

°C; MS, m/e 826 (M^+); 1H NMR ($CDCl_3/CH_2Cl_2$) δ 0.36 (s, 6 H), 0.96 (s, 4 H), 6.6-7.3 (m, 40 H). Anal. Calcd for $C_{60}H_{50}Si_2$: C, 87.12; H, 6.09. Found: C, 86.82; H, 6.29.

Photochemical Reactions of 3. A THF (500-mL) solution of **3a** (531 mg, 1.04 mmol in a Pyrex photochemical reactor) was bubbled with argon and irradiated with a 450-W high-pressure Hg lamp for 3 h. The yellow color changed to colorless. After evaporation of the solvent, white crystals (444 mg, 83.7%) of **8a** were obtained: mp 166-168 °C; MS, m/e 508 (M^+); 1H NMR ($CDCl_3/CH_2Cl_2$) δ 0.39 (s, 6 H), 0.39 (d, $J = 15$ Hz, 2 H), 4.60 (m, 2 H), 6.67 (m, 2 H), 6.9-7.4 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ -2.3, 0.3, 50.1, 52.9, 124.0, 126.4, 127.4, 128.2, 140.1, 143.2, 145.7, 147.5; ^{29}Si NMR ($CDCl_3$) δ 32.7. Anal. Calcd for $C_{35}H_{32}Si_2$: C, 82.62; H, 6.34. Found: C, 82.36; H, 6.37.

Similarly, **8b** (522 mg, 86.4%) was obtained from **3b** (604 mg, 1.15 mmol): mp 172-173 °C; MS, m/e 522 (M^+); 1H NMR ($CDCl_3$) δ -0.14 (s, 6 H), 1.32 (AA'BB', 4 H), 4.39 (m, 2 H), 6.7-7.3 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ -2.7, 7.4, 43.8, 50.4, 122.0, 124.6, 125.3, 126.5, 127.3, 137.9, 141.5, 143.6, 144.1; ^{29}Si NMR ($CDCl_3$) δ 16.8. Anal. Calcd for $C_{36}H_{32}Si_2$: C, 82.70; H, 6.55. Found: C, 82.90; H, 6.59.

By a similar procedure to that of **3a**, **3c** (611 mg, 1.14 mmol) was irradiated to give **8c** (518 mg, 84.8%): mp 162-163 °C; MS, m/e 536 (M^+); 1H NMR ($CDCl_3/CH_2Cl_2$) δ -0.18 (s, 6 H), 1.1-1.6 (m, 4 H), 1.9-2.3 (m, 2 H), 4.43 (m, 2 H), 6.7-7.1 (m, 2 H), 6.9-7.4 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 0.3, 16.5, 17.8, 48.5, 53.0, 124.2, 126.7, 126.9, 127.4, 128.7, 129.4, 144.0, 140.3, 144.2, 146.2; ^{29}Si NMR ($CDCl_3$) δ 21.3. Anal. Calcd for $C_{37}H_{36}Si_2$: C, 82.78; H, 6.76. Found: C, 82.91; H, 6.82.

Registry No. **1**, 7688-03-1; **2a**, 33492-52-3; **2b**, 33375-55-2; **2c**, 33375-56-3; **3a**, 87433-06-5; **3b**, 87433-07-6; **3c**, 87433-08-7; **4**, 55373-67-6; **5a**, 87433-09-8; **5b**, 3353-69-3; **5c**, 16957-21-4; **6**, 7641-40-9; **7**, 87433-10-1; **8a**, 87450-36-0; **8b**, 87433-11-2; **8c**, 87433-12-3; Me_2SiCl_2 , 75-78-5; (*Z,Z*)-1,4-dithio-1,2,3,4-tetra-phenyl-1,3-butadiene, 57956-30-6; bis(dichloromethylsilyl)methane, 4519-03-3; bis(trimethylsilyl)methane, 2117-28-4; bis-(diethoxymethylsilyl)methane, 18048-25-4; 1-(dichloromethylsilyl)-3-(diphenylmethylsilyl)propane, 87433-13-4; allylmethyl-diphenylsilane, 17922-43-9; dichloromethylsilyl, 75-54-7; 1,4-dibromo-1,4-diphenyl-1,3-butadiene, 55373-68-7; diphenylacetylene, 501-65-5.

Activation of C-H and C-C Bonds in Alkanes by First-Row Group 8 Atomic Transition-Metal Ions in the Gas-Phase. Mechanistic Details from a Study of Deuterium and ^{13}C -Labeled Hydrocarbons[†]

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The first step in the interaction of saturated hydrocarbons with atomic group 8 metal ions involves oxidative addition of either a C-H or a C-C bond to the metal. At low energies this is followed by unimolecular rearrangement and elimination of smaller alkanes or molecular hydrogen. The present report is a continuation of our ion beam studies of these processes, in which we make extensive use of deuterium and ^{13}C -labeled normal, branched, and cyclic alkanes to elucidate mechanistic details. While overall patterns of reactivity are similar, the labeling results reveal subtle differences in comparing the behavior of Fe^+ , Co^+ , and Ni^+ . For example, dehydrogenation of linear alkanes by Ni^+ proceeds exclusively via a 1,4-elimination process, while dehydrogenation by Fe^+ and Co^+ occurs via a mixture of 1,4 and 1,2 eliminations and seems to be accompanied by some scrambling. In several cases involving the reactions of Fe^+ , product distributions are best explained by assuming that β -alkyl transfers occur as one step in the decomposition of reaction intermediates. The fragmentation of a hydrocarbon molecule by reaction with a group 8 metal ion is highly specific and occurs without the extensive rearrangements that often accompany electron-impact ionization. This suggests the use of gas-phase metal ion reactions as a novel chemical ionization technique to determine not only the structure but also the original label distribution in a molecule.

Introduction

Considerable interest in the subject of C-H bond activation at transition-metal centers has developed in the past several years, stimulated by the observation that even saturated hydrocarbons can react with little or no activation energy under appropriate conditions.² Interestingly, gas-phase studies of the reactions of saturated hydrocarbons at transition-metal centers were reported as early as 1973.³ More recently, ion cyclotron resonance⁴⁻⁷ and ion beam experiments⁸⁻¹⁰ have provided many examples of activation of both C-H and C-C bonds of alkanes by transition-metal ions. Facile addition of C-H or C-C bonds to metal centers requires first that the process be energetically feasible, preferably exothermic (Scheme I). Metal-hydrogen bonds in the range of 60 kcal/mol would

Scheme I

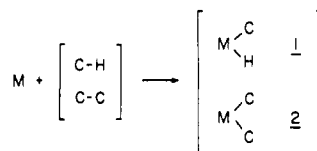


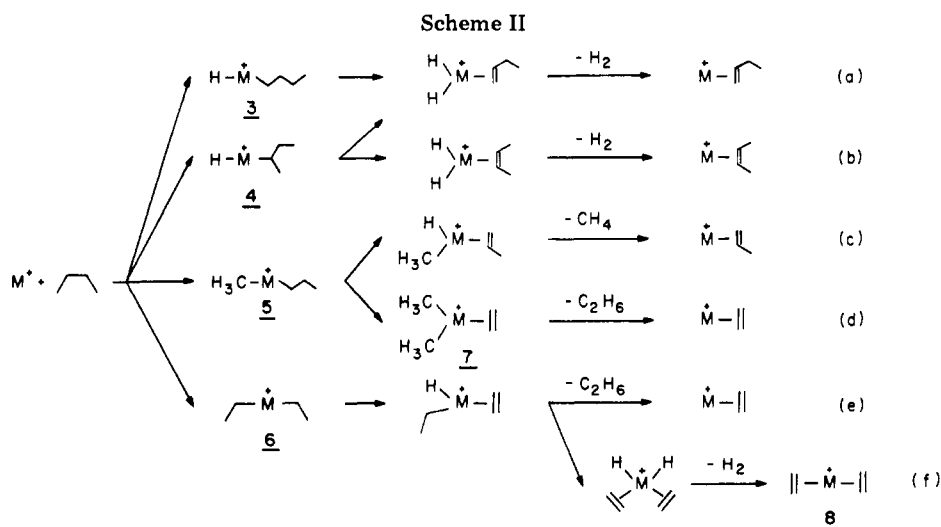
Table I. Thermochemical Data^{a, b}

bond energies	Fe^+	Co^+	Ni^+
$D^{\circ}(M^+-H)$	58 ± 5	52 ± 4	43 ± 2
$D^{\circ}(M^+-CH_3)$	69 ± 5	61 ± 4	48 ± 5
$D^{\circ}(M^+-CH_2)$	96 ± 5	85 ± 7	86 ± 6

^a All values in kcal/mol. ^b See ref 8, 9, and 16.

require metal-carbon bond energies greater than 35 kcal/mol for **1** to be more stable than the reactants.^{11,12}

[†]Contribution No. 6782.



While this is not an unreasonable value, the requirement that metal-carbon bond energies exceed 40–45 kcal/mol to render **2** energetically accessible might at first appear restrictive. However, there are several estimates of metal-carbon bond energies in this range.¹⁵ Recent studies in our lab have shown that metal-carbon bond energies in organometallic “fragment” ions can exceed the analogous metal-hydrogen bond strengths (Table I).^{8,9,16} In part this result must be regarded as unique and parallels involving coordinatively saturated complexes are not likely to be found. The polarizable methyl group stabilizes the charge more favorably than hydrogen, resulting in stronger metal-carbon bonds. This effect is diluted by additional polarizable ligands as well as by a dielectric medium in

condensed phases.

Along with a detailed examination of their electronic structure¹⁶ the above considerations argue against simple bond additivity in organometallic fragment ions. Hence, the metal-hydrogen and metal-carbon bond energies measured in our laboratory must be used cautiously in estimating the thermochemical changes attending formation of intermediates such as **1** or **2**. An important additional observation is the formation of $M(\text{CH}_3)_2^+$ as an exothermic reaction of Fe^+ , Co^+ , and Ni^+ with acetone.^{17,18} This requires that the sum of the first and second metal-carbon bond dissociation energies exceeds 96 kcal/mol.¹⁹ Hence, we remain firmly convinced that insertion of these metal ions into C-C bonds is an exothermic process. Consistent with these observations are products derived from reactions in which the metal ion cleaves the carbon chain of the alkane at low relative kinetic energies.^{4–10} These products, as well as those which occur via dehydrogenation processes, are listed in Table II for selected alkanes. The details of the product distributions have been discussed previously.^{8,9}

A general mechanism that has been proposed for the reaction of metal ions with hydrocarbons is shown in Scheme II for butane. Oxidative addition of C-H and C-C bonds to the metal yields reaction intermediates that further rearrange by β -H and β -alkyl shifts. The final step involves reductive elimination of hydrogen or an alkane from the metal center to yield observed products.

Several aspects of the proposed reaction mechanism shown in Scheme II deserve comment. The products are alkenes bound to the metal ion. Binding energies of group 8 metal ions to ethylene are in the range 40–70 kcal/mol.^{10,20} Hence, it is the stability of the products that render the overall process substantially exothermic when effected by a transition-metal ion.

Scheme II depicts a number of initial steps that arise from insertion of the metal ion into one of the two types of C-H bonds in butane (leading to structures **3** and **4**) or one of the two types of C-C bonds (structures **5** and **6**). A myriad of possible rearrangements can follow. Scheme II indicates what we believe to be the important subsequent rearrangement processes. To sort out which path-

(1) On leave from École Polytechnique Fédérale, CH 1007 Lausanne, Switzerland.

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(11) Supplementary heats of formation of hydrocarbons are taken from: Cox, J. D.; Pilcher, G. “Thermochemistry of Organic and Organometallic Compounds”; Academic Press: New York, 1970.

(12) It has been estimated that the activation energy for reductive elimination of cyclohexane from $(\text{C}_5\text{Me}_5)(\text{Me}_3\text{P})\text{Ir}(\text{H})(\text{C}_6\text{H}_{11})$ is approximately 30 kcal/mol and that the activation barrier for the reverse process is small in comparison (Bergman, R. G., private communication). This implies that the sum of the iridium carbon and hydrogen bonds is ~125 kcal/mol (using $D(\text{C}-\text{C}_6\text{H}_{11}-\text{H}) = 95.5 \pm 1$ kcal/mol from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493). This value is not inconsistent with known thermochemical data. A bond energy of 49 ± 11 kcal/mol has been measured for $D(\text{Ir}-\text{C}(\text{O})\text{CH}_3)$,¹³ and bond strengths of 65–70 kcal/mol for metal hydrogen bonds are not unreasonable.¹⁴

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(14) See: Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1982, 103, 190, for estimates of metal-hydrogen bond energies in protonated transition-metal complexes.

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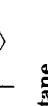
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(19) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493. $\Delta H_f(\text{CH}_3) = 35.1 \pm 0.15$ kcal/mol.

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	0.77	0.03	0.10	0.10	0.04
2,2-dimethylpentane	0.30	0.13	0.40	0.11	0.02
	0.64	0.09	0.18	0.06	0.03
	0.59	0.06	0.19	0.10	0.06
	0.49	0.09	0.29	0.09	0.05
	0.59	0.09	0.21	0.08	0.02
	0.58	0.07	0.23	0.10	0.02
	0.46	0.07	0.27	0.12	0.07
octane	0.23	0.16	0.29	0.15	0.03
octane-1,1,1,8,8,8-d ₆	0.69	0.03	0.10	0.11	0.01

^a For example, the "CH₄" column accounts for all methane losses, including ¹³C and deuterium-labeled molecules. ^b See ref 37. ^c The available amount of this compound was exhausted during the experiment. Consequently, the proportional loss of hydrogen could not be measured. ^d Loss of C₂H₄ is also observed, see text. ^e Trace amount observed. ^f Measured at 0.9 eV relative kinetic energy. ^g Product distributions listed are averages of two widely different data sets. Data taken at about the same time as labeled studies were performed show 73% dehydrogenation of pentane and 78% dehydrogenation of hexane.

ways occur for the different metal ions one needs information relating to the structure of the products. This can in part be obtained by varying the hydrocarbon structure. More sophisticated approaches include labeling the reactants,^{4a} ligand exchange reactions, and collision-induced dissociation studies of the product ions.^{4b,7,21}

Studies utilizing labeled hydrocarbons are few. Ridge and co-workers have reported that reaction of Fe⁺ with (CH₃)₃CD results in loss of CH₄ and HD, exclusively.^{4a} In particular, dehydrogenation occurs via a 1,2-elimination process analogous to a or b in Scheme II.²² There is no evidence in this case that β-H-transfer processes are reversible. In our laboratory the reaction of Co⁺ with CD₃CH₂CH₂CD₃ has been studied.⁸ Insertion of Co⁺ into the central C-C bond leads mainly to formation of Co-(C₂H₂D₂)⁺ although a minor amount of Co-(C₂HD₃)⁺ was noted and attributed to reversible β-hydrogen transfer processes (see also Table IV). At higher kinetic energies the amount of hydrogen scrambling was reduced, consistent with a shorter lifetime of the reaction intermediate expected with higher internal energies. Dehydrogenation to form the cobalt-butene ion indicates loss of H₂, HD, and D₂; product yields were not reported but did not vary significantly with reactant ion kinetic energy.

Details of dehydrogenation reactions of nickel ions with a number of deuterated alkanes have also been reported.¹⁰ The product distributions for these reactions are listed in Table III and indicate that at low energies, the dehydrogenation by Ni⁺ of linear alkanes with alkyl chains of four or more carbons occurs exclusively by a 1,4-elimination process leading to structure 8, Scheme II*f*. Metallacycle intermediates are not involved in these reactions. Instead, as shown for butane, the metal ion inserts into the internal carbon-carbon bond, followed by two β-hydrogen transfers onto the metal, resulting in loss of hydrogen atoms from the two end carbons. Reversible β-H transfers do not occur in these reactions. These results are supported by structural information obtained by Jacobson and Freiser using the technique of collision-induced dissociation (CID) of the product ions formed in a Fourier transform mass spectrometer (FT-MS).^{7,21} The CID technique involves acceleration of a particular ion to a high kinetic energy. Subsequent collisions with neutral molecules convert translational energy to internal energy which can lead to fragmentation. The fragmentation pattern, or CID spectrum, is often characteristic of a particular structure. In the FT-MS experiments, M(C₄H₈)⁺ ions, M = Fe, Co, Ni, were generated by reaction of M⁺ with several different reactants, such as butane and larger *n*-alkanes, 2,2-dimethylpropane, and cyclopentanone. By comparing the CID spectra of the various M(C₄H₈)⁺ ions, the authors concurred that Ni⁺ dehydrogenates linear alkanes exclusively via a 1,4-elimination process (Scheme II*f*). Their results indicate Co⁺ dehydrogenates butane 90 ± 5% via Scheme II*f* and 10 ± 5% by Scheme II*a,b*, while Fe⁺ dehydrogenates butane 30 ± 10% by Scheme II*f* and 70 ± 10% by Scheme II*a,b*.^{7,21}

In the present work we report reactions of first-row group 8 metal ions with a variety of deuterium and ¹³C-labeled hydrocarbons. Because there is little precedence for oxidative addition of unstrained C-C bonds to metal centers,²³ our specific interests in carrying out these studies included not only comparing in greater detail the reactivity of the different group 8 metal ions but also substantiating

(21) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* 1983, 105, 5197.

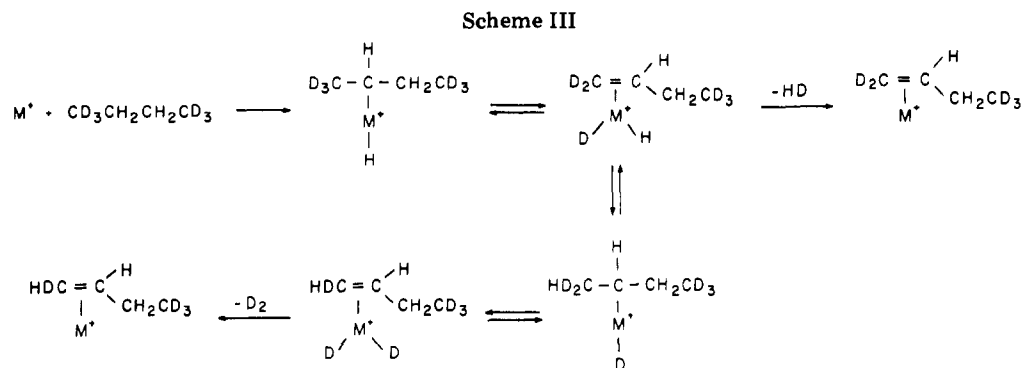
(22) Note that this is also true for the reaction of Ni⁺ with 2-methylpropane-2-d₁, see Table III.

(23) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* 1977, 24, 97.

Table V. Distribution of Labeled Products in the Reactions of Ni⁺ with ¹³C-Labeled Alkanes^a

alkane	neutral products corresponding to M(alkene) ⁺ products						
	C ₂ H ₆	¹³ CCH ₆	C ₃ H ₆	¹³ CC ₂ H ₈	C ₄ H ₁₀	¹³ CC ₃ H ₁₀	¹³ C ₂ C ₂ H ₁₀
hexane-1,6- ¹³ C ₂		1.0		1.0		1.0	
hexane-3,4- ¹³ C ₂ ^b	1.0			1.0			1.0
hexane-2- ¹³ C ₁	0.50	0.50	0.50	0.50	0.50	0.50	

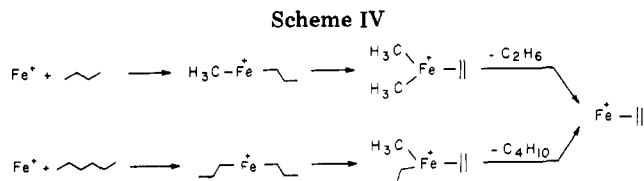
^a Measured at ~0.5 eV relative kinetic energy. ^b These spectra showed products due most likely to hexane-3-¹³C₁ (~15-25% impurity), not included in table.



product, such as loss of a smaller alkane, can most often be explained by processes analogous to c and e in Scheme II. As an example, consider the reaction of Ni⁺ with hexane-1,1,1,6,6,6-*d*₆. Little loss of methane is seen in the reactions of Ni⁺ with the linear alkanes, most likely because of the high terminal C-C bond energy. In analogy with c and e in Scheme II, loss of ethane would proceed via insertion of the metal ion into the C2-C3 bond of hexane followed by transfer of the β-hydrogen on C4. Consistent with this expectation, only C₂H₃D₃ is lost from the 1,6-labeled hexane. Similarly, propane is lost only as C₃H₅D₃ and butane is eliminated as C₄H₄D₄, incorporating a terminal methyl and one deuterium atom from the opposite end of the molecule.

Table V lists the losses of alkane from reaction of Ni⁺ with three ¹³C-labeled hexanes. The products observed in these cases also are those expected via c and e in Scheme II. For example, loss of ethane involves a terminal carbon atom along with its nearest neighbor. Thus, ¹³CCH₆ is lost from hexane-1,6-¹³C₂ and unlabeled ethane is lost from hexane-3,4-¹³C₂.

Dehydrogenation. Table III lists the products due to dehydrogenation of alkanes by Fe⁺, Co⁺, and Ni⁺. As mentioned above, nickel ions dehydrogenate linear alkanes larger than butane exclusively via a 1,4-elimination process at low energies.^{10,21} Iron and cobalt ions dehydrogenate alkanes by both this 1,4 pathway and the 1,2-elimination process depicted in a and b in Scheme II. The bond strengths of Ni⁺ to H and CH₃ (Table I) suggest that the overall energetics of insertion into a C-H bond may be unfavorable. Insertion into C-C bonds appears more reasonable on energetic grounds, which can explain the preference of Ni⁺ to react via the 1,4-elimination pathway.²⁵ Iron and cobalt ions have higher first bond energies to a hydrogen atom and undergo the "easier" 1,4-elimination process only part of the time. Jacobson and Freiser estimate from CID spectra that Co⁺ and Fe⁺ dehydrogenate butane 90 ± 5% and 30 ± 10% by Scheme III, respectively.⁷ It is more difficult to determine these pro-



portions from our data because a small amount of scrambling (see below) complicates the analysis. However, our results for loss of D₂ from butane-1,1,1,4,4,4-*d*₆, Table III (see also Table VI) with Fe⁺ and especially Co⁺ is less than what the CID results would predict.

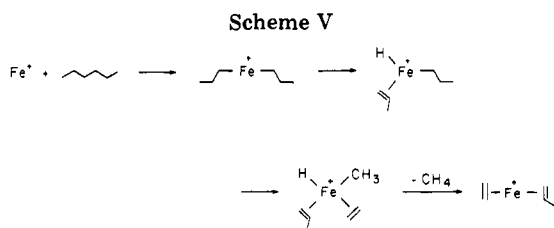
Data in Table VI indicate that as the relative kinetic energy is increased, the proportion of 1,4 loss (loss of D₂) decreases in the reaction of the three metal ions with butane-1,1,1,4,4,4-*d*₆. For Ni⁺, loss of H₂ becomes competitive with loss of D₂ above 1 eV, with equal amounts at 2 eV.

The small amount of H₂ loss from pentane-2,2,3,3,4,4-*d*₆ in the reactions of Co⁺ and Fe⁺ cannot be explained by either a strict 1,2 or 1,4 process. Either α-hydrogen elimination occurs or some scrambling takes place. The former is considered unlikely since no loss of H₂ is seen in reactions with 2,2-dimethylpentane.^{8,9} A plausible scrambling mechanism is shown in Scheme III. While scrambling processes seem to be negligible for both Fe⁺ and Ni⁺, they also account for some ionic products due to loss of alkanes in Co⁺ reactions⁸ as discussed below.

Loss of Alkane. Tables IV and V list the label distribution in alkane loss products from the interaction of the three group 8 ions with the *n*-alkanes. For each metal ion, slightly different sets of products are observed. The products of Ni⁺ reactions are strictly consistent with c and e in Scheme II, where the metal cation inserts into a C-C bond followed by a β-H transfer and elimination of an alkane. However, somewhat unexpected products arise in both the Fe⁺ and Co⁺ reactions. For example, focusing on the Fe⁺ reactions, 10% of the loss of ethane from butane-1,1,1,4,4,4-*d*₆ is C₂D₆, and 30% of the loss of butane from *n*-hexane involves the carbon atoms in the 1-, 2-, 3-, and 6-positions.²⁶ These products can be explained by

(25) Dehydrogenation of an alkane resulting in formation of two olefins requires ~20-30 kcal/mol more energy than dehydrogenation forming one olefin, for example, C₄H₁₀ → 2C₂H₄ + H₂ (ΔH = 55 kcal/mol) vs. C₄H₁₀ → C₄H₈ + H₂ (ΔH = 27 kcal/mol).¹¹ The extra metal-olefin bond more than compensates for the extra energy required.

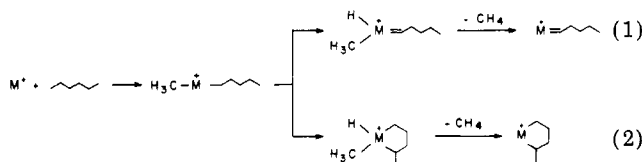
(26) Loss of butane from hexane involving carbon atoms in the 1-, 2-, 3-, and 6-positions vs. the 1-, 2-, 4-, and 6-positions could not be distinguished with the labeled compounds we had, but the latter case seems unlikely.



a mechanism in which Fe^+ inserts into the C1–C2 bond of butane or the C3–C4 bond of hexane, after which the terminal β -methyl group migrates onto the metal. This leads to elimination of ethane from butane and butane from hexane, as shown in Scheme IV (which is analogous to Scheme IId). This also accounts for the loss of $\text{C}_3\text{H}_6\text{D}_2$ from pentane-2,2,3,3,4,4- d_6 and $\text{C}_5\text{H}_9\text{D}_3$ from 2,2 dimethylpentane-5,5,5- d_3 (Table IX). Though rarely observed, β -alkyl transfers have been noted in solution studies as well.²⁷

Loss of C_2D_6 from reaction of butane-1,1,1,4,4,4- d_6 with Fe^+ increases in proportion to loss of $\text{C}_2\text{H}_2\text{D}_4$ (Scheme IIe) with increasing energy. Loss of C_2D_6 is also seen at higher energies in the reactions of Co^+ and Ni^+ with butane-1,1,1,4,4,4- d_6 . The occurrence of β -methyl transfers at very low energies in the Fe^+ reactions, and to a lesser extent in the Co^+ reactions (see Table IV), may be due to a higher methyl bond energy of the intermediates (5 or 7) involved in these reactions. However, thermochemical data for these more complex species are not known.

Table VII lists the methane losses expected via Scheme IIc as well as those experimentally observed. There are several mechanisms that can explain these products. For example, Fe^+ may insert into a terminal C–C bond followed by either an α - or δ -hydrogen transfer, processes 1 and 2.



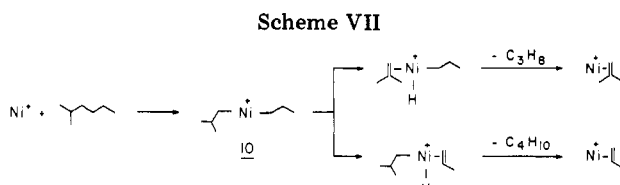
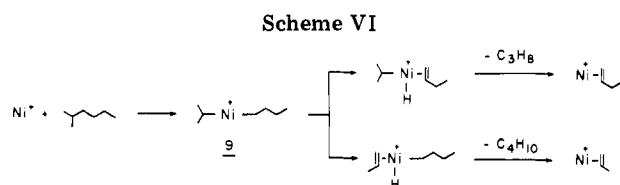
As discussed above, α -hydrogen transfers are not considered likely.⁸ Metallacycle intermediates²⁸ have been proposed in studies of the interactions of cobalt ions with cycloalkanes²⁹ and the dehydrogenation of 2,2,3,3-tetramethylbutane.^{8,9} We are not aware of any precedent that provides support for the possible existence of the high oxidation states required by the intermediates in processes 1 and 2. Scheme V also yields the observed methane losses and remains consistent with Schemes IId and IV. Here Fe^+ inserts into the central bond of hexane, followed by β -hydrogen and β -methyl transfers onto the metal center and reductive elimination of methane. This also accounts for the loss of CH_4 from pentane-2,2,3,3,4,4- d_6 (insertion into the C2–C3 bond followed by methyl [C1] and β -hydrogen [from C5] transfers) and CH_3D (and perhaps some CD_3H) from 2,2-dimethylpentane-5,5,5- d_3 , Table IX. It is surprising that an iron ion, which makes a bond of 68 kcal/mol to one methyl radical (Table I), preferentially inserts into an internal rather than a terminal C–C bond

(27) See, for example: Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

(28) For examples of metallacycles in solution-phase studies see: Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551.

(29) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

(30) The dehydrogenation of 2,2,4,4-tetramethylbutane can also be explained by a 1,4-elimination mechanism similar to Scheme IIc. Namely, the metal ion inserts into the central C–C bond followed by a β -H transfer from both ends and loss of H_2 off the metal center.



which is only ~ 4 kcal/mol stronger.^{11,31} It is possible that the second metal carbon bond is substantially weaker and accounts for this selectivity or that the metal ion alkyl bond strength is larger for the larger alkyls. However, this does not account for the relatively large amount of methane lost in the reaction of Fe^+ with butane.

As noted above, smaller amounts of products that may occur through Schemes IV and V appear in the reactions of Co^+ ions as well, as exemplified by the loss of CH_4 and $\text{C}_3\text{H}_6\text{D}_2$ in the reaction with pentane-2,2,3,3,4,4- d_6 . There are yet other products observed only in the Co^+ reactions, such as loss of $\text{C}_2\text{H}_3\text{D}_3$ from butane-1,1,1,4,4,4- d_6 and loss of $\text{C}_2\text{H}_4\text{D}_2$ and $\text{C}_3\text{H}_3\text{D}_5$ from pentane-2,2,3,3,4,4- d_6 which occur via other pathways. These products decrease in proportion to the c- and e-type products in Scheme II with increasing energy (also noted in ref 8). Their occurrence can be explained either by allowing for α -hydrogen transfers as in reaction 1, again considered unlikely for reasons discussed above or, as already mentioned, via a scrambling mechanism similar to Scheme III.⁸ Studies of the hexane reactions were not done in such detail due to limited amounts of the compounds, so that scrambling products could not be examined with certainty.

Reactions of Metal Ions with Branched Alkanes.

The product distributions for the reactions of the metal ions with the heptane isomers (Tables VIII and IX) display the expected influence of branching in the alkane, namely, an increase in the loss of CH_4 from the intermediate complex.^{8,9} This is due in part to the increased number of sites for methane loss, as well as the decrease in the terminal carbon–carbon bond energy.

The loss of alkane from the nickel(1+) isoheptane complex consists essentially of propane and butane in comparable amounts (Table II). The results obtained with labeled samples, Table VIII, indicate that these two products are both formed from the same intermediate 9, Scheme VI. It thus appears that Scheme VII involving insertion into the C3–C4 bond is not contributing to the formation of these products. This suggests that Ni^+ selectively inserts into the weakest carbon–carbon bond, resulting in the formation of intermediate 9 rather than 10.³² The small amount of ethane loss ($\sim 1\%$), however, must occur from insertion into the internal C4–C5 bond.

The reaction of Ni^+ with the tertiary heptane isomer, 2,2-dimethylpentane, displays product distribution and label retention compatible with the formation of intermediate 11 which subsequently loses either C_3H_8 or C_4H_{10} in accordance with c and e in Scheme II. In this case, no

(31) $\Delta H_f(n\text{-C}_5\text{H}_9)$ was calculated by assuming $D(n\text{-C}_5\text{H}_9\text{-H}) = D(n\text{-C}_3\text{H}_7\text{-H})$. $D(n\text{-C}_3\text{H}_7\text{-H}) = 97.9 \pm 1$ kcal/mol and $\Delta H_f(\text{CH}_3)$ from ref 19.

(32) The selectivity of Fe^+ , Co^+ , and Ni^+ in inserting into C–C bonds has been discussed previously in the literature.⁷⁻⁹ Note that in determining the proportion of insertion of Fe^+ into terminal C–C bonds, these references do not account for β -methyl transfers (Schemes IId, IV, and V).

Table VII. Loss of Methane in the Reaction of Fe⁺ with Deuterated Hexanes at ~0.5 eV Relative Kinetic Energy

hexane	1, 1, 1, 6, 6, 6-d ₆		2, 2, 5, 5, 5-d ₄		3, 3, 4, 4-d ₄	
	experimentally observed	CHD ₃	CH ₃ D	CH ₃ D	CH ₄	CH ₄
hexane						
2, 2, 5, 5, 5-d ₄		CHD ₃	CH ₃ D	CH ₃ D	CH ₄	CH ₄
3, 3, 4, 4-d ₄		CHD ₃	CH ₃ D	CH ₃ D	CH ₄	CH ₄
2, 2, 5, 5, 5-d ₄		CHD ₃	CH ₃ D	CH ₃ D	CH ₄	CH ₄

Table VI. Percentage of Loss of X₂ (X = H, D) in the Reactions of Fe⁺, Co⁺, and Ni⁺ with Butane-1, 1, 1, 4, 4, 4-d₆ at Several Energies

M ⁺	loss of H ₂ :HD:D ₂		
	0.26 ^a	0.52 ^a	2.0 ^a
Fe ⁺	71:5:25	46:30:24	60:26:14
Co ⁺	15:28:57	16:28:56	36:18:45
Ni ⁺	0:0:100	0:0:100	14:0:86
			50:?:50

^a Relative kinetic energy (eV).

Table VIII. Distribution of Labeled Products in the Reactions of Ni⁺ with ¹³C-Labeled 2-Methylhexane and 2,2-Dimethylpentane^a

alkane	neutral products											
	CH ₄	¹³ CH ₄	C ₂ H ₆	C ₃ H ₈	¹³ CC ₂ H ₈	¹³ C ₂ CH ₈	C ₄ H ₁₀	¹³ CC ₃ H ₁₀	C ₅ H ₁₂	¹³ CC ₄ H ₁₂	2CH ₄	CH ₄ + ¹³ CH ₄
	1.0		1.0	1.0				1.0	1.0			
	1.0		1.0	1.0				1.0	1.0			
	1.0		1.0	1.0				1.0	1.0			
	b		b	1.0				1.0	b			
	1.0		b	1.0				1.0	b			
	1.0	1.0	1.0	1.0				1.0	b			
	1.0		1.0	1.0				1.0	1.0			0.70
	1.0		1.0	1.0				1.0	1.0			1.0
	1.0		1.0	1.0				1.0	1.0			1.0
	1.0		1.0	1.0				1.0	b			b
	~0.60		~0.40	1.0				1.0	~0.50			~0.50










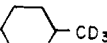
^a Measured at ~0.6 eV relative kinetic energy. ^b Distributions not measured (product peaks very small).

Table IX. Distribution of Labeled Products in the Reactions of Fe⁺ and Ni⁺ with 2,2-Dimethylpentane-5, 5, 5-d₃^a

M ⁺	neutral products										
	H ₂	HD	CH ₄	CH ₃ D	CD ₃ H	C ₃ H ₈ D ₃	C ₄ H ₁₀	C ₅ H ₁₂ D	C ₅ H ₉ D ₃	2CH ₄	CH ₄ + CHD ₃
Fe ⁺	0.76	0.24	0.09	0.27	0.64	1.0	1.0	0.44	0.56	0.43	0.57
Ni ⁺	1.0		b		1.0	1.0	1.0	0.64	0.64	0.64	0.36

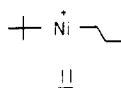
^a Measured at ~0.6 eV relative kinetic energy. ^b Distributions not measured (product peaks very small).

Table X. Product Distributions for Reactions of Ni⁺ with Cyclic Alkanes Measured at ~0.5 eV Relative Kinetic Energy

alkane	neutral products (irrespective of label)						
	H ₂	CH ₄	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	2H ₂	CH ₄ + H ₂
	0.41		0.48				
	0.61		0.30	0.03		0.05	
	0.20	0.46	0.01	0.05		0.03	0.24
	0.33	0.45		0.04			0.19
	0.18	0.58		0.04			0.20
	0.22	0.57	0.01	0.10			0.11
	0.24	0.46	0.01	0.08			0.21
	0.76			0.21		0.03	
	0.18	0.39		0.10	0.01	0.01	0.29
	0.26	0.47		0.06	0.02		0.19

^a Also observed at this energy is an 11% loss of CH₃, see ref 35.

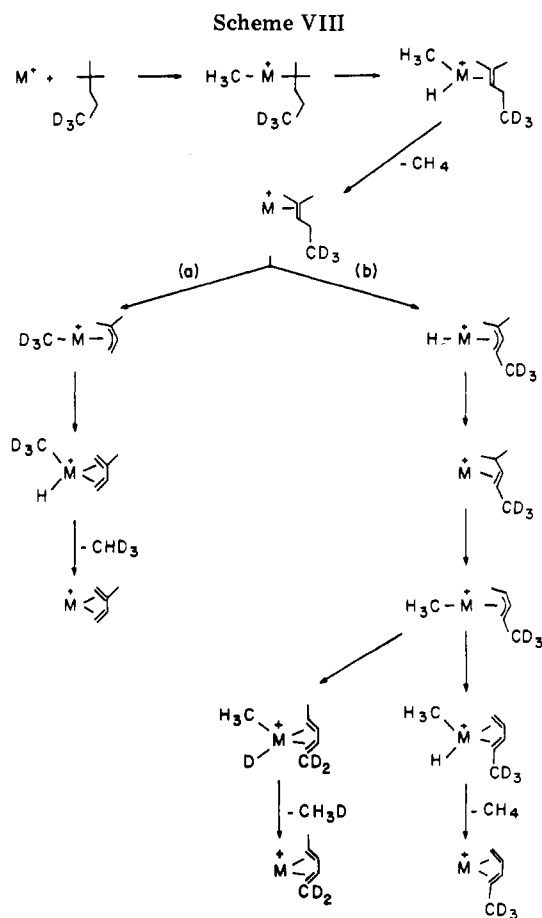
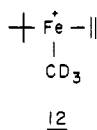
ethane is lost since there is no hydrogen in a β -position to the metal following insertion into the C3-C4 bond.



The loss of methane from both heptane isomers reacting with Ni⁺ occurs exclusively with a methyl group originating in the branched part of the alkane. This is in contrast to the behavior of Fe⁺ (Scheme V), since no CH₃D is lost from the tertiary isomer. Instead, insertion into the branched methyl-carbon bond is favored, followed by a β -hydrogen transfer.

The loss of two molecules of methane occurs in the reactions of both Fe⁺ and Ni⁺ with 2,2-dimethylpentane. The second step of this process may be related to the mechanism by which loss of methane is thought to occur in the reaction of Co⁺ with 2-methyl-2-butene.³³ This is illustrated in Scheme VIII for 2,2-dimethylpentane-5,5,5-d₃. The initial loss of CH₄ leads to formation of the internal olefin 2-methyl-2-pentene. Loss of CHD₃ can occur via process a. Rearrangement to give 4-methyl-2-pentene, process b, also takes place. The metal ion can then insert into an allylic C-C bond, abstract a β -hydrogen, and eliminate either CH₄ or CH₃D. The latter product was observed only as a very minor species at lower energies. This sequence of events has been proposed to be the general mode of reaction in the interactions of Co⁺ with alkenes.³³

One type of product not previously observed is the exothermic loss of ethylene, C₂H₄, in the reaction of Fe⁺



with 2,2-dimethylpentane-5,5,5-d₃. This product is probably formed via insertion into the C2-C3 bond followed by β -methyl transfer to give structure 12. Loss of ethylene (~18% of the product distribution at 0.3 eV relative kinetic energy) is preferred over loss of C₅H₉D₃ (5% at 0.3

Table XI. Product Distributions for Reactions of Ni⁺ with Labeled Methylcyclopentanes and Cyclohexane (Measured at ~0.6 eV Relative Kinetic Energy)^a

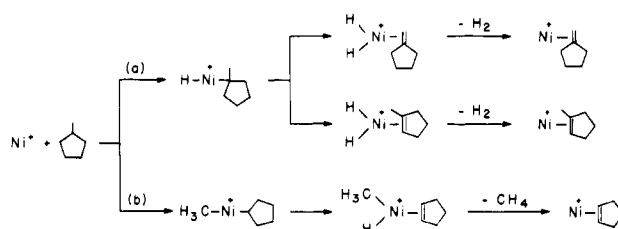
alkane	neutral products										
	H ₂	HD	CH ₄	CH ₃ D	C ₃ H ₆	C ₃ H ₃ D	C ₃ H ₄ D ₂	C ₃ H ₃ D ₃	C ₄ H ₃ D ₃	CH ₄ + HD, CH ₃ D + H ₂ , CH ₃ D ₂ + H ₂ , CH ₃ D ₃ + HD	CHD ₃ + H ₂
	0.70	0.30	1.0	1.0	0.30	?	0.50	0.70	0.50	1.0	1.0
	1.0	1.0	1.0	1.0	0.50	0.50	1.0	1.0	0.50	1.0	1.0
	0.60	0.40	1.0	1.0	0.50	0.50	1.0	1.0	0.50	1.0	1.0
	M		1.0	1.0	M	x	x	x	M	M	1.0

^a M's and x's are entered when it is difficult to separate mass peaks to determine product ratios. M indicates that most of the particular product is due to this species.
^b Spectrum seemed to show lingering amounts of previous sample.

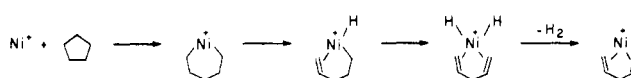
Table XII. Product Distribution for the Reaction of Ni⁺ with ¹³C-Labeled Cyclopentanone (Measured at 0.55 eV Relative Kinetic Energy)

alkane	neutral products				
	H ₂	¹³ CH ₄	C ₃ H ₆	¹³ CC ₂ H ₆	¹³ CH ₄ + H ₂
	1.0	1.0	0.50	0.50	1.0

Scheme IX



Scheme X



eV). This suggests that the activation energy for reductive elimination of the alkane is fairly high.

Reactions of Ni⁺ with Cycloalkanes. Table X lists the product distributions for reactions of Ni⁺ with several cycloalkanes. The reactions with cyclobutane, cyclopentane, and cyclohexane, both at low and high energies (high energy data are not presented³⁴), are virtually identical³⁵ with the analogous reactions of Co⁺ that were discussed in detail in a previous paper.²⁹ These data are presented here to compare to the reactions of Ni⁺ with methylcyclopentane and methylcyclohexane that were studied by using labeled compounds as well (Tables XI and XII). Table X indicates that dehydrogenation is a major process in reactions of Ni⁺ with simple cycloalkanes, accounting for 40% to over 70% of the reaction. The major product in reactions with the methylcycloalkanes is loss of methane and methane in combination with hydrogen. This pattern of reactivity suggests that methane is eliminated as a first step in the reactions of the methylcycloalkanes, followed by dehydrogenation.

Some mechanistic details can be elucidated with the aid of data given in Tables XI and XII for reaction of Ni⁺ with labeled methylcyclopentane and methylcyclohexane. Dehydrogenation appears to always involve the tertiary hydrogen as indicated by the methylcyclopentane-1-*d*₁ results in which only HD loss is observed. This process probably proceeds via insertion into the weak tertiary C-H (or C-D) bond, followed by a β-hydrogen transfer to the metal, most often the secondary β-hydrogen, Scheme IX. Loss of methane always involves the exocyclic carbon. The small amounts of cleavage products make verification of the pathways leading to these products (including the possibility of scrambling) difficult.

Nickel ions dehydrogenate 2-methylpropane-2-*d*₁, presumably in a process analogous to Scheme IX, producing

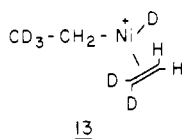
(34) Halle, L. F.; Beauchamp, J. L., unpublished results.

(35) In the reaction of Ni⁺ with cyclobutane, loss of CH₃ to yield a Ni(C₃H₅)⁺ ion accounts for 11% of the product distribution with a cross section of 4 Å² at ~0.5 eV relative kinetic energy. As an exothermic process, the formation of this product implies that D(Ni⁺-C₃H₅) > 67 kcal/mol (ΔH_f(C₃H₅) = 39.1 kcal/mol) from: Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* 1980, 101, 1223.^{11,19} Co(C₃H₅)⁺ accounts for less than 1% in the analogous reaction of Co⁺ at the same energy and appears as an endothermic product. Fe(C₃H₅)⁺ is not observed in the reaction of Fe⁺ with cyclobutane.³⁴

only loss of HD by a 1,2-elimination process. It was argued above that dehydrogenation by Ni^+ of linear alkanes larger than propane occurs via a 1,4 elimination in which the first step is insertion into a C-C rather than C-H bond. Insertion into a C-H bond in the case of 2-methylpropane and methylcyclopentane may be favored due to a low tertiary C-H bond strength. Unfortunately, these results yield no information on the mechanism of dehydrogenation of simple cycloalkanes, which may proceed in a similar pathway as depicted in Scheme IX or occur via a 1,4 process such as in Scheme X.

In contrast to the reactions of Co^+ and Ni^+ with cycloalkanes, loss of alkenes is not a prominent pathway in the reactions of Fe^+ with cyclopentane and cyclohexane.^{6,36} Single and multiple dehydrogenation account for greater than 95% of product distribution at low energies in these reactions.^{6,34} This may be due to a greater facility of Fe^+ to insert into C-H bonds resulting from a greater bond strength to hydrogen atoms (see Table I).

Isotope Effects. Deuterium or ^{13}C labeling of the alkanes does not appear to greatly alter the distribution of products, as shown in Tables II and X.³⁷ Because of the small fractional mass difference between a ^{13}C and ^{12}C nucleus, any isotope effect caused by this labeling is expected to be small. None can be inferred from the present data. Deuterium substitution might lead to observable isotope effects in at least three different processes. These include (1) insertion of the metal into C-H bonds, (2) transfer of β -hydrogen to the metal center, and (3) the rate of reductive elimination of alkanes from metal hydrido alkyl intermediates. Since the observed reaction processes are formulated as multistep sequences, it is difficult to establish isotope effects for individual steps, especially when different reaction pathways operate competitively. In the first instance the data for dehydrogenation of propane-2- d_1 by Ni^+ suggest no isotope effect on the relative probabilities of insertion into otherwise equivalent C-H and C-D bonds.^{37,38} This assumes, however, that insertion into the secondary C-H bond initiates the dehydrogenation process. In the reaction of Ni^+ with butane-1,1,1,4,4,4- d_6 , the decomposition of 13 involves reductive elimination of



$\text{CD}_3\text{CH}_2\text{D}$ occurring in competition with a β -D transfer. In four-center rearrangements of chemically activated species, transfer of a β -H can be favored over a β -D transfer by a factor ranging from 2 (at high levels of excitation) to 6 or more (near threshold), depending on the excess internal energy.³⁹ The loss of ethane from $\text{CD}_3\text{CH}_2\text{CH}_2\text{CD}_3$ in the reaction with Ni^+ is somewhat more prominent than from unlabeled butane (Table II). In light of the previous discussion this appears reasonable, provided that the isotope effect associated with reductive elimination of $\text{CH}_3\text{CH}_2\text{D}$ vs. CH_3CH_3 (in the case of unlabeled butane) from intermediate 13 is smaller than that for β -D vs. β -H

transfer. Halpern and co-workers have reported a comparison of the rates of reductive elimination of methane from $[\text{PtH}(\text{CH}_3)(\text{PPh}_3)_2]$ and $[\text{PtD}(\text{CH}_3)(\text{PPh}_3)_2]$ that reveals a primary isotope effect of $k^{\text{H}}/k^{\text{D}} = 3.3 \pm 0.3$.⁴⁰ This suggests that a marked isotope effect should be apparent in the loss of $\text{CH}_3\text{CH}_2\text{D}$ vs. CH_3CD_3 in the reaction of Ni^+ with butane-1,1,1- d_3 since the former involves both a β -D transfer and rupture of the Ni^+-D bond of $[(\text{CH}_2\text{CD}_2)\text{NiD}(\text{C}_2\text{H}_5)]^+$. Unfortunately, the labeled precursor that would confirm this conjecture was not readily available to us. This discussion makes it clear, however, that it is difficult to assign isotope effects on product distributions (Tables II and X) to isotope effects in individual reaction steps.

Conclusion

The specific goal of the present study was to understand the mechanistic details by which hydrocarbons are cleaved by first-row group 8 metal ions. Despite the apparent similarity of the reactions with alkanes, somewhat different pathways are significant for the three ions. This can in part be attributed to differences in reaction thermochemistry. For example, nickel ions dehydrogenate linear alkanes with a chain of four or more carbons via a 1,4-elimination process that has as its first step insertion into a C-C rather than C-H bond, Scheme Iif.^{7,10} This pathway is apparently favored due to the low nickel ion-hydrogen bond strength as discussed above (Table I). Iron and cobalt ions make stronger first bonds to hydrogen and undergo a mixture of both 1,2- and 1,4-dehydrogenation processes. In the alkane elimination reactions, β -methyl transfers seem to play an important role in the reactions of Fe^+ with alkanes and to a lesser extent in Co^+ reactions. This may be due to a higher Fe^+ -methyl bond energy of the intermediates (such as 5 or 7). The appearance of β -methyl-transfer products at higher energies in the reactions of Co^+ and Ni^+ lends support to this assumption. It is not clear why all of the loss of methane in the reaction of Fe^+ with hexane appears to occur via combined β -methyl- and β -hydrogen-transfer processes (Scheme V), while $\sim 20\%$ of the loss of methane in reaction with pentane is via a pathway analogous to Scheme Iic. Scrambling of the intermediates in the reactions of deuterated alkanes with Co^+ (and to a lesser extent with Fe^+) is a significant process at low energies.⁸ No scrambling is observed in reactions of Ni^+ with these alkanes.

Differences in reactivity among the three metal ions are also noted with the cycloalkanes. While a substantial amount of ring cleavage products (loss of alkene) occurs in the interaction of Co^+ ²⁹ and Ni^+ with cyclopentane and cyclohexane, multiple dehydrogenation accounts for almost all of the products seen in the analogous reactions of Fe^+ .^{6,34,36}

Marked bond insertion selectivity is also noted in these reactions.³² For example, little insertion into terminal C-C bonds is observed even in the reactions of Fe^+ , which has a high first bond energy to a methyl radical. This suggests that perhaps the second metal ion-ligand bond is weak enough to account for this selectivity, or that bonds to larger alkyl fragments are much greater than to methyl groups, or a combination of both effects.

The present studies reveal that group 8 metal ions react with ^{13}C and deuterium-substituted alkanes to give highly specific label retention in the products. This is in contrast to ion-molecule reactions of organic species, which can lead to totally scrambled products.⁴¹ This suggests the use of

(36) In the reaction of Fe^+ with cyclobutane, $\text{Fe}(\text{C}_2\text{H}_4)^+$ accounts for $\sim 85\%$ of the product distributions at energies from 0.5 to 1.0 eV relative kinetic energy.³⁴

(37) A similar branching ratio was observed for products of the reaction of Fe^+ with 2-methylpropane and 2-methylpropane- d_{10} studies using an ion cyclotron resonance spectrometer.⁴⁸

(38) It is strange that no loss of D_2 is observed in the reaction of Fe^+ or Co^+ with hexane-3,3,4,4- d_4 , a product expected via a 1,2-dehydrogenation process. (Less than 5% would go undetected.)

(39) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(40) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

(41) Franklin, J. L. "Ion Molecule Reactions"; Franklin, J. L., Ed.; Plenum Press: New York, 1972; Vol. 1.

these gas-phase metal ion reactions as a tool to determine the original label distribution in a molecule. For example, by looking at the product ratio for loss of methane to loss of ethane from butane in the reaction with nickel ions, we can determine the amount of ^{13}C at interior vs. exterior positions. Because mass spectrometry is used to detect the products, this technique could be quite useful for identifying isotopically labeled reactants when only small amounts of the compound are available.

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Registry No. FeCl_3 , 7705-08-0; CoCl_2 , 7646-79-9; NiCl_2 , 7718-54-9; Fe^+ , 14067-02-8; Co^+ , 16610-75-6; Ni^+ , 14903-34-5; propane, 74-98-6; 2-methylpropane, 75-28-5; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; 2,2-dimethylpentane, 590-35-2; heptane, 142-82-5; 2-methylhexane, 591-76-4; octane, 111-65-9; cyclobutane, 287-23-0; cyclopentane, 287-92-3; methylcyclopentane, 96-37-7; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2.

Fluorine Substituent Effects on Metal-Carbene Bond Dissociation Energies. Implications for Metathesis Reactions of Fluorinated Olefins[†]

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The reactions of singly charged atomic nickel ions with ethylene oxide, cyclopropane, ethene, and several fluorinated hydrocarbons are examined by using an ion beam apparatus. Analysis of the thresholds for endothermic processes leading to the formation of nickel ion carbene species yields the bond dissociation energies $D^0(\text{Ni}^+-\text{CH}_2) = 86 \pm 6$ kcal/mol and $D^0(\text{Ni}^+-\text{CF}_2) = 47 \pm 7$ kcal/mol. Although fluorine substitution results in a substantially weakened bond, the difluorocarbene is, in fact, more stable as judged by several criteria. For example, the reaction of NiCH_2^+ with C_2F_4 to yield NiCF_2^+ and CH_2CF_2 is exothermic by 20 kcal/mol. The implications of these carbene bond strengths for the metathesis of various fluorinated olefins is discussed.

Introduction

Metal carbenes are considered to be propagating intermediates in reactions such as olefin metathesis² and possibly olefin polymerization.³ Little is known about the strength of the metal-carbene bond. Estimates of the relative strengths of π bonds in these species are sometimes derived from measured rotational barriers.⁴ This analysis may lead to erroneous conclusions for metal systems in which more than a single d orbital is available for π bonding.⁵ Theoretical calculations for model metal carbene systems have provided some estimates of bond strengths.^{6,7} Where comparison with experiment has been possible, the agreement is sufficiently poor to suggest that caution must be used in regarding the calculated bond strengths as useful estimates.⁷⁻⁹ In our laboratory, we have developed experimental methods to directly measure carbene bond strengths to metal ions in the gas phase.^{9,11} The present study reports the results of ion beam reactions of Ni^+ with various organic compounds which yield the metal carbene ions NiCH_2^+ and NiCF_2^+ . Bond energies are derived from an examination of thresholds of endothermic reactions using theoretical techniques described previously. These bond strengths can be used to assess fluorine substituent effects on carbene stability and evaluate the energetics of gas-phase metathesis reactions of fluorinated olefins with NiCH_2^+ and NiCF_2^+ as the propagating intermediates.

Experimental Section

The ion beam apparatus is described in detail elsewhere.¹⁰ Ions from a surface ionization source are accelerated and focused into a 60° sector magnet for mass separation. The mass selected beam is decelerated to a chosen energy and focused into a collision chamber containing the reactant gas. Product ions scattered in the forward direction are focused into a quadrupole mass filter and detected by using a channeltron electron multiplier operated

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