Reactions of $FeOH^+$ and $CoOH^+$ with Alkanes in the Gas Phase

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Abstract: The gas-phase reactions of $FeOH^+$ and $CoOH^+$ with aliphatic alkanes up to C_6H_{14} were studied. As was the case in earlier studies on MH^+ and MCH_3^+ (M = Fe, Co), $FeOH^+$ is found to be less reactive than $CoOH^+$. For aliphatic alkanes, $CoOH^+$ reacts with species larger than ethane, while $FeOH^+$ only reacts with branched alkanes and hexane. Following initial C-H insertion, H_2O loss dominates the $FeOH^+$ reactions. For $CoOH^+$, however, H_2O loss leads to an activated Co^+–alkyl complex which decomposes further. In addition, dehydrogenation with no H_2O elimination also occurs in contrast to FeH^+, CoH^+, and $CoCH_3^+$ with alkanes, where complete loss of the initial ligand is seen. Initial C–C insertion is also a major pathway leading to $M(OH)(alkene)^+$ species, and for $FeOH^+$, pressure-dependent adduct formation is also observed with hexane and several branched alkanes. Both $FeOH^+$ and $CoOH^+$ react with cyclopropane and cyclobutane by initial C–C insertion. For cyclopentane and cyclohexane, $CoOH^+$ reacts exclusively by C–H insertion, while $FeOH^+$ is unreactive. As expected on the basis of thermodynamic calculations, the overall reactivity of MOH^+ is intermediate to that of MH^+ and MCH_3^+.

Several recent studies have shown that the reactivity of a gas-phase atomic metal ion is dramatically altered by the addition of a ligand. For example, while $Fe^{+\,1-4}$ and $Co^{+\,3-5}$ react with alkanes predominantly by oxidative addition of the metal into C–C bonds, C–H insertion occurs almost exclusively in the reactions of MD^+,[6] MCH_3^+,[7,8] MO^+,[9] and MCH_2^+[10] with alkanes (M = Fe, Co). The overall reactivity of a metal ion may be either increased or decreased by the presence of a ligand.

In this paper the results of a study of the reactions of $FeOH^+$ and $CoOH^+$ with alkanes are presented. In solution, metal complexes are often used as catalysts in the oxidation of organic compounds.[11] Metal–hydroxide intermediates are thought to play an important role in these processes. In particular, metal–hydroxides have frequently been invoked in homolytic catalysis mechanisms. For example, Groves et al.[12,13] have proposed electron transfer process 1 as a step in the hydroxylation of organic substrates in biological systems. However, Sharpless et al.[14] have

$$O{=}Fe^{V} + RH \rightarrow [HO{-}Fe^{IV}{\cdot}R] \rightarrow Fe^{III} + ROH \quad (1)$$

suggested that this reaction occurs via an electrophilic substitution, process 2, which also involves a metal–hydroxide intermediate. The mechanism proposed by Sharpless, with attack of the nu-

$$O{=}Fe^{V} + RH \rightarrow [HO{-}Fe^{V}{-}R] \rightarrow Fe^{III} + ROH \quad (2)$$

cleophile on the metal center to form an organometallic intermediate, is in contrast to the generally accepted mechanism involving oxygen attack.[11] Regardless of the mechanism, the end result of these solution studies is incorporation of a hydroxy group at a metal center into a hydrocarbon chain. Thus, one of the interesting aspects of the work discussed here was to determine if any similar process occurs in the gas-phase reactions of $FeOH^+$ and $CoOH^+$ with alkanes.

Experimental Section

All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer which has previously been discussed in detail.[15] The mass spectrometer is 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 has a 0.25-in.-diameter hole in one of the transmitter plates to allow various light sources access to the inside of the cell. Metal ions were generated by focusing the frequency-doubled beam (532 nm) of a Quanta Ray Nd:YAG laser onto high-purity metal foils which were supported by the opposite transmitter plate. Details of the laser ionization experiment have been described elsewhere.[16,17]

Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. Sample pressures were on the order of 2×10^{-7} Torr and were monitored with a Bayard-Alpert ionization gauge.

Collision-induced dissociation experiments using the FTMS[3,15] employed argon as the collision gas at a pressure of $\sim 5 \times 10^{-6}$ Torr. Under these conditions multiple collisions with the target gas can occur. The collision energy of the ions can be varied typically in the lab frame between 0 and 100 eV. Plots of CID product intensities vs. kinetic energy (E_{max}) are reproducible to ±10% absolute. 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.[18] Collision-induced dissociation (as well as other structural techniques) with FTMS can only be applied to ions having relatively long lifetimes (>1 ms). Reaction intermediates, therefore, are assigned as reasonable as opposed to proven.

MOH^+ ions were formed by the reaction of Fe^+ and Co^+ with nitromethane, reaction 3. Nitromethane was introduced into the vacuum

$$M^+ + CH_3NO_2 \rightarrow MOH^+ + CH_2NO \quad (3)$$

chamber through a General Valve Corp. Series 9 pulsed solenoic valve.[19]

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Table I. Product Distributions for the Reactions of $FeOH^+$ and $CoOH^+$ with Linear Alkanes

	products		rel abundance		
alkane	ion	neutral(s)	$FeOH^+$	$CoOH^+$	
methane			NR[a]	NR	
ethane			NR	NR	
propane	$M(C_3H_6)(OH)^+$	H_2	NR	100[b]	
butane	$MC_3H_5^+$	H_2O, CH_4	NR	5	
	$M(OH)(C_2H_4)^+$	C_2H_6		18	
	$MC_4H_7^+$	H_2O, H_2		48	
	$M(OH)(C_4H_8)^+$	H_2		29	
pentane	$MC_3H_5^+$	H_2O, C_2H_6	NR	11	
	$M(OH)(C_2H_4)^+$	C_3H_8		4	
	$M(OH)(C_3H_6)^+$	C_2H_6		20	
	$MC_5H_9^+$	H_2O, H_2		51	
	$M(OH)(C_5H_8)^+$	$2H_2$		5	
	$M(OH)(C_5H_{10})^+$	H_2		9	
hexane	$MC_3H_5^+$	H_2O, C_3H_8	0	4	
	$M(OH)(C_2H_4)^+$	C_4H_{10}	0	3	
	$MC_4H_7^+$	H_2O, C_2H_6	0	12	
	$M(OH)(C_3H_6)^+$	C_3H_8	0	12	
	$M(OH)(C_4H_8)^+$	C_2H_6	0	11	
	$MC_6H_9^+$	$H_2O, 2H_2$	0	11	
	$MC_6H_{11}^+$	H_2O, H_2	22	42	
	MC_6H_{13}	H_2O	14	0	
	$M(OH)(C_6H_{12})^+$	H_2	0	5	
	$M(OH)(C_6H_{14})^+$		64	65	0

[a] NR indicates that no reaction occurs. [b] The reaction with propane is slow relative to that with the other compounds.

Initially, a concurrent laser and valve pulse occurs. Nitromethane 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 $\sim$250 ms. The MOH^+ ions formed by reaction 3 are then isolated by swept double resonance techniques[20] and allowed to react with a static pressure of reagent gas without complicating reactions with nitromethane. This sequence of events is illustrated in Figure 1 for the generation of $CoOH^+$ and its reaction with 2-methylpropane. As can be seen from Figure 1D, enough signal intensity remains to allow CID[3,15] and double-resonance[20] experiments to be performed on primary reaction products. Unless otherwise noted, all of the reactions reported are presumed to be at thermal energies.

The MOH^+ ions may exist as a hydroxide bound to the metal ion as written or, conceivably, as the hydrido-oxide structure HMO^+. We recently reported $D(Fe^+-OH) = 73 \pm 3$ kcal/mol and $D(Co^+-OH) = 71 \pm 3$ kcal/mol[21] from which $D(FeO^+-H) = 107$ kcal/mol and $D(CoO^+-H) = 109$ kcal/mol can be estimated. These latter bond energies are much more representative of an O–H bond than either $D(Fe^+-H) = 58$ kcal/mol or $D(Co^+-H) = 52$ kcal/mol.[22] Furthermore, we observe hydroxide loss as the only fragment upon both collisional excitation and photoexcitation.[21] The complete absence of H loss in the CID and photodissociation experiments further suggests that an activated rearrangement to the hydrido-oxide structure does not occur.

Results and Discussion

The primary products for the reactions of $FeOH^+$ and $CoOH^+$ with linear, branched, and cyclic alkanes are presented in Tables I–III, respectively. Since neutrals are not directly monitored, they are inferred from the ionic products. Prior to a discussion of the reactions of specific alkanes, several general observations can be made about the overall reactivities of $FeOH^+$ and $CoOH^+$ with alkanes.

As is evident from the tables, two types of products are formed in these reactions: products that retain the OH to form $M(OH)(alkene)^+$ or $M(OH)(alkane)^+$ and products that lose the OH as H_2O to form $M(alkyl)^+$ or $M(allyl)^+$. With the exception of the reactions of cyclopropane and cyclobutane, both types of products are present for all of the alkanes studied, with OH loss dominating. In general, OH loss is seen to a greater extent with $FeOH^+$ than with $CoOH^+$. Typically on the order of 30–40% of the products retain the OH. In contrast, almost no initial ligand retention occurs in the reactions of MD^+ [6] and MCH_3^+ [7,8] with alkanes, while FeO^+ reacts with alkanes to form products resulting from both retention and elimination of O.[9] For comparison, the reactions of a series of ML^+ species with butane and 2-methylpropane are given in Tables IV and V.

Table II. Product Distributions for the Reactions of $FeOH^+$ and $CoOH^+$ with Branched Alkanes

	products		rel abundance	
alkane	ion	neutral(s)	$FeOH^+$	$CoOH^+$
2-methyl-propane	$MC_3H_5^+$	H_2O, CH_4	0	5
	$MC_4H_7^+$	H_2O, H_2	0	65
	$MC_4H_9^+$	H_2O	38	0
	$M(OH)(C_3H_6)^+$	CH_4	0	6
	$M(OH)(C_4H_8)^+$	H_2	36	24
	$M(OH)(C_4H_{10})^+$		26	0
2,2-dimethyl-propane	$M(OH)(CH_4)^+$	C_4H_8	15	8
	$MC_4H_7^+$	H_2O, CH_4	5	76
	$MC_5H_{11}^+$	H_2O	80	0
	$M(OH)(C_4H_8)^+$	CH_4	0	16
2-methyl-butane	$MC_3H_5^+$	H_2O, C_2H_6	0	7
	$M(OH)(C_2H_4)^+$	C_3H_8	0	4
	$MC_4H_7^+$	H_2O, CH_4	0	11
	$M(OH)(C_3H_6)^+$	C_2H_6	0	13
	$MC_5H_9^+$	H_2O, H_2	10	54
	$MC_5H_{11}^+$	H_2O	50	0
	$M(OH)(C_4H_8)^+$	CH_4	0	3
	$M(OH)(C_5H_{10})^+$	H_2	28	8
	$M(OH)(C_5H_{12})^+$		12	0
2,3-dimethyl-butane	$MC_3H_5^+$	H_2O, C_3H_8	0	16
	$M(OH)(C_3H_6)^+$	C_3H_8	13	50
	$MC_5H_9^+$	H_2O, CH_4	0	5
	$MC_6H_{11}^+$	H_2O, H_2	27	29
	$MC_6H_{13}^+$	H_2O	39	0
	$M(OH)(C_6H_{12})^+$	H_2	16	0
	$M(OH)(C_6H_{14})^+$		5	0
2,2-dimethyl-butane	$M(OH)(CH_4)^+$	C_5H_{10}	6	0
	$MC_4H_7^+$	H_2O, C_2H_6	0	26
	$MC_5H_9^+$	H_2O, CH_4	4	39
	$M(OH)(C_4H_8)^+$	C_2H_6	0	24
	$MC_6H_{13}^+$	H_2O	90	0
	$M(OH)(C_5H_{10})^+$	CH_4	0	11
2,2,3,3-tetra-methyl-butane	$MC_4H_7^+$	H_2O, C_4H_{10}	0	19
	$M(OH)(C_4H_8)^+$	C_4H_{10}	36	37
	$MC_7H_{11}^+$	H_2O, CH_4, H_2	0	16
	$MC_7H_{13}^+$	H_2O, CH_4	7	12
	$MC_8H_{15}^+$	H_2O, H_2	0	11
	$MC_8H_{17}^+$	H_2O	57	0
	$M(OH)(C_7H_{14})^+$	CH_4		5

Table III. Product Distributions for the Reactions of $FeOH^+$ and $CoOH^+$ with Cyclic Alkanes

	products		rel abundance	
alkane	ion	neutral(s)	$FeOH^+$	$CoOH^+$
cyclopropane	$MC_3H_5^+$	H_2O	100	100
cyclobutane	$M(OH)(C_2H_4)^+$	C_2H_4	100	100
cyclopentane	$MC_5H_5^+$	$H_2O, 2H_2$	NR[a]	16
	$MC_5H_7^+$	H_2O, H_2		33
	$M(OH)(C_5H_6)^+$	$2H_2$		28
	$M(OH)(C_5H_8)^+$	H_2		23
cyclohexane	$MC_6H_7^+$	$H_2O, 2H_2$	NR	63
	$M(OH)(C_6H_6)^+$	$3H_2$		5
	$M(OH)(C_6H_8)^+$	$2H_2$		6
	$M(OH)(C_6H_{10})^+$	H_2		26
methylcyclohexane	$MC_7H_9^+$	$H_2O, 2H_2$	29	83
	$MC_7H_{11}^+$	H_2O, H_2	18	0
	$MC_7H_{13}^+$	H_2O	34	0
	$M(OH)(C_7H_8)^+$	$3H_2$	0	6
	$M(OH)(C_7H_{10})^+$	$2H_2$	0	5
	$M(OH)(C_7H_{12})$	H_2	7	6
	$M(OH)(C_7H_{14})^+$		12	0

[a] NR indicates that no reaction occurs.

The $M(allyl)^+$ product ions readily react with the alkane. These reactions, which are given in Table VI, occur almost exclusively

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Table IV. Product Distributions for the Reactions of FeL^+ with Butane and 2-Methylpropane

		relative abundance		
FeL^+	products	butane	2-methylpropane	ref
Fe^+	$FeC_2H_4^+ + C_2H_6$	60	0	3, 4
	$FeC_3H_6^+ + CH_4$	29	62	
	$FeC_4H_6^+ + 2H_2$	3	0	
	$FeC_4H_8^+ + H_2$	8	38	
FeD^+	$FeC_4H_7^+ + HD + H_2$	60	55	6
	$FeC_4H_9^+ + HD$	40	45	
$FeCH_3^+$		NR[a]	NR	7
$FeCH_2^+$	$Fe^+ + C_5H_{12}$	10	17	10a
	$FeC_2H_4^+ + C_3H_8$	17	1	
	$FeC_3H_6^+ + C_2H_6$	9	16	
	$FeC_4H_6^+ + CH_4 + H_2$	54	0	
	$FeC_4H_8^+ + CH_4$	10	66	
FeO^+	$Fe^+ + H_2O + C_4H_8$	10	0	9
	$FeC_2H_4^+ + H_2O + C_2H_4$	30	0	
	$FeC_4H_6^+ + H_2O + H_2$	60	0	
	$FeC_4H_8^+ + H_2O$	0	35	
	$Fe(OH)(C_3H_6)^+ + CH_3$	0	65	
$FeOH^+$	$FeC_4H_9^+ + H_2O$	NR	38	
	$Fe(OH)(C_4H_8)^+ + H_2$		36	
	$Fe(OH)(C_4H_{10})^+$		26	

[a] NR indicates that no reaction occurs.

Table V. Product Distributions for the Reactions of CoL^+ with Butane and 2-Methylpropane

		relative abundance		
CoL^+	products	butane	2-methylpropane	ref
Co^+	$CoC_2H_4^+ + C_2H_6$	74	0	3, 4
	$CoC_3H_6^+ + CH_4$	8	77	
	$CoC_4H_8^+ + H_2$	18	23	
CoD^+	$CoC_4H_7^+ + HD + H_2$	100	100	6
$CoCD_3^+$	$CoC_4H_7^+ + CD_3H + H_2$	97	96	7
	$CoCD_3H + C_4H_9^+$	3	4	
$CoCH_2^+$	$Co^+ + C_5H_{12}$	6	11	10a
	$CoC_2H_4^+ + C_3H_8$	10	5	
	$CoC_3H_6^+ + C_2H_6$	21	7	
	$CoC_4H_6^+ + CH_4 + H_2$	52	20	
	$CoC_4H_8^+ + CH_4$	11	57	
$CoOH^+$	$CoC_3H_5^+ + H_2O + CH_4$	5	5	
	$Co(OH)(C_2H_4)^+ + C_2H_6$	18	0	
	$CoC_4H_7^+ + H_2O + H_2$	48	65	
	$Co(OH)(C_3H_6)^+ + CH_4$	0	6	
	$Co(OH)(C_4H_8)^+ + H_2$	29	24	

by C–H insertion resulting in loss of H_2 and $2H_2$. In general, $Co(allyl)^+$ species are more reactive than $Fe(allyl)^+$ species, while $Fe(alkyl)^+$ species do not react. Due to low signal intensity and the limited number of frequency pulses available for ion ejection, the structures of these secondary ions were not probed. However, the structures of similar ions which are formed in the reactions of $CoCH_3^+$ with alkanes have been studied in detail.[7]

Primary product ions that retain OH do not react further with the alkane. These ions also do not undergo H/D exchange with D_2, while many of the $Co(allyl)^+$ products readily H/D exchange. Ligand displacement reactions with CH_3CN were performed on a representative group of $M(OH)(alkene)^+$ and $M(OH)(alkane)^+$ ions. In all cases, CH_3CN displaced the hydrocarbon, leaving $M(OH)(CH_3CN)^+$. In addition, CID was performed on the major $M(OH)(alkene)^+$ products. With two exceptions, which will be discussed later, all of the $M(OH)(alkene)^+$ ions studied dissociate to give loss of H_2O at low energies, MOH^+ at higher energies, and M^+ at the highest energies available. If any other CID products are seen at all, they are in low abundance and appear to be products from secondary dissociation of the low-energy product $M(alkene-H)^+$. An exemplary CID breakdown curve, for $Co(OD)(C_3H_6)^+$ generated from 2,3-dimethylbutane, is given in Figure 2. At low energies, the Co–π-allyl ion dominates arising due to rearrangement and loss of water. As the collision energy increases, direct cleavage of propene from the complex to form $CoOD^+$ competes more effectively with rearrangement. The remaining ions shown result from the further decomposition of either $CoOD^+$ or $CoC_3H_5^+$.

Table VI. Product Distributions for the Reactions of $MC_xH_y^+$ (M = Fe, Co) with Alkanes

		products		rel abundance[a]	
alkane	reactant ion	ion	neutral(s)	FeL^+	CoL^+
butane	$MC_3H_5^+$	$MC_7H_{11}^+$	$2H_2$	–[b]	44
		$MC_7H_{13}^+$	H_2		56
	$MC_4H_7^+$	$MC_8H_{13}^+$	$2H_2$	–	21
		$MC_8H_{15}^+$	H_2		79
pentane	$MC_3H_5^+$	$MC_6H_{11}^+$	C_2H_6	–	25
		$MC_8H_{13}^+$	$2H_2$		30
		$MC_8H_{15}^+$	H_2		45
	$MC_5H_9^+$	$MC_{10}H_{17}^+$	$2H_2$	–	66
		$MC_{10}H_{19}^+$	H_2		34
hexane	$MC_3H_5^+$	$MC_9H_{15}^+$	$2H_2$	–	46
		$MC_9H_{17}^+$	H_2		54
	$MC_4H_7^+$	$MC_{10}H_{17}^+$	$2H_2$	–	73
		$MC_{10}H_{19}^+$	H_2		27
	$MC_6H_9^+$	$MC_{12}H_{21}^+$	H_2	–	100
	$MC_6H_{11}^+$	$MC_{12}H_{21}^+$	$2H_2$	64	70[c]
		$MC_{12}H_{23}^+$	H_2	36	30
	$MC_6H_{13}^+$			NR[d]	–
2-methylpropane	$MC_3H_5^+$	$MC_7H_{13}^+$	H_2	–	100
	$MC_4H_7^+$	$MC_8H_{15}^+$	H_2	–	100
	$MC_4H_9^+$			NR	–
2,2-dimethylpropane	$MC_4H_7^+$	$MC_8H_{15}^+$	CH_4	NR	55
		$MC_9H_{15}^+$	$2H_2$		10
		$MC_9H_{17}^+$	H_2		35
2-methylbutane	$MC_3H_5^+$	$MC_8H_{13}^+$	$2H_2$	–	50
		$MC_8H_{15}^+$	H_2		50
	$MC_4H_7^+$	$MC_9H_{15}^+$	$2H_2$	–	59
		$MC_9H_{17}^+$	H_2		41
	$MC_5H_9^+$	$MC_{10}H_{17}^+$	$2H_2$	50	41
		$MC_{10}H_{19}^+$	H_2	50	59
	$MC_5H_{11}^+$			NR	–
2,3-dimethylbutane	$MC_3H_5^+$	$MC_9H_{15}^+$	$2H_2$	–	58
		$MC_9H_{17}^+$	H_2		42
	$MC_5H_9^+$	$MC_{10}H_{17}^+$	CH_4, H_2	–	14
		$MC_{11}H_{19}^+$	$2H_2$		67
		$MC_{11}H_{21}^+$	H_2		19
	$MC_6H_{11}^+$	$MC_{12}H_{21}^+$	$2H_2$	80	39
		$MC_{12}H_{23}^+$	H_2	20	61
	$MC_6H_{13}^+$			NR	–
2,2-dimethylbutane	$MC_4H_7^+$	$MC_8H_{15}^+$	C_2H_6	–	18
		$MC_9H_{15}^+$	CH_4, H_2		20
		$MC_{10}H_{17}^+$	$2H_2$		28
		$MC_{10}H_{19}^+$	H_2		34
	$MC_5H_9^+$	$MC_9H_{17}^+$	C_2H_6	NR	9
		$MC_{10}H_{17}^+$	CH_4, H_2		24
		$MC_{11}H_{19}^+$	$2H_2$		38
		$MC_{11}H_{21}^+$	H_2		29
	$MC_6H_{13}^+$			NR	–
2,2,3,3-tetramethylbutane	$MC_4H_7^+$			–	NR
	$MC_7H_{11}^+$			–	NR
	$MC_7H_{13}^+$			NR	NR
	$MC_8H_{15}^+$			–	NR
	$MC_8H_{17}^+$			NR	–
cyclopropane	$MC_3H_5^+$	$MC_4H_7^{+}$[e]	C_2H_4	100	100
cyclopentane	$MC_5H_5^+$	$MC_{10}H_{11}^+$	$2H_2$	–	100
	$MC_5H_7^+$	$MC_{10}H_{13}^+$	$2H_2$	–	100
cyclohexane	$MC_6H_7^+$	$MC_{12}H_{15}^+$	$2H_2$	–	8
		$MC_{12}H_{17}^+$	H_2		92
methylcyclohexane	$MC_7H_9^+$	$MC_{13}H_{19}^+$	CH_4	NR	10
		$MC_{14}H_{17}^+$	$3H_2$		5
		$MC_{14}H_{19}^+$	$2H_2$		15
		$MC_{14}H_{21}^+$	H_2		70
	$MC_7H_{11}^+$	$MC_{13}H_{21}^+$	CH_4	13	–
		$MC_{14}H_{19}^+$	$3H_2$	87	
	$MC_7H_{13}^+$			NR	–

[a] Product distributions are reproducible to ±10%. [b] – indicates that this ion was not formed in the primary MOH^+ reactions. [c] 75% of this ion is unreactive. [d] NR indicates that no secondary reaction was observed. [e] This ion reacts further with cyclopropane, as discussed in the text.

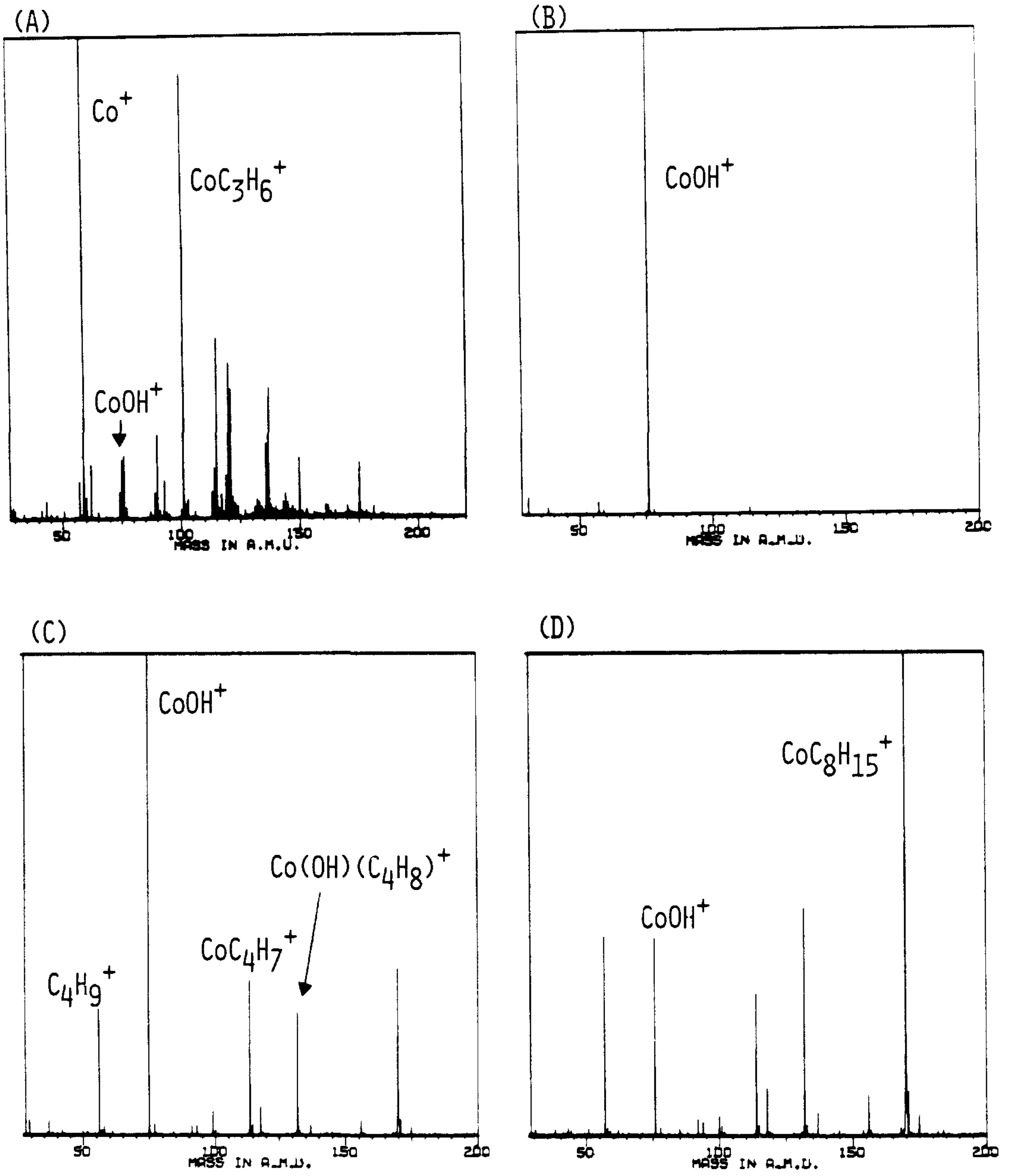
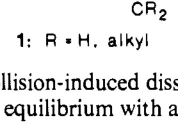
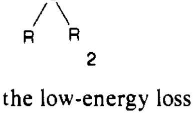


Figure 1. Generation and reaction of $CoOH^+$: (A) mass spectrum obtained when Co^+ is allowed to react with CH_3NO_2 (pulsed) and 2-methylpropane (static, 2×10^{-7} Torr) after a 400 ms initial reaction time, (B) same as part a with subsequent isolation of $CoOH^+$, (C) a 500 ms final reaction period following isolation, and (D) a 1 s final reaction period following isolation.

The CID results, together with the CH_3CN reactions, indicate that no incorporation of the OH into the hydrocarbon chain occurs, pointing to a hydroxy–alkene structure **1**. No H/D scrambling is observed in products arising from MOD^+, either during ion–molecule reactions or collision-induced dissociation. This indicates that structure **1** is not in equilibrium with an aquo–π-allyl complex, **2**, in analogy to the hydrido–π-allyl complex proposed for $RhC_3H_6^+$.[16] However, the low-energy loss of H_2O from **1** under CID conditions suggests that **2** must be an easily accessible activated complex. In the reactions of FeO^+ with alkanes,[9] M(OH)(alkene)$^+$ ions are also formed and react identically to the ions generated in this study. In several cases, Fe(OH)(alkane)$^+$ adducts are generated in the reactions with $FeOH^+$. When collisionally activated, these ions yield $FeOH^+$ at low energies and Fe^+ at higher energies. They do not react with D_2 or the precursor alkane, and the intact alkane is readily lost in ligand displacement reactions with CH_3CN. These observations point to a hydroxy–alkane structure. This lack of formation of ROH for M(OH)(alkene)$^+$ and M(OH)(alkane)$^+$ ions is, therefore, contrary to what is observed in metal-catalyzed oxidation reactions,[11-14] as discussed above.

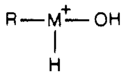


1: R = H, alkyl



2

The dominant pathway for the reactions of $FeOH^+$ and $CoOH^+$ with alkanes appears to involve initial insertion into a C–H bond leading presumably to intermediate complex **3**. Alternatively, a four-center intermediate involving the OH moiety and yielding complex **2** directly can also be postulated for product ions involving water loss. Carbon–hydrogen insertion also dominates for other ML^+ species, as shown in Tables IV and V. For MOH^+, one of the major C–H insertion pathways leads to H_2O loss. For $FeOH^+$,



$R-\overset{+}{M}(H)-OH$

3

H_2O loss alone is the dominant process; however, $CoOH^+$ forms no products corresponding to only H_2O loss, with loss of H_2O and H_2 dominating instead. This may indicate that H_2O loss from $CoOH^+$ is more exothermic than from $FeOH^+$, leaving an activated Co^+-alkyl complex that dissipates energy by eliminating H_2 or small alkanes. An alternative possibility is that the bond energies of Co^+-allyl species are greater than those of similar Fe^+-allyl species, making Co^+-allyl formation more energetically favorable relative to Fe^+-allyl formation. In addition, Co^+ appears to be a more facile β-hydride abstractor than Fe^+,[3] which might also lead to an enhanced ability of Co^+-alkyl intermediates to eliminate H_2 and small alkanes. Finally, electronic structure may play a role in the differences in reactivity.

In general, $FeOH^+$ is less reactive with alkanes than $CoOH^+$, and in fact it does not react with some linear and cyclic alkanes, as is evident from the tables. In contrast, assuming $D(Fe^+-CH_3) = 69 \pm 5$ kcal/mol and $D(Co^+-CH_3) = 61 \pm 4$ kcal/mol[22] are representative of M^+-R bond strengths, formation of $M(alkyl)^+$ ions is ~5 kcal/mol more exothermic for $FeOH^+$ than for $CoOH^+$.[21] Therefore, it is unclear as to whether the decreased reactivity for $FeOH^+$ is a result of the overall energetics of the reactions or of the energetics of initial bond insertion. A decreased reactivity of FeL^+ relative to CoL^+ is also seen with D[6] and CH_3[7] ligands, as is evident from Tables IV and V. FeD^+ reacts with alkanes larger than ethane, but it does not show as many multiple loss products as CoD^+.[6] $FeCH_3^+$, however, does not react with alkanes (except cyclopropane and cyclobutane), while $CoCH_3^+$ is reactive with alkanes larger than ethane.[7,8] The intermediate reactivity of MOH^+ between MD^+ and MCH_3^+ is expected on the basis of the thermodynamics of reaction 4. For the various FeL^+ species, loss of H_2O is ~1 kcal/mol less exothermic than

$$ML^+ + C_nH_{2n+2} \rightarrow MC_nH_{2n+1}^+ + HL \qquad (4)$$

HD loss, but it is ~8 kcal/mol more exothermic than CH_4 loss.[21-23] For CoL^+, H_2O loss is again intermediate in energy, being ~4 kcal/mol less exothermic than HD loss and ~5 kcal/mol more exothermic than CH_4 loss.[21-23]

In addition to the products listed in the tables, MOH^+ also reacts with some alkanes at 2×10^{-7} Torr to yield alkyl ions formed by either hydride or methyl abstraction. These ions do not form when an inert gas, such as argon, is present at a static pressure of $\sim 10^{-5}$ Torr. This may suggest that MOH^+ is formed with excess energy and is thermalized by collisions with the inert gas, similar to the cooling of excited-state metal ions.[24] The reactions of Fe^+ and Co^+ with nitromethane to form $FeOH^+$ and $CoOH^+$ are roughly 20 kcal/mol exothermic.[21,23] Thus, MOH^+ may retain up to 20 kcal/mol of excess energy. Some quenching of this excess energy may occur during the high-pressure CH_3NO_2 pulse; however, this pulse is only at a total pressure of $\sim 10^{-5}$ Torr for ~100 ms. On the basis of studies of excited M^+, this time may not be long enough to thermalize the ions.[24] Alkyl ions are also pressure-dependent products in the reactions of alkanes with CoO^+ and NiO^+ generated from ozone,[25] where MO^+ formation is exothermic by 39 kcal/mol for Co^+ and 19 kcal/mol for Ni^+.[22,23] However, alkyl ions are not observed in the reactions of alkanes with FeO^+ generated from N_2O[9] in a process that is only ~6 kcal/mol exothermic.[22,23] In addition, the intensities of minor alkyl product ions in the reactions of alkanes with $CoCH_3^+$ are not dependent on pressure.[7] In this study $CoCH_3^+$ was generated from methyl iodide in a reaction that is only ~5 kcal/mol exothermic.[22,23] An alternative explanation for the pressure dependence of alkyl ion formation is that collisional stabilization of a long-lived reaction intermediate occurs.[26] The product intensities for the MOH^+ reactions listed in the tables are taken at a pressure of 2×10^{-7} Torr and are for the metal-containing products only, neglecting organic products. The relative intensities of metal-containing products are generally not affected by changing the pressure, except for a few specific cases noted later in the text.

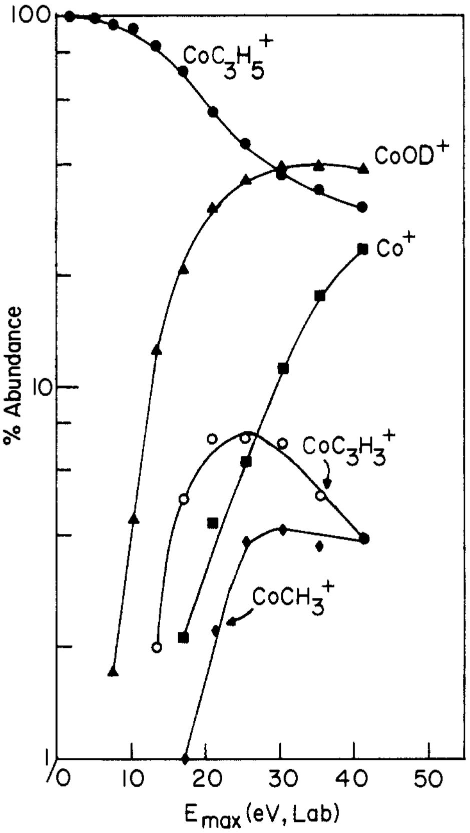
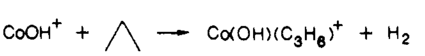


Figure 2. Distribution of CID product intensities vs. kinetic energy for $Co(OD)(C_3H_6)^+$ generated from 2,3-dimethylbutane.

Linear Alkanes

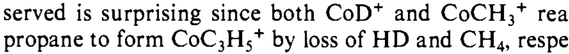
$FeOH^+$ and $CoOH^+$ exhibit markedly different reactivities with linear alkanes. Hexane is the only linear alkane studied which reacts with $FeOH^+$, while $CoOH^+$ reacts with all linear alkanes except methane and ethane. The reaction of $CoOH^+$ with propane, process 5, occurs at a substantially slower rate than the reactions with larger alkanes.



(5)

The fact that only dehydrogenation is observed is surprising since both CoD^+ and $CoCH_3^+$ react with propane to form $CoC_3H_5^+$ by loss of HD and CH_4, respectively. Formation of $CoC_3H_5^+$ should also be exothermic for $CoOH^+$ (in fact, more exothermic than its formation from $CoCH_3^+$); thus, this lack of reactivity is not due to the overall energetics of the process.

$CoOH^+$ readily reacts with butane, reactions 6 through 9, at a rate that is at least an order of magnitude faster than the reaction with propane. Reactions 6 and 7 can be explained by initial insertion of $CoOH^+$ into a C–H bond. Reaction 7, which involves dehydrogenation with no H_2O loss, is unexpected since similar processes do not occur in the reactions of CoD^+[6] and $CoCH_3^+$[7] with alkanes. Its presence suggests that combination of H and OH to form H_2O on the metal center is slow relative to CH_4 and



(6)
(7)
(8)
(9)

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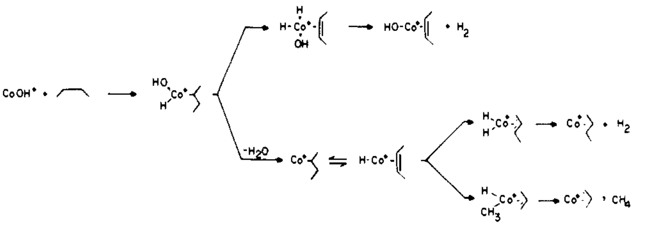
(23) Supplementary thermochemical information is taken from the following: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*.

(24) Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 2765.

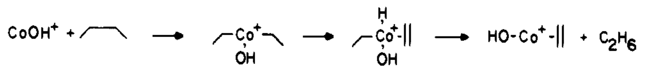
(25) Jackson, T. C.; Ph.D. Thesis, Purdue University, 1985.

(26) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 1573.

Scheme I

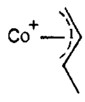


Scheme II



HD formation. The lack of H/D scrambling in $CoOD^+$ reactions indicates that once D and OH combine, HDO loss occurs with no equilibration to regenerate the hydroxy complex. A mechanism for product formation following H_2O loss to yield $CoC_4H_9^+$ as a reaction intermediate is given in Scheme I. The C–C bond cleavage product, $CoC_3H_5^+$, may also be formed by decomposition of the $CoC_4H_9^+$, as shown in Scheme I. The other product involving C–C cleavage, $Co(OH)(C_2H_4)^+$, could be the result of decomposition of a reaction intermediate of C–H insertion, i.e., $Co(OH)(C_4H_8)^+$. This mechanism seems unlikely, however, since activated intermediates typically follow CID elimination pathways and no $M(OH)(alkene)^+$ or $M(OH)(alkane)^+$ species involved in this study decompose under CID conditions by C–C bond cleavage pathways. An alternative explanation is that reaction 9 involves initial oxidative addition of $CoOH^+$ into a C–C bond, as shown in Scheme II. On the basis of the relative lack of C–C insertion pathways in the reactions of ML^+ species with alkanes, C–C insertion by ML^+ is probably a higher energy process than C–H insertion. An initial C–C bond cleavage in reaction 9 is supported by the fact that this reaction has a significant pressure dependence, accounting for 18% of the total product intensity at 2×10^{-7} Torr and 7% at 5×10^{-6} Torr. This may suggest that reaction 9 is a higher energy process than the other primary reaction pathways.

The structure of the major butane product, $CoC_4H_7^+$, was probed by reaction with D_2. At least three H/D exchanges occur, suggesting equilibrating methallyl, **4**, and hydrido-butadiene, **5**, structures. No CID was observed for this ion; however, product ions from low-efficiency processes may have been lost in the background.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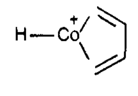
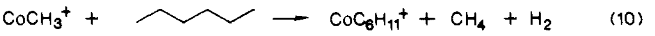

5

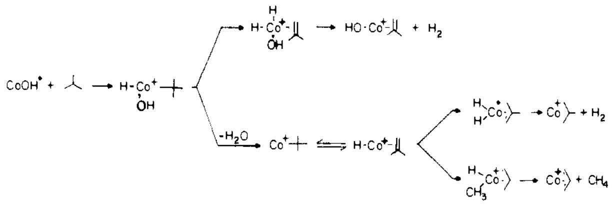
The $CoOH^+$ reactions with pentane can be envisioned as proceeding through processes similar to those outlined for butane. Again, the intensities of OH-containing C–C cleavage products decrease slightly with increasing pressure. Also interesting is the production of $Co(OH)(C_5H_8)^+$ with loss of $2H_2$, which further indicates that formation of H_2O on the metal may be slow relative to H_2 formation.

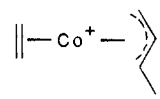
The major pentane product, $CoC_5H_9^+$, undergoes CID to yield H_2 loss at low energy and $2H_2$ loss at higher energies as the dominant processes. This ion also exchanges at least three hydrogens with D_2, which is consistent with equilibrating allyl and hydrido-pentadiene structures.[7]

The reactions of $CoOH^+$ with hexane can be explained by the mechanisms proposed for butane. The major product, $CoC_6H_{11}^+$, undergoes at least 3 H/D exchanges with D_2. This ion reacts with hexane by loss of H_2 and $2H_2$ to produce $CoC_{12}H_{23}^+$ (30%) and $CoC_{12}H_{21}^+$ (70%). However, only ~25% of the $CoC_6H_{11}^+$ ions are reactive. Similar behavior has been observed for $CoC_6H_{11}^+$ generated by reaction 10,[7] where ~30% of the ions react. The reactive species is believed to be an intact allylic species which is in equilibrium with a hydrido-hexadiene ion. CID on $CoC_6H_{11}^+$ from $CoOH^+$ yields loss of C_2H_4 at low energies and loss of C_6H_{11} at higher energies, with several other minor high-energy processes also occurring. This behavior is identical with that of $CoC_6H_{11}^+$ generated by reaction 10, where the unreactive species is thought to have structure **6**.[7]

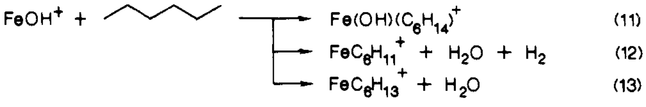

$CoCH_3^+ +$ $\longrightarrow CoC_6H_{11}^+ + CH_4 + H_2$ (10)

Scheme III




6

$FeOH^+$ also reacts with hexane, reactions 11 through 13, but at a slower rate than $CoOH^+$. For $FeOH^+$, C–H insertion dominates, with no C–C cleavage observed. Adduct formation, reaction 11, is the major reaction and occurs readily within 500 ms at 2×10^{-7} Torr. This is the only process observed for $FeOH^+$ reacting with butane and pentane, where it occurs at substantially slower rates than with hexane. The addition of relatively high pressures (10^{-5}–10^{-6} Torr) of an inert gas increases adduct formation relative to reactions 12 and 13, suggesting collisional stabilization of the adduct at higher pressures. Since internal C–H bond energies decrease as the length of the carbon chain increases,[27] $FeOH^+$ may react with hexane, but not with smaller linear alkanes, because the metal is able to insert into the weaker internal C–H bonds of hexane. The overall energetics, however, may also be more favorable for hexane.


$FeOH^+ +$

$\longrightarrow Fe(OH)(C_6H_{14})^+$ (11)

$\longrightarrow FeC_6H_{11}^+ + H_2O + H_2$ (12)

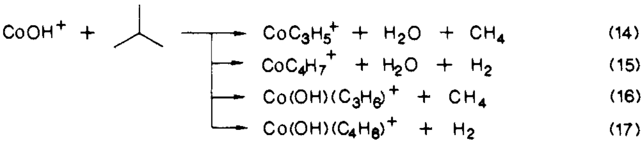
$\longrightarrow FeC_6H_{13}^+ + H_2O$ (13)

The products of hexane reactions 12 and 13, $FeC_6H_{11}^+$ and $FeC_6H_{13}^+$, do not react with D_2. However, this does not confirm a structure, since FeH^+, an ion of obvious hydride character, does not react with D_2.[6] In addition, none of the other Fe^+ products generated in this study react with D_2, which may indicate that D_2 cannot oxidatively add to these species.

Branched Alkanes

Both $FeOH^+$ and $CoOH^+$ react with the six branched alkanes studied (Table II). $CoOH^+$, however, is more reactive with multiple loss processes dominating while single loss processes dominate for $FeOH^+$. $FeOH^+$ may be reactive with branched alkanes because it can insert into the C–H and C–C bonds at the branch points, which are weak relative to the bonds in linear alkanes.[27]

While $CoOH^+$ reacts very slowly with propane, it reacts readily with 2-methylpropane, reactions 14 through 17. This may be due to the weakness of the $(CH_3)_3C$–H bond (84.1 kcal/mol[27]) relative to the $(CH_3)_2CH$–H bond (85.7 kcal/mol[27]). A mechanism for product formation following initial insertion into this bond is given in Scheme III. Again, C–C cleavage products may result from either elimination of CH_4 from an activated intermediate or initial


$CoOH^+ +$

$\longrightarrow CoC_3H_5^+ + H_2O + CH_4$ (14)

$\longrightarrow CoC_4H_7^+ + H_2O + H_2$ (15)

$\longrightarrow Co(OH)(C_3H_6)^+ + CH_4$ (16)

$\longrightarrow Co(OH)(C_4H_8)^+ + H_2$ (17)

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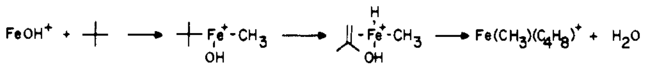
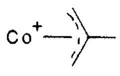
(27) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

Scheme IV



C-C insertion. The major product, $CoC_4H_7^+$, does not H/D exchange with D_2. Although no CID products were seen for this ion, low-efficiency processes may have been unobserved in the background. The most probable structure of this ion is a 2-methallyl complex, **7**.



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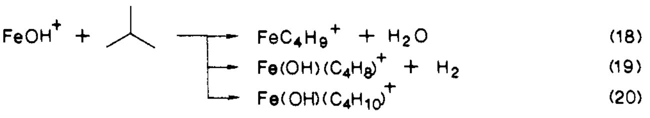
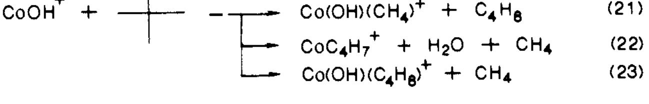
$FeOH^+$ reacts with 2-methylpropane, reactions 18 through 20, but at a substantially slower rate than it reacts with other branched



alkanes. Only single loss products form, suggesting that following the initial loss the activated complex does not have enough energy to fragment further. As is the case with hexane, adduct formation from 2-methylpropane is dependent on pressure. Adding argon at 5 × 10^{-6} Torr increases the relative intensity of $Fe(OH)(C_4H_{10})^+$ from 26% to 58%, indicating that collisions are able to thermalize the complex prior to fragmentation.

$CoOH^+$ reacts with 2,2-dimethylpropane to give three products, reactions 21 through 23. In this case, after insertion of $CoOH^+$

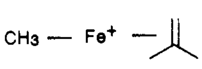


into a C-H bond, there are no β-hydrogens present to shift onto the metal. Thus, rather than loss of H_2 and H_2O, the major process involves CH_4 and H_2O loss. Elimination of methane may proceed by a β-methyl shift; however, initial C-C insertion cannot be ruled out. The major product, $CoC_4H_7^+$, does not react with D_2 and dissociates when collisionally activated to lose CH_4 at low energies and C_4H_7 at higher energies. Elimination of H_2 and C_3H_4 are also minor high energy processes. These results suggest a Co(2-methallyl)$^+$ species.[7]

$FeOH^+$ reacts with 2,2-dimethylpropane predominantly by H_2O loss, forming $FeC_5H_{11}^+$. This ion does not react with D_2 or 2,2-dimethylpropane. It undergoes CID, reactions 24 through 26, to yield $FeC_4H_7^+$ as the initial product, with $FeCH_3^+$ starting

$$FeC_5H_{11}^+ \xrightarrow{Ar} FeC_4H_7^+ + CH_4 \qquad (24)$$
$$\longrightarrow FeCH_3^+ + C_4H_8 \qquad (25)$$
$$\longrightarrow Fe^+ + C_5H_{11} \qquad (26)$$

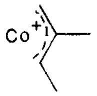
at slightly higher energies and Fe^+ forming at the highest energies studied. In addition, CH_3CN displaces C_4H_8 from $FeC_5H_{11}^+$. These results indicate that the ion has a methyl-isobutene structure **8**. This structure implies that $FeC_5H_{11}^+$ is not formed by initial metal insertion into a relatively strong C-H bond (100 kcal/mol[27]), but instead it results from insertion into a relatively weak C-C



8

bond (84.1 kcal/mol[27]), as shown in Scheme IV. Initial C-C insertion might be expected to yield CH_3OH elimination; however, no evidence is found in this study to indicate that a hydroxy-alkyl combination can occur at the metal. Therefore, the lack of a CH_3OH loss product is not indicative of a mechanism. Also, the formation of structure **8** from initial insertion of the metal into a C-H bond, followed by a β-methyl shift, cannot be ruled out.

$CoOH^+$ reacts with 2-methylbutane to give seven products, as listed in Table II. These products may form from processes similar to those outlined for butane and 2-methylpropane. Oxidative addition of the metal into C-C bonds, followed by alkane loss, generates three products since three different types of C-C bonds are present in 2-methylbutane. The major process, however, involves H_2O and H_2 loss to yield $CoC_5H_9^+$. This ion reacts with excess D_2 to give at least three H/D exchanges. CID yields loss of C_2H_4 at low energies, with H_2 and $2H_2$ loss at higher energies. These results suggest equilibrating allylic and hydrido-diene structures, **9** and **10**.



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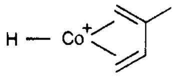
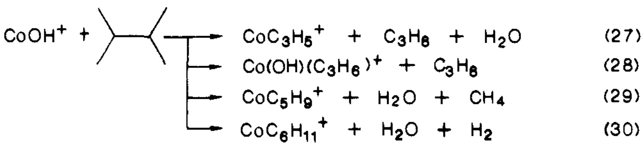


10

$FeOH^+$ reacts with 2-methylbutane predominantly by H_2O loss, with no C-C cleavage products forming. In addition, adduct formation occurs and increases in intensity when an inert gas is added at 5 × 10^{-6} Torr. Adduct formation is surprising since a weak C-H bond is present at the branch point and would be expected to make C-H insertion favorable. The major product $FeC_5H_{11}^+$ does not react with D_2 and undergoes CID to lose H_2 at low energies and C_5H_{10} at higher energies. These results suggest an intact Fe(alkyl)$^+$ complex.

The reaction of $CoOH^+$ with 2,3-dimethylbutane is unusual since C_3H_8 loss, process 28, dominates over loss of H_2O and H_2, process 30. This can be attributed to the weakness of the internal



C-C bond (79.0 kcal/mol[27]) which may make C-C insertion thermodynamically favorable relative to C-H insertion.

Water loss dominates in the reaction of $FeOH^+$ with 2,3-dimethylbutane, but some internal C-C cleavage is also observed. In addition, two processes, adduct formation and dehydrogenation, are present which do not occur for $CoOH^+$. CID on the dehydration product, $FeC_6H_{13}^+$, gives H_2 loss as the major process at all energies, with minor products corresponding to C_3H_8 loss and C_5H_{10} loss forming at higher energies. This ion does not react with CH_3CN. These results suggest an intact Fe(alkyl)$^+$ species.

Loss of CH_4 and H_2O is the dominant process for the reaction of $CoOH^+$ with 2,2-dimethylbutane. In this case, initial C-H insertion may generate a Co(alkyl)$^+$ species which does not have two β-hydrogens available for H_2 elimination. Thus, a β-methyl shift and loss of CH_4 may occur instead. The CID breakdown curve of the major product ion, $CoC_5H_9^+$, is identical (within experimental error) with that of $CoC_5H_9^+$ generated from 2-methylbutane and $CoC_5H_9^+$ formed in the reactions of $CoCH_3^+$ with these compounds.[7] This ion also undergoes at least three exchanges with D_2, suggesting equilibrating allylic and hydrido-diene structures, **9** and **10**.

Loss of H_2O dominates for the reaction of $FeOH^+$ with 2,2-dimethylbutane. The ion formed in this process, $FeC_6H_{13}^+$, does not react with the precursor alkane or with D_2. It dissociates when collisionally activated to yield a variety of products, reactions 31 through 37, with reaction 33 as the major low-energy process, reaction 34 as a major process at moderate energies, and reaction 36 dominating at higher energies. In addition, CH_3CN displaces C_5H_{10} from $FeC_6H_{13}^+$. These results suggest a methyl-alkene structure, $Fe(CH_3)(C_5H_{10})^+$.

$$FeC_6H_{13}^+ \xrightarrow{Ar} FeC_5H_9^+ + CH_4 \qquad (31)$$
$$\longrightarrow FeC_5H_7^+ + CH_4 + H_2 \qquad (32)$$
$$\longrightarrow FeC_5H_5^+ + CH_4 + 2H_2 \qquad (33)$$
$$\longrightarrow FeC_3H_5^+ + C_3H_8 \qquad (34)$$
$$\longrightarrow FeC_3H_3^+ + C_3H_8 + H_2 \qquad (35)$$
$$\longrightarrow FeCH_3^+ + C_5H_{10} \qquad (36)$$
$$\longrightarrow Fe^+ + C_6H_{13} \qquad (37)$$

$CoOH^+$ reacts with 2,2,3,3-tetramethylbutane to give six products, as shown in Table II. The major product, $Co(OH)(C_4H_8)^+$, probably results from oxidative addition of $CoOH^+$ into the very weak internal C–C bond (71.2 kcal/mol[27]). The four allylic products, $CoC_8H_{15}^+$, $CoC_7H_{13}^+$, $CoC_7H_{11}^+$, and $CoC_4H_7^+$, may result from initial C–H insertion followed by H_2O loss forming a $CoC_8H_{17}^+$ intermediate which retains sufficient internal energy to dissociate further. These products do not react with either the precursor alkane or D_2.

$FeOH^+$ reacts with 2,2,3,3-tetramethylbutane by three pathways, with H_2O loss dominating. No adduct formation occurs with either this compound or 2,2-dimethylpropane and 2,2-dimethylbutane, while adducts form in the reactions of $FeOH^+$ with 2-methylpropane, 2-methylbutane, and 2,3-dimethylbutane, which have considerably weaker C–H bonds at the branch point. This suggests that $FeOH^+$ may attack the C–C bonds in species containing strong C–H bonds and weak C–C bonds (as shown in Scheme IV for 2,2-dimethylpropane). However, initial C–H insertion cannot be ruled out.

As was the case for $CoOH^+$, the primary products of the $FeOH^+$ reaction with 2,2,3,3-tetramethylbutane do not react with the precursor alkane or D_2. $FeC_8H_{17}^+$ dissociates via eight channels, reactions 38 through 45, with CH_4 loss, reaction 38, and $FeCH_3^+$ formation, reaction 44, as the major processes at low and high energies, respectively. This suggests a methyl–alkene structure, $Fe(CH_3)(C_7H_{14})^+$.

$$FeC_8H_{17}^+ \xrightarrow{Ar} FeC_7H_{13}^+ + CH_4 \qquad (38)$$
$$\rightarrow FeC_7H_{11}^+ + CH_4 + H_2 \qquad (39)$$
$$\rightarrow FeC_7H_9^+ + CH_4 + 2H_2 \qquad (40)$$
$$\rightarrow FeC_6H_{11}^+ + C_2H_6 \qquad (41)$$
$$\rightarrow FeC_6H_9^+ + C_2H_6 + H_2 \qquad (42)$$
$$\rightarrow FeC_6H_7^+ + C_2H_6 + 2H_2 \qquad (43)$$
$$\rightarrow FeCH_3^+ + C_7H_{14} \qquad (44)$$
$$\rightarrow Fe^+ + C_8H_{17} \qquad (45)$$

Cyclic Alkanes

The reactions of $FeOH^+$ and $CoOH^+$ with cyclic alkanes are given in Table III. Both $FeOH^+$ and $CoOH^+$ react with cyclopropane to yield only H_2O loss (reaction 46). Cyclopropane has extremely strong C–H bonds (106.3 kcal/mol[27]); however, the

$$MOH^+ + △ \rightarrow MC_3H_5^+ + H_2O \qquad (46)$$

C–C bonds are very weak due to ring strain. Thus, while $MC_3H_5^+$ may form following oxidative addition of MOH^+ into a C–H bond, a more probable mechanism is C–C insertion followed by a β-hydride shift and loss of H_2O, as shown in Scheme V. In contrast to the MOH^+ reactions, Fe^+,[2] Co^+,[5] and FeO^+[9] do not react with cyclopropane, while $FeCH_3^+$ and $CoCH_3^+$[8] react to generate predominantly $MC_2H_5^+$ (loss of C_2H_4).

$MC_3H_5^+$ ions from both $FeOH^+$ and $CoOH^+$ do not H/D exchange with D_2, but they do undergo CID to form $MC_3H_3^+$, MCH_3^+, and M^+, suggesting $M(allyl)^+$ structures.[7] $MC_3H_5^+$ reacts further with cyclopropane to generate $MC_4H_7^+$ (reaction 47). A mechanism for the formation of this ion following initial

$$MC_3H_5^+ + △ \rightarrow MC_4H_7^+ + C_2H_4 \qquad (47)$$

C–C insertion is given in Scheme VI. CID on $FeC_4H_7^+$, reactions 48 through 50, yields $FeC_2H_3^+$ as the major low-energy product

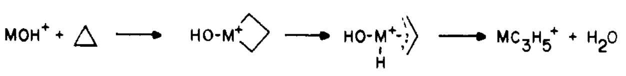
$$FeC_4H_7^+ \xrightarrow{Ar} FeC_2H_3^+ \; C_2H_4 \qquad (48)$$
$$\rightarrow FeH^+ + C_4H_6 \qquad (49)$$
$$\rightarrow Fe^+ + C_4H_7 \qquad (50)$$

and FeH^+ as the major high-energy product. $CoC_4H_7^+$ dissociates, reactions 51 through 54, to give $CoC_3H_3^+$ as the lowest energy

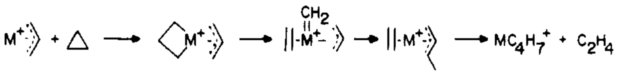
$$CoC_4H_7^+ \xrightarrow{Ar} CoC_4H_5^+ + H_2 \qquad (51)$$
$$\rightarrow CoC_3H_3^+ + CH_4 \qquad (52)$$
$$\rightarrow CoC_2H_3^+ + C_2H_4 \qquad (53)$$
$$\rightarrow Co^+ + C_4H_7 \qquad (54)$$

product with $CoC_2H_3^+$ forming at slightly higher energies. The CID breakdown curve for $CoC_4H_7^+$ is identical (within experimental error) with that of $Co(methallyl)^+$.[7] Most likely, $FeC_4H_7^+$ also has a methallyl structure. $MC_4H_7^+$ undergoes a series of sequential reactions with cyclopropane via a mechanism probably involving oxidative addition of the metal into a C–C bond followed by reductive elimination of C_2H_4 or C_2H_4 and H_2, with the end result being the addition of CH_2 units to the carbon chain on the metal. In general, Fe^+ species eliminate predominantly C_2H_4, while for Co^+ species the major process is loss of C_2H_4 and H_2. At a trapping time of 5 s, $MC_9H_{11}^+$ and $MC_9H_{13}^+$ are present in the mass spectrum for $FeOH^+$ and $CoOH^+$, with $FeC_9H_{15}^+$ and $FeC_9H_{17}^+$ also forming for $FeOH^+$.

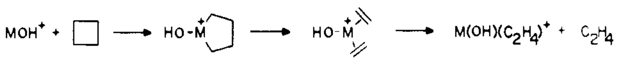
Scheme V



Scheme VI



Scheme VII



$FeOH^+$ and $CoOH^+$ react with cyclobutane to generate only $M(OH)(C_2H_4)^+$ (reaction 55). This reaction may occur by ox-

$$MOH^+ + □ \rightarrow M(OH)(C_2H_4)^+ + C_2H_4 \qquad (55)$$

idative addition of MOH^+ into a C–C bond forming a metallacyclopentane intermediate which undergoes symmetric ring cleavage to eliminate C_2H_4. This mechanism, presented in Scheme VII, has previously been proposed to explain the reaction of MCH_3^+ with cyclobutane.[8] The product of reaction 55 undergoes CID to generate only MOH^+, with no H_2O loss at low energies. In addition, this ion does not react with cyclobutane or D_2. However, C_2H_4 is readily displaced by background water present in the cyclobutane sample. These results indicate that the OH is not incorporated into the ethene ligand. In contrast, FeO^+ reacts with cyclobutane to form $Fe(OC_2H_4)^+$ (loss of C_2H_4) as the major product. CID on this ion yields only Fe^+, suggesting that it contains an intact C_2H_4O ligand.[9]

Cyclopentane and cyclohexane do not contain exceptionally weak C–C or C–H bonds. While $CoOH^+$ readily reacts with both of these compounds exclusively by C–H insertion, $FeOH^+$ does not react. In analogy, $CoCH_3^+$ also reacts with cyclopentane and cyclohexane, but $FeCH_3^+$ does not.

$CoOH^+$ reacts with cyclopentane to form four products, reactions 56 through 59. When argon is added at 5×10^{-6} Torr, a slight decrease in intensity of processes 56 and 58, involving $2H_2$ loss, occurs relative to $1H_2$ loss processes 57 and 59, suggesting collisional stabilization of a reaction intermediate.[26] In the

$$CoOH^+ + ⬠ \rightarrow CoC_5H_5^+ + H_2O + 2H_2 \qquad (56)$$
$$\rightarrow CoC_5H_7^+ + H_2O + H_2 \qquad (57)$$
$$\rightarrow Co(OH)(C_5H_6)^+ + 2H_2 \qquad (58)$$
$$\rightarrow Co(OH)(C_5H_8)^+ + H_2 \qquad (59)$$

presence of excess D_2, $CoC_5H_7^+$ undergoes two H/D exchanges. Similar results have previously been reported for $Co\text{-}c\text{-}C_5H_7^+$, and a mechanism for this exchange proceeding through cyclopentenyl and hydridocyclopentadiene intermediates has been proposed.[8] $CoC_5H_7^+$ generated from reaction 57 dissociates when collisionally activated to yield H_2 loss at low energies and C_5H_7 loss at higher energies, again exhibiting behavior identical with that previously observed for $Co\text{-}c\text{-}C_5H_7^+$.[8]

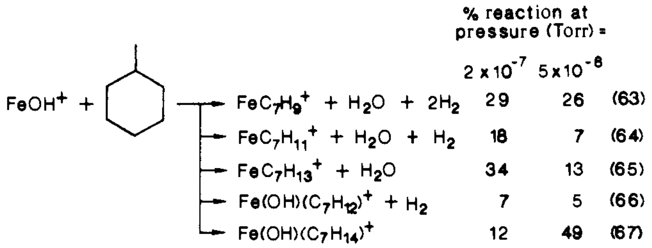
Formation of $CoC_6H_7^+$ dominates in the reaction of $CoOH^+$ with cyclohexane; however, products corresponding to loss of $3H_2$,

$2H_2$, and H_2 are also observed. $CoC_6H_7^+$ undergoes one rapid H/D exchange with D_2 and dissociates when collisionally activated to yield $CoC_6H_6^+$ at low energies and CoH^+ at higher energies. This behavior is indicative of a hydrido–benzene complex.[8] The major cyclohexane product involving OH retention is the single dehydrogenation product, $Co(OH)(C_6H_{10})^+$. Surprisingly, CID on this ion does not yield H_2O loss and MOH^+ products, as it does for other $M(OH)(alkene)^+$ species. Instead, reaction 60, Co(benzene)$^+$ formation, is a high-efficiency process at all energies, with reactions 61 and 62 occurring in low intensity at higher energies. Since $D(Co^+–OH) > D(Co^+–C_6H_6)$,[8,21] reaction 60 apparently involves initial HDO loss, as opposed to OD loss.

$$Co(OD)(C_6H_{10})^+ \xrightarrow{Ar} CoC_6H_6^+ + HDO + H_2 + H \qquad (60)$$
$$\rightarrow CoH^+ + HDO + C_6H_8 \qquad (61)$$
$$\rightarrow Co^+ + OD + C_6H_{10} \qquad (62)$$

$CoOH^+$ reacts with methylcyclohexane to generate the methyl analogues of the products observed for cyclohexane. The major product, $CoC_7H_9^+$, undergoes one rapid H/D exchange with D_2. CID on this ion results in $CoC_7H_8^+$ and $CoC_7H_6^+$ at low energies, with CoH^+ and Co^+ forming at higher energies. These results suggest a hydrido–toluene complex and imply that $D(Co^+–C_7H_8) > D(Co^+–H) = 52 \pm 4$ kcal/mol.[22]

While $FeOH^+$ is unreactive with cyclohexane, it does react with methylcyclohexane, processes 63 through 67. This implies that the reactions occur by oxidative addition of $FeOH^+$ into the C–H bond either at the branch point or in the methyl group. These processes are pressure dependent, with adduct formation increasing in intensity with the addition of relatively high pressures of inert gas. However, while the formation of products resulting from H_2O and H_2O/H_2 elimination is dependent on pressure, formation of $FeC_7H_9^+$ from H_2O and $2H_2$ elimination is not. This reaction may be driven by the formation of a hydrido–toluene product, which should be a very stable species.



$FeOH^+$ + methylcyclohexane →	% reaction at pressure (Torr) = 2×10^{-7}	5×10^{-8}	
$FeC_7H_9^+ + H_2O + 2H_2$	29	26	(63)
$FeC_7H_{11}^+ + H_2O + H_2$	18	7	(64)
$FeC_7H_{13}^+ + H_2O$	34	13	(65)
$Fe(OH)(C_7H_{12})^+ + H_2$	7	5	(66)
$Fe(OH)(C_7H_{14})^+$	12	49	(67)

Conclusions

While Fe^+ and Co^+ react with alkanes predominantly by initial insertion across C–C bonds, various ML^+ species (L = H, CH_3, CH_2, O) have been found to attack primarily C–H bonds. For $FeOH^+$ and $CoOH^+$, C–H insertion is again the major pathway, but C–C insertion also plays a role in the chemistry.

Following initial C–H insertion, H_2O loss dominates the $FeOH^+$ reactions. For $CoOH^+$, however, H_2O loss leads to an activated Co^+–alkyl complex which decomposes further. In addition, dehydrogenation, with no H_2O elimination, also occurs for species in which C–H insertion leads to an intermediate containing hydrogens β to the metal. This is in contrast to the reactions of FeD^+,[6] CoD^+,[6] and $CoCH_3^+$[7,8] with alkanes, where complete loss of the initial ligand is seen. This suggests that the combination of OH and H at the metal to form H_2O may be slow relative to HD and CH_4 formation.

Initial C–C insertion is also a major pathway in the MOH^+ reactions. This mechanism leads to $M(OH)(alkene)^+$ species, which behave identically to the analogous ions generated in the reactions of FeO^+ with alkanes.[9] Structure studies indicate that these ions have intact hydroxy–alkene structures, with no rearrangement to a aquo-π-allyl form. No evidence was found in this study for any incorporation of the hydroxide ligand into the alkane. This lack of ROH formation is surprising since metal–hydroxides are thought to be intermediates in solution processes involving metal-catalyzed oxidation of organic compounds.[11-14]

As was the case with MD^+ and MCH_3^+, $FeOH^+$ was found to be less reactive than $CoOH^+$. For aliphatic alkanes, $CoOH^+$ reacts with species larger than ethane, while $FeOH^+$ only reacts with branched alkanes and linear alkanes larger than pentane. $FeOH^+$ is apparently reactive with branched alkanes because it can insert into the C–H and C–C bonds at the branch points, which are weak relative to the bonds in linear alkanes. In addition, adduct formation also occurs in the reactions of $FeOH^+$ with hexane and several branched alkanes, with an increase in pressure resulting in an increase in adduct intensity relative to neutral loss products, suggesting collisional stabilization of the adduct. Both $FeOH^+$ and $CoOH^+$ react with cyclopropane and cyclobutane, with insertion across the weak C–C bonds being the only reaction pathway. For cyclopentane and cyclohexane, $CoOH^+$ reacts by exclusively C–H insertion, while $FeOH^+$ is unreactive. However, both MOH^+ species react with methylcyclohexane via initial C–H insertion. As expected on the basis of thermodynamic calculations, the overall reactivity of MOH^+ is intermediate to that of MD^+ and MCH_3^+.

Acknowledgement 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 the National Science Foundation (CHE-8310039) for providing funds for the purchase of the FTMS.

Registry No. $FeOH^+$, 15092-05-4; $CoOH^+$, 12323-82-9; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; 2-methylpropane, 75-28-5; 2,2-dimethylpropane, 463-82-1; 2-methylbutane, 78-78-4; 2,3-dimethylbutane, 79-29-8; 2,2-dimethylbutane, 75-83-2; 2,2,3,3-tetramethylbutane, 594-82-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; methylcyclohexane, 108-82-7.