimination from **4** involving the endo hydrogen yields the product ion, $(CD_3)C_5H_4Ni^+$. The sequence of Scheme I is repeated four times and is facilitated by the increasing activation of the cyclopentadienyl ring toward electrophilic substitution with each successive alkylation.[21] The appealing feature of the proposed mechanism is that it allows for only four alkylations since the fifth step would require HBr elimination to involve the exo hydrogen from **5**. Apparently in this case the reaction intermediate reverts to reactants, if it is formed at all.

Scheme II

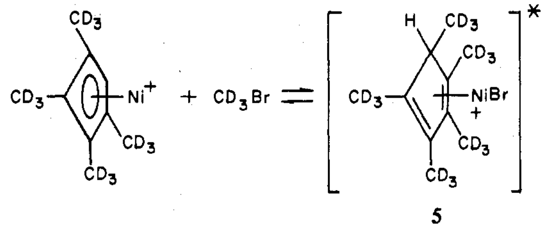


Table II. Enthalpy of Reaction for the Process $CH_3X \rightarrow CH_2 + HX^a$

X	$\Delta H_f(CH_3X)^b$	$\Delta H_f(HX)^c$	ΔH_r
F	−55.9	−64.8	83.2
Cl	−20.6	−22.0	90.7
Br	−9.1	−8.7	92.5
I	3.4	6.3	95.0

[a] Reaction 12 in the text; all values in kcal/mol; $\Delta H_f(CH_2) = 92.1 \pm 1.0$ (D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971)). [b] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970. [c] J. L. Franklin, J. G. Dillard, N. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969).

The proposed mechanism does not require expansion of the valence shell of nickel beyond 18 electrons;[22] the situation with $CpFe^+$ is even less restrictive and consequently the similar reactivity is not surprising. The differential reactivity of the methyl halides is puzzling, since CH_3F, CH_3Cl, and CH_3I sequentially alkylate $CpNi^+$ in very small yield compared to CD_3Br. The thermochemistry of the alkylation reactions 5 and 11 may be compared for the different methyl halides by examining the enthalpy of reaction 12 for the series (Table II). While the reaction with CH_3F will be somewhat more

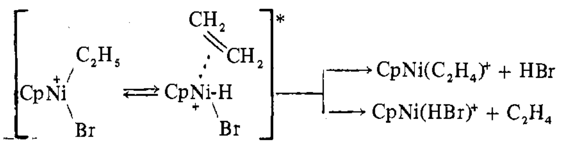
$$CH_3X \rightarrow CH_2 + HX \qquad (12)$$

exothermic than with the remaining methyl halides, there is no indication of unusual behavior to be expected for CH_3Br. The internal excitation of **1** depends on the metal–ligand bond dissociation energy. Also for the oxidative addition to be exothermic (formation of **2**) it is required that $D(CH_3\text{–}CpNiBr^+) + D(Br\text{–}CpNiCH_3^+) \geq D(CH_3\text{–}Br)$, with the extent of inequality determining the internal excitation available to effect further rearrangement of **2**. Assuming a metal–carbon bond dissociation energy of approximately 40 kcal/mol[23] and using available data for nickel–halogen[24] and carbon–halogen[25] bond dissociation energies, the internal excitation of **2** is estimated to be 55 kcal/mol for CH_3Br and

53 and 45 kcal/mol for CH_3I and CH_3Cl, respectively. Considering the uncertainties in the data it appears that the oxidative–addition reaction is exothermic for all three methyl halides, with CH_3Br being distinguished only by being slightly more exothermic.

C_2H_5Br reacts with $CpNi^+$ in a somewhat different manner than CD_3Br. This is attributed to the rapid β-hydrogen atom shift onto Ni^+ (eq 13 and 14), which is a facile process both

$CpNi^+ + C_2H_5Br \rightarrow$



(13)

(14)

in the gas phase[17] and in solution.[18] It is noted, however, that Lewis acids such as Li^+ also effect dehydrohalogenation reactions of alkyl halides analogous to processes 6 and 7.[26] Consequently an oxidative-addition step is not required.

That the metal ion plays a decisive role in the alkylation reactions 5 and 11 is confirmed by the observation that ions produced from both cyclopentadiene and benzene are not alkylated by CH_3Br. Court and Werner[27] have recently synthesized and isolated $[CpNi^+]BF_4^-$. The solution chemistry of this organometallic salt may exhibit alkylation reactions similar to those discussed herein.

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Registry No. $C_5H_5Ni^+$, 52668-78-7; $(CD_3)C_5H_4Ni^+$, 64381-81-3; $(CD_3)_2C_5H_3Ni^+$, 64365-04-4; $(CD_3)_3C_5H_2Ni^+$, 64365-03-3; $(CD_3)_4C_5HNi^+$, 64381-80-2; CD_3Br, 1111-88-2; C_2H_5Br, 74-96-4; $CpFe^+$, 61827-27-8; CH_3F, 593-53-3; CH_3Cl, 74-87-3; CH_3I, 74-88-4; CH_3Br, 74-83-9.

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(16) $D(CD_3Br{-}CpNi^+) \approx 40 \pm 5$ kcal/mol $\approx E^*$ is calculated by taking $PA(CD_3Br) \approx PA(CH_3Br) = 163$ kcal/mol and using the data of ref 3.

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