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Reactions of FeCH_2^+ and CoCH_2^+ with Aliphatic Alkanes in the Gas Phase. Activation of C-H and C-C Bonds by Naked Transition-Metal Carbene Ions

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Abstract: Gas-phase reactions of the title carbenes with several aliphatic alkanes using Fourier transform mass spectrometry (FTMS) are described. CoCH_2^+ reacts with alkanes larger than methane whereas FeCH_2^+ reacts with alkanes larger than ethane. Both FeCH_2^+ and CoCH_2^+ react predominantly by initial C-H bond insertion with some C-C bond insertion also observed. As a consequence of facile carbene-alkyl coupling, C-C bond cleavage processes proceed predominantly with elimination of the original carbene incorporated into the departing alkane neutral. In addition a small amount of C-C bond formation product is also observed. Finally, a greater degree of H/D scrambling is observed for CoCD_2^+ than for FeCD_2^+ .

Gas-phase techniques have proven to be particularly well suited for studying the reactivity of transition-metal ions in the absence of complicating ligand and solvent perturbations. A great deal of fundamental information, for example, has been obtained on the first-row groups 8-10 transition-metal ions with hydrocarbons.¹⁻⁸ More recently, the development of increasingly sophisticated experimental methodology has facilitated the study of organometallic fragment ions yielding information on the effect of various ligands on metal ion reactivity. The gas-phase reactivities and bond energies associated with the species MH^+ and MCH_3^+ , for example, have been a center of focus^{2,9-12} due to the importance of transition-metal hydrides¹³ and alkyls¹⁴ as proposed intermediates in catalytic reactions. Likewise, transition-metal methylidenes have been the subject of an increasing number of studies.^{9a,15-19} In this paper we add to this growing body of knowledge by reporting the reactions of FeCH_2^+ and CoCH_2^+ with a variety of alkanes. NiCH_2^+ was not studied due to the difficulty in generating it in sufficient amounts. Structures of the major product ions were investigated by collision-induced dissociation (CID).²⁰

Experimental Section









The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectroscopy²¹ and Fourier transform mass spectrometry (FTMS)²² have been discussed elsewhere. All experiments were performed with a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail²³ and equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and utilizes 80% neutral density screens as the transmitter plates which permit irradiation with various light sources. High-purity foils of the appropriate metals were attached to one of the transmitter screens. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a metal foil. Details of the laser ionization technique have been described elsewhere.^{5,24}

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-

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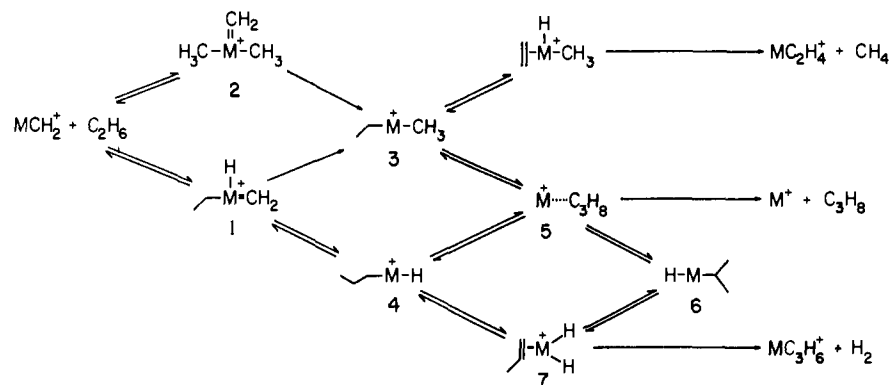
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Table I. Distributions of Neutral(s) Lost for the Reactions of FeCH_2^+ and CoCH_2^+ with Aliphatic Alkanes^a

alkane	carbene	neutral(s) lost, %											
		H_2	2H_2	CH_4	$\text{CH}_4 + \text{H}_2$	C_2H_6	$\text{C}_2\text{H}_6 + \text{H}_2$	C_3H_8	$\text{C}_3\text{H}_8 + \text{H}_2$	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}
C_2H_6	FeCH_2^+ ^b												
	CoCH_2^+	14		28				58					
C_3H_8	FeCH_2^+	4	2	70		8				16			
	CoCH_2^+	9	1	59		13				18			
	FeCH_2^+			10	54	9		17			10		
	CoCH_2^+	t ^c	t	11	52	21		10			6		
	FeCH_2^+			66	t	16		1			17		
	CoCH_2^+			57	20	7		5			11		
	FeCH_2^+			4	3	2	17	45		15		14	
	CoCH_2^+			3	8	8	24	44		9		4	
	FeCH_2^+			5	7	2	26	42		9		9	
	CoCH_2^+			3	18	6	41	25		4		3	
	FeCH_2^+					79	t	5		1		15	
	CoCH_2^+			2	12	37	26	11		7		5	
	FeCH_2^+			3			6	39	11	27	9		5
	CoCH_2^+			1			4	3	37	15	31	7	2
	FeCH_2^+				4	2	12	51	9	13	4		5
	CoCH_2^+			2	3	4	27	34	12	9	8		1
	FeCH_2^+			3	6		32	6	5	40	1		7
	CoCH_2^+			1	8	2	37	20	8	20	2		2

^a Product distributions are reproducible to $\pm 10\%$. ^b No reaction is observed for FeCH_2^+ with ethane. ^c "t" stands for trace ($< 1\%$).

Scheme I



condensable gases. $\text{C}_2\text{D}_4\text{O}$ (>98 atom % D) was obtained from MSD Isotopes, Merck Chemical Division. Sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for the collision-induced dissociation (CID) experiments at a total sample pressure of approximately 5×10^{-6} torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.^{23,25}

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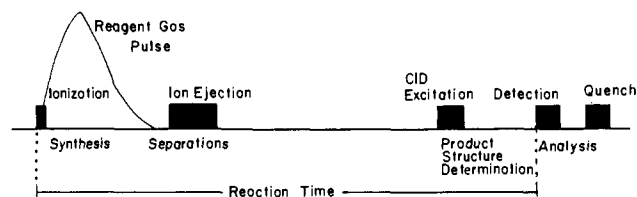
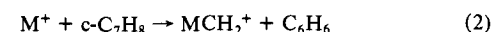
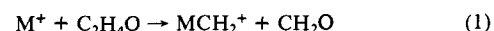


Figure 1. Sequence of events for pulsed valve addition of reagent gas for the FTMS experiment. See the Experimental Section for a more detailed explanation.

The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. kinetic energy can be made. These plots are reproducible to $\pm 5\%$ absolute and yield additional structural information. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.²⁶

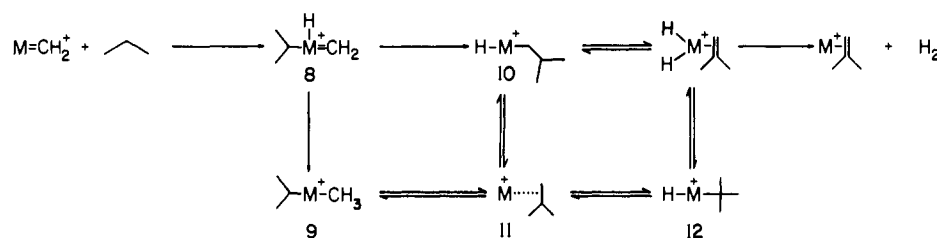
The MCH_2^+ ions were generated by reacting laser desorbed Fe^+ and Co^+ with ethyleneoxide²⁷ and cycloheptatriene,²⁹ reactions 1 and 2. The



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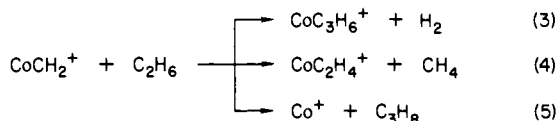
Scheme II



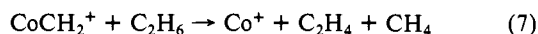
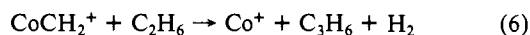
carbenes generated in reactions 1 and 2 yield identical results. Labeled carbene (MCD_2^+) was formed by reaction with deuterated ethylene oxide. The carbene reagent gas (ethylene oxide or cycloheptatriene) was introduced into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.²⁹ The sequence of events using the pulsed valve for addition of a reagent gas is illustrated in Figure 1. Initially, a concurrent laser (metal ionization) and valve pulse occurs. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of $\sim 10^{-5}$ torr and is pumped away by a high-speed 5-in. diffusion pump in ~ 250 ms. The MCH_2^+ (MCD_2^+) ions are then isolated by swept double resonance ejection techniques²² and allowed to react with a static pressure of a reagent gas without complicating reactions with ethylene oxide or cycloheptatriene. Product distributions for the reactions of MCH_2^+ and MCD_2^+ with aliphatic alkanes are summarized in Tables I and II and are reproducible to $\pm 10\%$ relative abundance. The products resulting from reactions with the static reagent gas can be isolated by additional swept ejection pulses to allow their further chemistry to be studied or their CID spectra to be obtained.

Results and Discussion

Reactions with Linear Alkanes. Ethane and Propane. Ethane is unreactive with FeCH_2^+ , while CoCH_2^+ yields three products, reactions 3–5. A mechanism for the reactions of CoCH_2^+ with



ethane is presented in Scheme I. Initially the carbene inserts into a C–H bond or a C–C bond forming **1** and **2**, respectively. Hydride migration onto the methylene of **1** yields **3** (a methyl-ethyl species). Methylene insertion into the ethyl of **1** generates **4** and methylene insertion into the methyl of **2** yields **3**. Intermediate **3** can decompose by a β -hydride shift followed by reductive elimination of methane. Dehydrogenation and C_3H_8 elimination probably proceed by either initial formation of **4** or by formation of propane from **3** generating intermediate **5** in which propane and Co^+ are held together by weak electrostatic forces. Species **4**, **5**, and **6** can undergo rapid interconversion by a series of facile oxidative addition/reductive elimination processes. β -Hydride abstraction from intermediates **4** and **6** generates **7** which reductively eliminates hydrogen. Formation of Co^+ may proceed by direct elimination of propane from intermediate **5** or by the sequential elimination processes, reactions 6 and 7. Formation

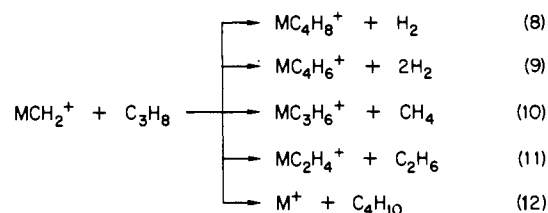


of Co^+ is believed to proceed predominantly by direct elimination

of propane since the sequential elimination reactions 6 and 7 are calculated to be endothermic by 8 ± 7 and 9 ± 7 kcal/mol, respectively.³⁰ Methylidene incorporation (migratory insertion) of an alkyl has also been implicated for reactions of MCH_3^+ ($\text{M} = \text{Fe}, \text{Co}$) with cyclic alkanes^{12b} and for reactions of RhCH_2^+ with alkanes in the gas phase.¹⁹ Migratory insertion of an alkyl to an alkylidene is well supported in solution for cationic alkylidene/alkyl complexes.^{31–37} In those studies the alkylidene/alkyl insertions were facilitated by a positive charge on the metal center. It has been suggested that the positive charge renders the unsaturated carbon center electrophilic and accelerates a migratory insertion which is best regarded as a migration of the alkyl group with its bonding electron pair onto the unsaturated carbon.³⁷ Such a process is analogous to the well-characterized alkyl/carbonyl migratory insertions.³⁸

H/D scrambling occurs for reaction of CoCD_2^+ with ethane (Table II). Total scrambling would yield a dehydrogenation (H_2 :HD: D_2) ratio of 15:12:1. The actual ratio of 9:4:<1 suggests that considerable H/D scrambling occurs prior to dehydrogenation. This scrambling can be accounted for by invoking an equilibrium between intermediates **4**, **5**, and **6** in Scheme I. Random scrambling would result in a methane (CH_4 : CH_3D : $\text{C}_2\text{H}_5\text{D}$) ratio of 1:2.7:1. The actual ratio of 1:1:2 (Table II) indicates that considerable methane elimination proceeds by direct β -hydride abstractions from intermediates **1** and **3** in Scheme I. In this case, H/D scrambling occurs as above for dehydrogenation generating intermediate **5** with the label scrambled. Oxidative addition into a C–C bond again generates **3** which eliminates methane as CH_4 , CH_3D , and CH_2D_2 depending on location of the label.³⁹ Methane elimination as CH_4 may also proceed by initial C–C bond insertion forming intermediate **2** in Scheme I.

Propane reacts with both carbenes, yielding the products in reactions 8–12 (Table I). Only a trace of H/D scrambling is seen



for FeCD_2^+ ; however, scrambling is again observed for CoCD_2^+ . Elimination of C_4H_8 is the only fragment observed under collisional activation of CoC_4H_8^+ and FeC_4H_8^+ formed in reaction 8, sug-

(27) This reaction for Co^+ was first reported by Armentrout and Beauchamp in ref 15. Using the bond energies from ref 9b and 15 and the heats of formation in ref 28, formation of FeCH_2^+ and CoCH_2^+ from ethylene oxide is calculated to be 17 ± 5 and 6 ± 7 kcal/mol exothermic, respectively, assuming formaldehyde as the natural product.

(28) Supplementary thermochemical information taken from: Rosenstock, H. M.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supplement No. 1. $\Delta H_f(\text{CH}_2)$ taken as 92.4 kcal/mol from: Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverund, A. N. *J. Phys. Chem. Ref. Data* **1975**, *4*, No. 1.

(29) This reaction for Co^+ was first reported by Jacobson, Byrd, and Freiser in ref 8c. Using the bond energies from ref 9b and 15 and the heats of formation in ref 28, formation of FeCH_2^+ and CoCH_2^+ from cycloheptatriene is calculated to be exothermic by 27 ± 5 and 16 ± 7 kcal/mol, respectively, assuming benzene as the neutral product.

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







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







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(38) For a general review of CO insertion reactions see: Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(39) Co^+ reacts with propane to yield both dehydrogenation and methane loss products. See, for example, ref 2.

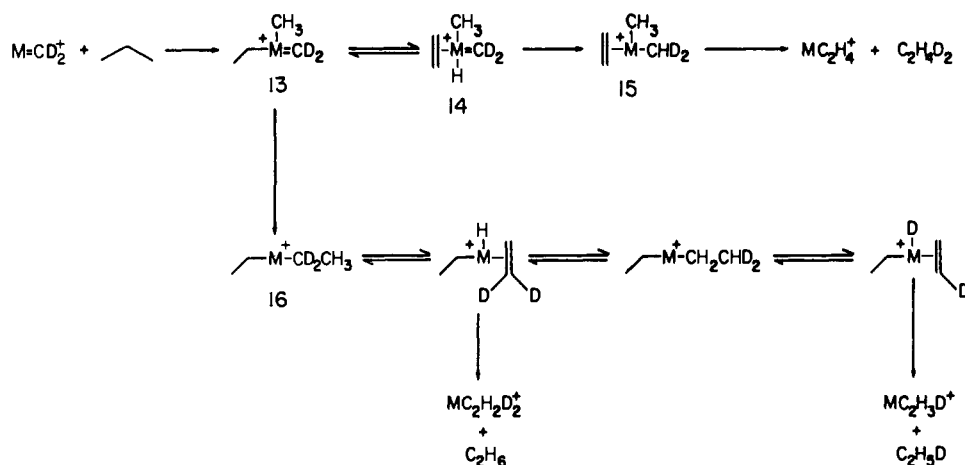
Table II. Distributions of Neutral(s) Lost for the Reactions of FeCD_2^+ and CoCD_2^+ with Aliphatic Alkanes^a

alkane	carbene	neutral(s) lost, %														
		H_2	HD	D_2	2H_2	CH_4	CH_3D	CH_2D_2	$\text{CH}_4 + \text{H}_2$	$\text{CH}_3\text{D} + \text{H}_2$	$\text{CH}_2\text{D}_2 + \text{H}_2$	C_2H_6	$\text{C}_2\text{H}_5\text{D}$	$\text{C}_2\text{H}_4\text{D}_2$	$\text{C}_2\text{H}_6 + \text{H}_2$	
C_2H_6	$\text{FeCD}_2^+, ^b$															
	CoCD_2^+	9	4	t ^c		6	6	12								
C_3H_8	FeCD_2^+	3	t	t	2			71								
	CoCD_2^+	8	2	t		12	6	45				3	2	7		
	FeCD_2^+							11								
	CoCD_2^+						1	14			7	43	10	4	6	
	FeCD_2^+							69						t	10	
	CoCD_2^+						3	61			2	10		1	7	
	FeCD_2^+							7								
	CoCD_2^+							5				8	6	4	3	
	FeCD_2^+							7								
	CoCD_2^+							5				17	2		6	
	FeCD_2^+														84	
	CoCD_2^+					2				5	5	t		3	35	26
	FeCD_2^+							3								
	CoCD_2^+							1					2		2	
	FeCD_2^+									3					3	
	CoCD_2^+							4					1	2		8
	FeCD_2^+							3							1	
	CoCD_2^+							2							6	

alkane	carbene	neutral(s) lost, %													
		$\text{C}_2\text{H}_5\text{D} + \text{H}_2$	$\text{C}_2\text{H}_4\text{D}_2 + \text{H}_2$	C_3H_8	$\text{C}_3\text{H}_7\text{D}$	$\text{C}_3\text{H}_6\text{D}_2$	$\text{C}_3\text{H}_7\text{D} + \text{H}_2$	$\text{C}_3\text{H}_6\text{D}_2 + \text{H}_2$	C_4H_{10}	$\text{C}_4\text{H}_9\text{D}$	$\text{C}_4\text{H}_8\text{D}_2$	$\text{C}_5\text{H}_{11}\text{D}$	$\text{C}_5\text{H}_{10}\text{D}_2$	$\text{C}_6\text{H}_{12}\text{D}_2$	$\text{C}_7\text{H}_{14}\text{D}_2$
C_2H_6	$\text{FeCD}_2^+, ^b$														
	CoCD_2^+					63									
C_3H_8	FeCD_2^+												17		
	CoCD_2^+											16			
	FeCD_2^+							19						10	
	CoCD_2^+						1	8					5		
	FeCD_2^+													21	
	CoCD_2^+						2	1	2				8		
	FeCD_2^+													8	
	CoCD_2^+												18	6	6
	FeCD_2^+													12	6
	CoCD_2^+													4	5
	FeCD_2^+							4	1						10
	CoCD_2^+							1	3					2	3
	FeCD_2^+														
	CoCD_2^+														
	FeCD_2^+														
	CoCD_2^+														
	FeCD_2^+														
	CoCD_2^+														

^a Product distribution are reproducible to $\pm 10\%$. ^b No reaction is observed for FeCD_2^+ with ethane. ^c "t" stands for trace ($<1\%$).

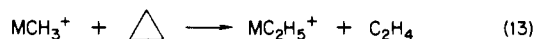
Scheme III



gesting that these ions have a metal-isobutene structure.⁴⁰ A mechanism for $\text{M}(\text{isobutene})^+$ formation is presented in Scheme II and involves initial insertion into a secondary C-H bond forming **8**. Intermediate **8** rearranges to **9** by a hydride shift or to **10** by methylene insertion into the propyl ligand. Reductive elimination in **10** generates **11** (formally a metal-isobutane complex) which can be in equilibrium with the hydrido-alkyl species **10** and **12**. β -Hydride abstraction and reductive elimination of hydrogen generates $\text{M}(\text{isobutene})^+$. Little H/D scrambling suggests that dehydrogenation proceeds predominantly by direct formation of **10** instead of through intermediate **11**. The small amount of MC_4H_6^+ formation probably proceeds via initial insertion of MCH_2^+ into a terminal C-H bond followed by rearrangement to a linear C_4 structure which generates $\text{M}(\text{butadiene})^+$ upon elimination of 2H_2 . Formation of $\text{M}(\text{butadiene})^+$ in this manner requires D° ($\text{M}^+-\text{C}_4\text{H}_6$) to exceed 55 ± 5 and 44 ± 7 kcal/mol for Fe^+ and Co^+ , respectively.^{30,41}

Methane elimination as CH_2D_2 occurs exclusively for FeCD_2^+ and also dominates with CoCD_2^+ . Initial insertion into a C-H bond followed by two sequential β -hydride shifts would result in complete loss of label. Elimination of methane as CH_4 and CH_3D for CoCD_2^+ may proceed by initial formation of intermediate **11** in Scheme II followed by insertion into a C-C bond. Elimination of CH_4 may also proceed by initial insertion into a C-C bond of propane, generating an ethyl-methyl-methylene complex. Coupling of methylene to ethyl followed by reductive elimination of methane would result in retention of the label.

Surprisingly, ethane elimination as $\text{C}_2\text{H}_4\text{D}_2$ occurs exclusively for FeCD_2^+ with some H/D scrambling seen for CoCD_2^+ . Ethane elimination probably proceeds by initial insertion into a C-C bond, generating **13** in Scheme III. Reversible β -hydride shifts generates **14** with rapid incorporation of hydride into methylene followed by reductive elimination of ethane. This mechanism requires that hydride transfer forming **15** must be rapid with respect to methyl-methylene and ethyl-methylene coupling, methylene-ethylene coupling via a metallacyclobutane intermediate,¹⁹ and reductive elimination of methane. Methyl-methylene coupling has been proposed as the key step in the reaction of MCH_3^+ ($\text{M} = \text{Fe}, \text{Co}$) with cyclopropane,^{12b} resulting in ethene elimination, reaction 13. H/D scrambling for CoCD_2^+ may proceed by initial



methyl-methylene coupling forming the bis(ethyl) complex **16** in Scheme III. Reversible β -hydride shifts result in H/D scrambling with elimination of ethane as C_2H_6 , $\text{C}_2\text{H}_5\text{D}$, and $\text{C}_2\text{H}_4\text{D}_2$.

Formation of M^+ probably proceeds by direct C_4H_{10} elimination since any sequential eliminations are calculated to be endothermic.³⁰

Butane, Pentane, and Hexane. Reactions of the carbenes with the larger linear alkanes can be explained predominantly by the mechanisms described above for ethane and propane. Again, some H/D scrambling is seen for CoCD_2^+ but not for FeCD_2^+ . Formation of MC_4H_6^+ from MCD_2^+ , for example, dominates for reactions with butane (Table II). This presumably is formed by initial C-H bond insertion followed by β -hydride abstraction with reductive elimination of methane generating an activated $\text{M}(\text{linear butene})^+$ species which dehydrogenates to $\text{M}(\text{butadiene})^+$.^{8a,b}

Two C-C bond cleavage products are observed, MC_3H_6^+ and MC_2H_4^+ . Reaction with FeCD_2^+ results in complete loss of label with some scrambling seen for CoCD_2^+ (Table II). The results for FeCD_2^+ can be explained by mechanisms similar to Scheme III where insertion into a terminal C-C bond results in $\text{C}_2\text{H}_4\text{D}_2$ elimination and insertion into the central C-C bond yields $\text{C}_3\text{H}_6\text{D}_2$ elimination. With CoCD_2^+ , considerable amounts of C_2H_6 and $\text{C}_2\text{H}_5\text{D}$ elimination are also observed. These results can best be interpreted by invoking a methylene-methyl coupling similar to that in Scheme III for propane.

Cleavage of the C-C bond framework dominates for reactions with pentane and hexane in contrast to butane and propane described above. In addition, these products generally result in loss of label with MCD_2^+ . These results can best be explained by invoking initial insertion into a C-H bond with reductive elimination of methane resulting in loss of label and formation of an activated $\text{M}(\text{olefin})^+$ species. With pentane, for example, both 1- and 2-pentene metal species are formed upon methane elimination. These activated $\text{M}(\text{olefin})^+$ complexes retain sufficient energy for subsequent fragmentation. The 1-pentene complexes decompose predominantly by elimination of C_2H_4 or C_3H_6 while the 2-pentene species loses CH_4 , C_2H_4 , and C_3H_6 .³² Alternative mechanisms involving initial C-C bond insertion analogous to Scheme III are also possible. CID of the MC_4H_8^+ formed from reaction with both pentane and hexane indicate formation of linear butene bound to the metal ion.⁴⁰

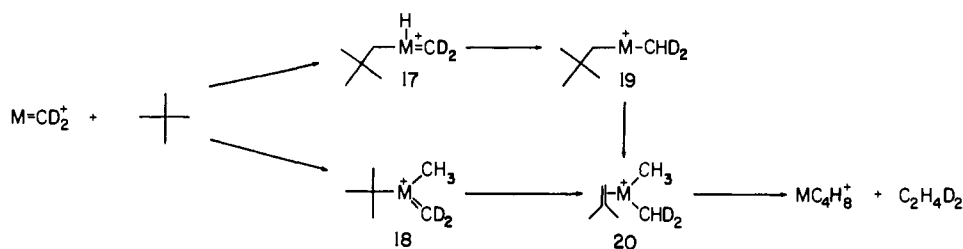
Reactions with Branched Alkanes. 2-Methylpropane and 2,2-Dimethylpropane. Formation of MC_4H_8^+ is the dominant process for reaction with 2-methylpropane. The CID spectra of this ion suggest formation of $\text{M}(\text{isobutene})^+$. A significant amount of CoC_4H_8^+ is also produced. This is probably formed by initial methane elimination forming an activated $\text{Co}(\text{isobutene})^+$ species which subsequently eliminates hydrogen.⁴¹ As with propane, ethane elimination as $\text{C}_2\text{H}_4\text{D}_2$ occurs exclusively for FeCD_2^+ with some H/D scrambling observed for CoCD_2^+ . These results can be explained by processes similar to those outlined in Scheme III.

Reaction of FeCH_2^+ and FeCD_2^+ with 2,2-dimethylpropane yields predominantly FeC_4H_8^+ . CID of this ion is again consistent with formation of $\text{Fe}(\text{isobutene})^+$. This ion may be generated by either initial C-H or C-C bond insertion generating intermediates **17** and **18**, respectively (Scheme IV). Intermediate **17** forms **19**

(40) Both $\text{Co}(\text{isobutene})^+$ and $\text{Fe}(\text{isobutene})^+$ species eliminate C_4H_8 exclusively upon collisional activation in FTMS while linear butenes bound to either cobalt or iron cations readily dehydrogenate at moderate collision energies in FTMS. See, for example, ref 6.

(41) Diene bond strengths appear to be in the range of 45–55 kcal/mol for Fe^+ and Co^+ . See, for example: ref 8 and 12.

Scheme IV



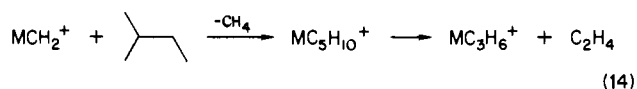
which converts to **20** by a β -methyl shift. Reductive elimination of $C_2H_4D_2$ (for reaction with $FeCD_2^+$) generates $M(\text{isobutene})^+$. Insertion into a C–C bond generates **18** which rearranges to **20** by a β -hydride shift with reductive elimination of $C_2H_4D_2$, again generating $M(\text{isobutene})^+$.

With $CoCH_2^+$, significant amounts of $CoC_4H_8^+$ and $CoC_4H_6^+$ are produced. Structural studies indicate that $CoC_4H_8^+$ consists of isobutene bound to Co^+ . Reaction with $CoCD_2^+$ yields $CoC_4H_8^+$ and $CoC_4H_4D_2^+$ as the major products, both nominally mass 115, with no $CoC_4H_6D_2^+$ observed. Formation of $CoC_4H_8^+$ probably proceeds by both initial C–H bond insertion and by initial C–C bond insertion (Scheme IV). Formation of $CoC_4H_6^+$ and $CoC_4H_4D_2^+$ from $CoCH_2^+$ and $CoCD_2^+$, respectively, probably proceed by initial formation of a methyl–neopentyl complex, **19**, which generates an activated $Co(2,2\text{-dimethylbutane})^+$ by reductive elimination. Oxidative addition and reductive elimination generates the corresponding $CoC_4H_6^+$ and $CoC_4H_4D_2^+$ species. Elimination of methane, propane, and butane may also occur from the activated $Co(\text{alkane})^+$ complex.^{2a}

2-Methylbutane, 2,2-Dimethylbutane, and 2,3-Dimethylbutane.

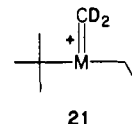
The neutral losses for the reactions of MCH_2^+ and MCD_2^+ with the methylbutanes are summarized in Tables I and II. Methane loss and methane loss plus dehydrogenation proceeds with nearly exclusive loss of label with MCD_2^+ for all three methylbutanes. This suggests initial insertion into a C–H bond, β -hydride abstraction, and reductive elimination of methane generating an activated $M(\text{olefin})^+$ species.

Cleavage of the methylbutane framework proceeds with nearly exclusive loss of the label with MCD_2^+ . This may occur by either initial insertion into a C–H bond followed by elimination of two methanes or by initial insertion into a terminal C–C bond followed by ethane and H_2 elimination. The dominant elimination of $C_3H_6D_2$ for reaction of MCD_2^+ with 2-methylbutane probably proceeds by initial C–H insertion resulting in loss of CH_2D_2 generating an activated $M(\text{methylbutene})^+$ species. This then decomposes further predominantly by ethene elimination,^{8a,b} reaction 14. This reaction sequence requires $D^0(M^+-C_3H_6)$ to be $>29 \pm 7$ and $>40 \pm 5$ kcal/mol for Co^+ and Fe^+ , respectively.^{12,43}



(42) Cobalt and iron cations react with linear olefins larger than butene predominantly by insertion into allylic C–C bonds: see, for example, ref 6 and 8.

$MC_4H_8^+$ is the dominant ion generated with 2,2-dimethylbutane. CID indicates that it consists of isobutene bound to the metal ion. With MCD_2^+ , elimination of $C_3H_6D_2^+$ forming $MC_4H_8^+$ occurs predominantly. This may be generated by initial insertion into the central C–C bond generating **21**. β -Hydride



transfer from *tert*-butyl followed by reductive elimination of $C_3H_6D_2$ generates $M(\text{isobutene})^+$. With 2,3-dimethylbutane, C_3H_8 ($C_3H_6D_2$ with MCD_2^+) loss generates $MC_4H_8^+$ which consists of linear butene bound to the metal ion.

Conclusions

Fe^+ and Co^+ react with aliphatic alkanes predominantly by attacking C–C bonds.^{1–8} In contrast to this behavior FeH^+ , CoH^+ , and $CoCH_3^+$ attack C–H bonds exclusively with $FeCH_3^+$ being unreactive toward alkanes.^{10–12} Both $FeCH_2^+$ and $CoCH_2^+$ are found to react with aliphatic alkanes predominantly by initial C–H bond insertion with some C–C bond cleavages also observed. As a consequence of facile carbene–alkyl coupling, C–C bond cleavage processes proceed predominantly with elimination of the original carbene incorporated into the departing alkane neutral. In addition, a small amount of C–C bond formation is also observed. A greater degree of H/D scrambling occurs for $CoCD_2^+$ than $FeCD_2^+$ (in analogy with other results).^{2,19} Finally, CID on $MC_4H_8^+$ structures was used to distinguish $M(\text{isobutene})^+$ from $M(\text{linear butene})^+$, yielding information on reaction mechanisms.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (CHE-8310039) for supporting the development of FTMS methodology.

Registry No. $FeCH_2^+$, 90143-30-9; $CoCH_2^+$, 76792-07-9; C_2H_6 , 74-84-0; C_3H_8 , 74-98-6; C_4H_{10} , 106-97-8; C_5H_{12} , 109-66-0; C_6H_{14} , 110-54-3; $FeCD_2^+$, 93604-57-0; $CoCD_2^+$, 93604-58-1; 2-methylpropane, 75-28-5; 2,2-dimethylpropane, 463-82-1; 2-methylbutane, 78-78-4; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8.

(43) Alkene bond energies appear to be in the range of 35–40 kcal/mol for Fe^+ and Co^+ . See, for example, ref 7a and 7b.

Generation and Reactions of Atomic Metal Anions in the Gas Phase. Determination of the Heterolytic and Homolytic Bond Energies for VH, CrH, FeH, CoH, and MoH

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Abstract: The atomic transition-metal anions V^- , Cr^- , Fe^- , Co^- , Mo^- , and W^- have been generated in the gas phase by collision-induced dissociation of the corresponding metal carbonyl negative ions in a Fourier transform mass spectrometer. Isolation of each ion by double resonance ejection techniques has enabled an examination of their ion-molecule reactions with added neutral substrates. Each atomic ion reacts with the parent metal carbonyl by dissociative electron transfer to produce mononuclear metal carbonyl anions while the cobalt ion gives both mononuclear and dinuclear product ions by metal-metal and metal-carbon bond cleavage, respectively. Vanadium, chromium, and molybdenum anions also produce dinuclear cluster ions in reactions with their parent neutral hexacarbonyls. The proton affinities of several of the atomic ions have been determined by bracketing methods and are found to be the following (kcal/mol): V^- , 339.4 ± 3 ; Fe^- , 339.4 ± 3 ; Cr^- , 339.4 ± 3 ; Co^- , 340.5 ± 3 ; Mo^- , 342.4 ± 3 . Combining these data with measured electron affinities of the metal yields homolytic bond energies for the hydrides $D[M-H]$ (kcal/mol): $V-H$, 37.9 ± 3 ; $Fe-H$, 29.6 ± 3 ; $Cr-H$, 41.2 ± 3 ; $Co-H$, 42.2 ± 3 ; $Mo-H$, 46.0 ± 3 . The new monohydride bond energies compare favorably with other experimental and theoretical data in the literature and have been used to derive additional thermodynamic properties for metal hydride ions and neutrals.

One of the most active frontiers for gas-phase ion research over the last decade has been the study of ion-molecule reactions involving transition-metal complexes and the chemistry of atomic and coordinated metal ions. The incentives for the considerable effort dedicated to this research are clearly illuminated in the current literature. Recent gas-phase studies involving inorganic and organometallic compounds have produced a wealth of important and useful thermodynamic data such as homolytic and heterolytic metal-hydrogen, metal-carbon, and metal-oxygen bond strengths,¹⁻⁹ relative ligand binding energies for atomic and molecular metal cations,¹⁰⁻¹⁵ and gas-phase basicities,¹⁶⁻¹⁸ hydride affinities,^{19,20} electron affinities,²¹⁻²⁵ and ionization potentials^{3,11,26}

for neutral transition-metal complexes. By far, the majority of this research has focused on the chemistry of coordinated and atomic metal *cations*. This is mainly due to the fact that these species can be generated readily by a variety of ionization methods such as laser desorption,^{27,28} surface ionization,⁸ and electron impact ionization²⁹ of volatile inorganic compounds such as metal carbonyls. Until fairly recently,³⁰⁻³⁴ only a relatively few studies of gas-phase ion-molecule reactions involving transition-metal negative ion complexes had been reported.^{1,12,16,35-40} Moreover,

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