the temperature range scale in addition to the provided coarse adjustments. This enabled smaller temperature fluctuations near the ends of the original temperature ranges. The temperature of the sample was determined before and after each run by replacing the sample with an identical tube containing a calibrated ethanol thermometer. If the two temperatures were not within ±0.2 °C, the spectrum was rerun.

Line-Shape Calculations. The theoretical spectra were calculated by using in-house two-site and three-site exchange programs based on the modified Bloch equations.[17] Exchange rates were obtained by a visual comparison of calculated and observed spectra. The errors quoted for the activation parameters only include errors from the least-squares fit of the data.

Appendix

The modified Bloch equations used for calculating the line shapes are based on 2.14, 2.17, and 2.26 of ref 17. After substitution of the lifetime, $\tau_{M'}$ and relative populations from Table I, these become

nonexchange

$$iC_0 = -\alpha_A G_A$$

two-site (3:1)

$$\begin{bmatrix} i(0.75)C_0 \\ i(0.25)C_0 \end{bmatrix} = \begin{bmatrix} (-\alpha_A - (^1/_3)k) & k \\ ^1/_3 k & (-\alpha_B - k) \end{bmatrix} \begin{bmatrix} G_A \\ G_B \end{bmatrix}$$

two-site (2:2)

$$\begin{bmatrix} i(0.5)C_0 \\ i(0.5)C_0 \end{bmatrix} = \begin{bmatrix} (-\alpha_A - (^2/_3)k) & ^2/_3 k \\ ^2/_3 k & (-\alpha_B - (^2/_3)k) \end{bmatrix} \begin{bmatrix} G_A \\ G_B \end{bmatrix}$$

three-site (2:1:1)

$$\begin{bmatrix} i(0.5)C_0 \\ i(0.25)C_0 \\ i(0.25)C_0 \end{bmatrix} = \begin{bmatrix} (-\alpha_A - (^2/_3)k) & ^2/_3 k & ^2/_3 k \\ ^1/_3 k & (-\alpha_B - k) & ^1/_3 k \\ ^1/_3 k & ^1/_3 k & (-\alpha_C - k) \end{bmatrix} \begin{bmatrix} G_A \\ G_B \\ G_C \end{bmatrix}$$

where C_0 = scaling factor, $\alpha_M = 1/T_{2M} - 2\pi i (\nu_M - \nu)$, ν_M = resonance frequency of site $M = \sum m_1$ for each face in units of J (Hz), as given in Table I, k = exchange rate, as discussed in the text, and G_M = magnetization due to site M.

Gas-Phase Transition Metal Ion Chemistry: The Reactivity and Specificity of Atomic Iron(I), Chromium(I), and Molybdenum(I) Ions with Alcohols

Sunkwei Huang, Robert W. Holman, and Michael L. Gross*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

The reactions of gas-phase atomic transition-metal ions Fe$^+$, Cr$^+$ and Mo$^+$, generated by multiphoton dissociation ionization (MPD/MPI), with a series of aliphatic alcohols were studied by using Fourier transform mass spectrometry. The concepts of reactivity and specificity are used to correlate the different insertion reaction chemistry of each metal ion. These metal ions undergo three classes of bond insertion reactions: C–O insertion (dehydration), C–H or O–H insertion (dehydrogenation), and C–C insertion. The total reactivity of each metal ion is a function of its electronic configuration and the aliphatic chain length and degree of branching of the alcohols. For straight-chain alcohols containing three carbons or more, the order of reactivity is Fe$^+$ > Mo$^+$ > Cr$^+$. For shorter alcohols Mo$^+$ is the most reactive species while Cr$^+$ is unreactive with methanol and ethanol.

Introduction

In recent years the literature covering gas-phase metal ion reactions, particularly those of metal ions of catalytic interest, has grown steadily. The growing volume of experimental data dealing with transition-metal ions reacting with alkanes, cycloalkanes,[1a–c] bifunctional,[2] and multi-

functional,[3] organic substrates as well as studies of ligand effects at the metal center[3,4] and metal cluster reactions[5] reflects this trend.

Transition-metal ions are reactive toward many organic substrates because their valence electron configurations make it possible for the metal ion to insert into organic

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bonds.[6a] Following insertion, H migration and/or expulsion of ligands occur to yield new organic species.[7] Recent theoretical studies, such as those of Ziegler–Natta type catalysis,[8] Fisher–Tropsch reactions,[9] and metal surface reactions,[10] support the above-mentioned, insertion/elimination scheme. It has been proposed that thermodynamics is a major factor governing the reactions;[7,11] however, electronic configuration of the metal ion and the polarization of the accompanying organic molecules may also need to be considered.

Although thermodynamic measurements of bond strengths, proton affinities, heats of formation, etc. are important approaches in the study of gas-phase metal ion–molecule reactions, a complete understanding of how metal ions interact with organic substrates will also require systematic studies of ion chemistry. For example, some issues addressed in this work are how the chain length and the position of functional groups on the organic species affect the specificity of metal ion–organic molecule reactions and how the electronic configuration at the metal center modifies the specificity and reactivity of the metal ion.

The transition-metal ions Cr^+ and Mo^+ were chosen for this study because they have the same ground electronic states and are useful models for gaining insight into homogeneous catalysis. In addition, Fe^+ was chosen as a reference point for comparing the reactivity and specificity of Cr^+ and Mo^+ in a set of common reactions with alcohols because more is known of the reactivity of Fe^+ and organic molecules. Reactions of other metal ions (Au^+, Ag^+, Cu^+) with alcohols were recently reported.[12]

Multiphoton dissociation/multiphoton ionization (MPD/MPI), a soft ionization technique, was chosen to ionize the metal carbonyls of chromium, molybdenum, and iron. One advantage of MPI is its ability to generate a clean population of bare metal ions without interference by other reactant ions such as $M(CO)_n^+$. An additional advantage of MPD/MPI may be its ability to produce a more homogeneous population of electronic states than does electron ionization as was recently demonstrated for Cr^+ from $Cr(CO)_6$.[13] The cell of a Fourier transform mass spectrometer was used for both conducting the chemical reactions and mass analyzing the product ions. Fourier transform mass spectrometry (FTMS) is particularly compatible with pulsed laser ionization methods because of its multichannel advantage.[14]

Experimental Section

Low-pressure, ion–molecule reactions were carried out with a FT mass spectrometer consisting of a Nicolet Analytical Instruments FTMS 1000 console interfaced to a custom-built spectrometer.[15] A 5.08-cm cubic cell situated in a 1.2 T magnetic field was used for all experiments. The trap voltage was maintained at 1 V to avoid ion evaporation.[16] Total pressure in the cell was

2 × 10⁻⁷ torr as measured by using a Bayard Alpert ionization gauge near the cell. The partial pressure ratio of organic to metal carbonyl was kept at 1:1.

The source of ultraviolet laser radiation used for MPD/MPI was a Quanta Ray (Mountain View, CA) DCR-2 Nd:YAG laser equipped with a Model HG-2 harmonic generator. The 266-nm fourth harmonic was used for all experiments. The laser produces a pulse of 5–6 ns in duration at this wavelength. Pulse energies at 266 nm were measured by using a disk calorimeter (Scientech, Boulder, CO) and were approximately 15 mJ/pulse.

For the optical arrangement, a UV-grade fused silica prism (ESCO Products) and the principles of total internal reflection were used to steer the laser output with 90% transmission. The focusing lens and optical window (ESCO Products) were also made of UV-grade fused silica. The prism was mounted on a tilt table at 67.5° and affixed to an optical rail with a vertically adjustable base. The lens was in a gimbal mount and was attached (via a linearly adjustable mounting) to the flange containing the optical window. The laser beam was focused to 0.5-mm diameter at the edge of the ion trap of the FT mass spectrometer. The laser beam entered the cell on diagonal, and the ions were made along this diagonal axis. The laser was triggered by the quench pulse of the FTMS system.

The determination of the reactivities of the metal ions with the various alcohols required several experiments. First, the rate constant for the disappearance of M^+ as a function of time was measured for each metal ion in reaction with its precursor neutrals (no organic present). In a separate experiment, the rate constant for disappearance of M^+ was measured for each metal ion in reaction with a given alcohol and with its neutral precursor. The difference between the rate constants in the above two experiments for each metal ion was taken as the experimental rate constant for the metal ion/alcohol reaction. These relative rate constants are plotted as a function of chain length in Figure 1.

The branching ratios (Tables II–IV) were calculated after a reaction time of 250 ms. This time was chosen because a plot of log branching rates vs. time is linear in this time range and has no significant contribution from successive reactions.

All reagents were purchased, of analytical grade, and were used without further purification. $Mo(CO)_6$, $Cr(CO)_6$, and $Fe(CO)_5$ and the organic alcohols were obtained from Aldrich Chemical Co., Milwaukee, WI. Their purity was established to be adequate by using mass spectrometric techniques.

Results and Discussion

Previous investigations of transition-metal ion–molecule reactions successfully dealt with reaction specificity; i.e., the mode of metal ion insertion and subsequent ligand expulsions that take place. Such studies were based on analysis of the branching ratios of product ions. However, branching ratios may only reflect the relative stability of product ions for each reaction channel. For a comparison of the reactions of several different metal ions with a common series of organic substrates, not only branching ratios but also relative reactivities of the metal ions were measured as part of this study.

This paper is divided into two parts. First, the overall reactivity of the MPI-produced bare metal ions of chromium, molybdenum, and iron with alcohols will be discussed. Second, the reaction specificity of the ions in their common reactions with alcohols ranging from methanol to hexanol will be addressed.

Results: Overall Reactivity of Cr^+, Mo^+, And Fe^+. The inherent reactivity of a metal ion with an organic substrate is likely to be a function of both the electronic configuration of the metal ion and the nature of the organic substrate. It is expected that, as the overall reactivity of a metal ion increases, its reaction specificity will decrease. A corollary of this axiom is that, as the metal ion reactivity increases, the sensitivity to structural alteration of the

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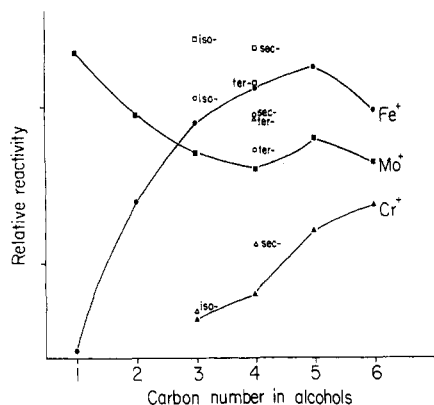
$$M^+ + \quad \diagdown\diagup OH \longrightarrow \quad Y^{\overset{+}{M}} \diagdown_{OH} \overset{\beta\text{-}H}{\longrightarrow} \quad \| \overset{+}{M} \cdots H_2O \longrightarrow MH_2O^+$$
$$\searrow MC_3H_6^+$$

Figure 1. Overall reactivity of Cr^+, Fe^+, and Mo^+ with alcohols.

organic substrate decreases.

The relative reactivities of Cr^+, Mo^+, and Fe^+ as a function of carbon chain length in their common reactions with alcohols are plotted in Figure 1. The relative reactivity of each metal ion was obtained from the difference of relative rate constants of metal ion reactions with and without the organic substrate present (see Experimental Section).

In reactions with short-chain alcohols, Mo^+ is the most reactive, while Cr^+ is entirely unreactive with both methanol and ethanol. For larger alcohols, Fe^+ is the most reactive species while Cr^+ is the least reactive.

A clear dependence on the structure of the organic molecule is seen for each metal ion. As straight-chain alcohols are changed to branched isomers, both Cr^+ and Mo^+ reactivities increase, while such alteration of the organic substrate causes a decrease in the reactivity of Fe^+. The magnitude of this structural dependence is greatest for Cr^+ and least for Fe^+, which is in accord with the aforementioned axiom.

The overall reactivity of the metal ion also changes dramatically as a function of aliphatic chain length. Both Cr^+ and Fe^+ reactivities increase with increasing chain length while that of Mo^+ decreases. The magnitude of this chain length effect is greater for Cr^+ and Fe^+ and less for Mo^+.

Discussion: Reactivity. A reason for the above results must lie with the electronic configuration of the reacting metal ions and with the way in which metal–organic bond formation takes place.

It was suggested that bonding between first-row transition metals and organic substrates involves s orbital electrons.[17] If a ground-state metal ion is of $3d^n$ electronic configuration, one or more electrons from a d orbital must be promoted to an s or p orbital for the metal to be reactive. The electronic configuration of these excited states would be either $3d^{n-1}4s^1$ [17] or $3d^{n-2}4s^1p^1$,[18] and a characteristic promotion energy is required for such transitions to take place.

On the basis that s electrons are used in bonding of first-row transition-metal ion reactions with organics,[17] it is expected that the ground state of $Cr^+(d^5)$ would be unreactive. Work in our laboratory indicates that MPI of $Cr(CO)_6$ yields a nearly ground state population of Cr^+ ions.[13] This is reasonable since the promotion energy from ground-state ^6S $Cr^+(d^5)$ to ^6D $Cr^+(s^1d^4)$ is 34.2 kcal/mol[19] and the transition is symmetry-forbidden. Although Cr^+
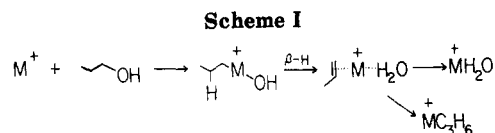
is unreactive with alkanes, MPI-produced Cr^+ is clearly reactive with alcohols.

Recently, Goddard et al.[20a] investigated theoretically a covalent $Cr=CH_2^+$ double bond between ground-state ^6S Cr^+ and $^3B_1$ CH_2 by using general valence-bond (GVB) theory. The metal–organic σ-bond was predicted to have 47% 4sp and 53% 3d character.[20a] Such quantum mechanical hybridization or orbital mix requires less energy than promotion of a d electron and may be an explanation for the reactivity of Cr^+ with alcohols. Recently, Harrison et al.[20b] also studied the electronic and organic structure of $CrCH_2^+$ by using ab initio MCSCF and CI techniques. The result is in fair agreement with Goddard's.

The ground state of $Fe^+(s^1d^6)$ requires neither promotion of one or more electrons to an excited state nor hybridization in order to achieve sufficient s character to interact with organic substrates. Moreover, Fe^+ has many low-lying, easily accessible, and reactive excited states,[19] which are probably populated when $Fe(CO)_5$ is multiphoton ionized. Thus, the high reactivity of Fe^+ with alcohols can be readily understood.

Second-row transition metals, such as Mo^+, have larger d orbitals relative to their s orbitals than do first-row transition metals. It is thought that bonding between second-row transition metals and organic substrates occurs through interactions involving expanded size d orbitals.[6,21] Empirically, Mo^+ is more reactive than Cr^+ and less reactive than Fe^+. Other second-row transition-metal ions whose electronic ground states involve no s electrons exhibit nearly pure d character in bonding.[6b,21]

It is clear that electronic configuration considerations cannot be used to explain completely the structural and chain length dependences seen in Figure 1. In addition, we note that on the basis of ADO theory,[22] the collision frequency for an ion and neutral molecule is a function of polarizability and molecular mass. Increases in the molecular mass of the neutral cause frequency decreases, but polarizability also increases with molecular mass and its relation to collision frequency is direct. Polarizability may have a more important role because MPI-produced Cr^+ is unreactive toward the smaller alcohols studied here. It is known that as a neutral metal approaches an organic substrate, the total energy of the chemical system decreases.[8] In a metal ion–organic molecule reaction, the magnitude of the energy decrease (coordination energy) should be larger because of interaction with the permanent dipole or with the charge-induced dipole of the organic.[22] In fact, the resulting coordination energy is considered to give rise to the lowest point of an energy surface.[23] Hence, the structure of the organic affects the coordination energy and, in turn, the reactivity of the metal ion. Furthermore, energy barriers for isomerization and/or decomposition of the initially formed metal ion–organic complex will determine whether the complex returns to starting materials or goes on to products. These barriers are expected to be

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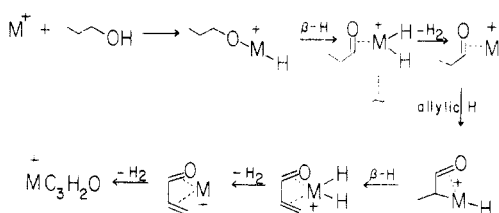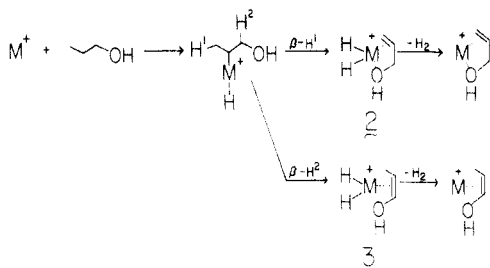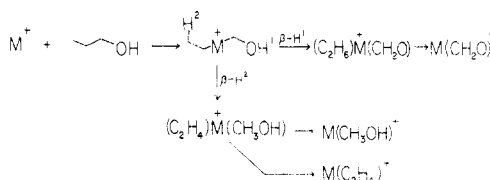
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Scheme II

Scheme III

Scheme IV

Table I. Bond Dissociation Energies (kcal/mol)[a]

bond	energy	bond	energy
CH_3–CH_2CH_2OH	84.6	CH_3–$CH_2CH_2CH_2OH$	83.87
CH_3CH_2–CH_2OH	77.1	CH_3CH_2–CH_2CH_2OH	78.3
CH_3CH_2CH–OH	91.1	$CH_3CH_2CH_2$–CH_2OH	76.37
$CH_3CH_2CH_2O$–H	101.4	$CH_3CH_2CH_2CH_2$–OH	89.74
		$CH_3CH_2CHCH_3$ (OH)	89.17
CH_3CHCH_2OH (H)	92.2	$CH_3CH_2CH_2CH_2O$–H	101.6
		$CH_3CHCH_2CH_2OH$ (H)	91.47
		$CH_3CH_2CH(OH)$–CH_3	86.47
$CH_2CH_2CH_2OH$ (H)	97.47	CH_3CH_2–$CH(OH)CH_3$	80.9
		$CH_3CH_2CH(O)CH_3$ (H)	103.3
CH_3CH_2CHOH (H)	95.37		
		$(CH_3)_3C$–OH	87.9
		CH_3–$C(CH_3)_2(OH)$	81.2
		$(CH_3)_3CO$–H	98.3

[a] Values are calculated by using the group equivalence data in ref 26–28.

influenced in part by stabilization arising from polarization of the organic by the charged metal after bond insertion has occurred.[24]

Results: Reaction Specificity. Three general types of metal ion–organic alcohol reactions are identified here: (a) C–O bond insertions (dehydration), (b) C–H or O–H bond insertions (dehydrogenation), and (c) C–C bond insertions.

One accepted mechanism for dehydration is shown in Scheme I.[25] The metal ion initially inserts into a polar C–O bond followed by a β-hydrogen shift and subsequent fragmentation.

Dehydrogenation, depicted in Schemes II and III, probably involves an initial metal insertion into an O–H (Scheme II) or C–H bond (Scheme III), followed by a β-hydrogen shift and expulsion of a hydrogen molecule (via structures 1, 2, or 3). Metal ion insertion into O–H bonds may not be thermodynamically favored because of the high O–H bond energy (see Table I). However, insertion into a C–H bond to give 2 or 3, in which the metal ion can interact with both the double bond and hydroxyl group, may be more favored. Additional losses of hydrogen molecules can occur via intramolecular allylic C–H insertions or cyclizations followed by β-H shifts to expel H_2 units. Multiple dehydrogenations are probably sequential and thermodynamically controlled; i.e., the formation of product ions from multiple dehydrogenations is highly exothermic. The reactions of Au^+, Ag^+, and Cu^+ with

alcohols was recently reported to involve an α-C–H bond insertion followed by H_2 elimination.[12]

Insertion into C–C bonds, as depicted in Scheme IV, involves bonds weaker than C–H or O–H, particularly those that are internal (nonterminal) bonds (Table I). This insertion is again followed by a β-H shift and subsequent fragmentation.

The percentages of total ion current for each of the three processes: dehydration, dehydrogenation, and C–C bond insertion, are the basis for the following discussion of specificity. The data are compiled in Tables II–IV for the reactions of Cr^+, Mo^+, and Fe^+ with alcohols up to 1-hexanol. These branching ratios were calculated from the product ion abundances after a reaction time of 250 ms (see Experimental Section).

It is clear from these results that mechanistic specificity is a function of not only the metal ion itself but also the nature of the aliphatic portion of the alcohol.

Reaction Specificity of Cr^+. The effect of aliphatic chain length can be seen most dramatically for the reaction of Cr^+ and straight-chain alcohols. For the smaller alcohols methanol and ethanol, no products are seen at all, whereas Cr^+ is quite reactive with larger alcohols. The reaction of Cr^+ with 1-propanol is highly specific; the only detectable product is $Cr(C_3H_6O)^+$ formed via dehydrogenation. As the chain length increases, the reactions of Cr^+ and alcohols involve predominantly C–C bond insertions (nearly 80% of the products from the reactions of Cr^+ with 1-butanol, 1-pentanol, and 1-hexanol are formed by C–C bond insertions.

The decomposition pathway for the Cr^+–alcohol adduct changes when the alcohol is changed to a branched isomer. For Cr^+ and *tert*-butyl alcohol, the major product is from dehydration (83%), whereas with 1-butanol, C–C bond insertion is favored (80%). A 50/50 mixture of products from dehydration and dehydrogenation is formed in the reaction with 2-propanol. The reactivity of Cr^+ with 2-butanol is intermediate to those with 1-propanol and 1-butanol; competitive C–O and C–C bond insertions in the ratio of ca. $\simeq$80:20 occur.

Reaction Specificity of Mo^+. A different chain length effect can be seen for the reactivity of Mo^+ with alcohols. Specificity is high for the reactions with small primary

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Table II. Dehydrogenation (O–H or C–H Insertions) of Alcohols by Fe^+, Cr^+, and Mo^+

alcohols	ions formed	neutrals	% product distributn		
			Fe^+	Cr^+	Mo^+
CH_3OH	MCH_2O^+	H_2	...	...	100
C_2H_5OH	$MC_2H_2O^+$	$2H_2$	...	...	60
	$MC_2H_4O^+$	H_2	...	...	40
C_3H_7OH	$MC_3H_2O^+$	$3H_2$	...	...	27
	$MC_3H_4O^+$	$2H_2$	...	...	73
	$MC_3H_6O^+$	H_2	...	100	...
$i\text{-}C_3H_7OH$	$MC_3H_2O^+$	$3H_2$	...	...	24
	$MC_3H_4O^+$	$2H_2$	...	...	56
	$MC_3H_6O^+$	H_2	2	50	...
C_4H_9OH	$MC_4H_4O^+$	$3H_2$	...	...	20
	$MC_4H_6O^+$	$2H_2$	...	...	59
	$MC_4H_8O^+$	H_2	37	8	...
$s\text{-}C_4H_9OH$	$MC_4H_4O^+$	$3H_2$	...	...	31
	$MC_4H_6O^+$	$2H_2$	...	...	20
	$MC_4H_8O^+$	H_2	7	...	...
$t\text{-}C_4H_9OH$	$MC_4H_4O_+$	$3H_2$	...	...	14
	$MC_4H_6O^+$	$2H_2$	...	...	trace
	$MC_4H_8O^+$	H_2	...	...	trace
$C_5H_{11}OH$	$MC_5H_6O^+$	$3H_2$	...	...	70
	$MC_5H_{10}O^+$	H_2	17	6	...
$C_6H_{13}OH$	$MC_6H_6O^+$	$4H_2$	...	...	66
	$MC_6H_8O^+$	$3H_2$	...	...	trace
	$M_6H_{10}O^+$	$2H_2$	...	...	trace
	$MC_6H_{12}O^+$	H_2	10	12	...

Table III. Dehydration (C–O Insertion) of Alcohols by Fe^+, Cr^+, and Mo^+

alcohols	ions formed	neutrals lost	% product distributn		
			Fe^+	Cr^+	Mo^+
CH_3OH	...	...	...	...	...
C_2H_5OH	MH_2O^+	C_2H_4	13	...	...
	$MC_2H_4^+$	H_2O	83	...	...
C_3H_7OH	MH_2O^+	C_3H_6	13	...	...
	$MC_3H_6^+$	H_2O	54	...	...
$i\text{-}C_3H_7OH$	MH_2O^+	C_3H_6	40	24	8
	$MC_3H_6^+$	H_2O	58	26	12
C_4H_9OH	MH_2O^+	C_4H_8	4	...	...
	$MC_4H_6^+$	H_2O, H_2	46	12	...
	$MC_4H_8^+$	H_2O	4	...	19
$s\text{-}C_4H_9OH$	MH_2O^+	C_4H_8	27	19	20
	$MC_4H_6^+$	H_2O, H_2	57	...	23
	$MC_4H_8^+$	H_2O	9	64	5
$t\text{-}C_4H_9OH$	MH_2O^+	C_4H_8	19	27	18
	$MC_4H_6^+$	H_2O, H_2	...	...	68
	$MC_4H_8^+$	H_2O	81	56	trace
$C_5H_{11}OH$	MH_2O^+	C_5H_{10}	...	...	...
	$MC_5H_8^+$	H_2O, H_2	8	15	3
	$MC_5H_{10}^+$	H_2O	...	...	10
$C_6H_{13}OH$	MH_2O^+	C_6H_{12}	...	...	trace
	$MC_6H_8^+$	$H_2O, 2H_2$	...	...	8
	$MC_6H_{10}^+$	H_2O, H_2	...	8	trace
	$MC_6H_{12}^+$	H_2O	...	...	...

alcohols, methanol, ethanol, and 1-propanol. All yield nearly quantitative dehydrogenation products. As the chain length increases in going to 1-butanol, 1-pentanol, and 1-hexanol, the specificity decreases monotonically; i.e., 79%, 70%, and 66% of the respective products originate via dehydrogenation. For 1-pentanol and 1-hexanol, C–C and C–O insertions account for 17% and 26%, and 13% and 8%, of the total product ion current, respectively.

The reaction of Mo^+ with *tert*-butyl alcohol shows a unique branching effect whereby 68% of the products are $Mo(C_4H_6)^+$ ions which are presumably formed by consecutive dehydration and dehydrogenation reactions. The [Mo–*tert*-butyl alcohol⁺]* also undergoes 18% dehydration and 14% dehydrogenation. The branching leads to lower specificity in contrast to Cr^+, which maintains specificity as a function of branching even though the category of reaction changes.

Changing the position of the hydroxyl group as in going from 1- to 2-propanol or from 1- to 2-butanol also causes a decrease in the overall specificity of the reaction. A near 50/50 mix of dehydration and dehydrogenation are seen for the reaction of Mo^+ and 2-butanol as opposed to 19/79 mix for 1-butanol.

Reaction Specificity of Fe^+. A significant chain length effect can also be seen for reactions of Fe^+ and alcohols. Fe^+ is unreactive with methanol toward dehydration and dehydrogenation. With ethanol and 1-propanol, Fe^+ yields largely dehydration products at 96% and 67%, respectively. As chain length increases in going to butanol, products from small amounts of C–C insertions (9%) begin to emerge, along with those from dehydration (54%) and dehydrogenation (37%). For five- and six-carbon alcohols, C–C bond insertion dominates, accounting for 75% and 90% of the total products formed in reactions with 1-pentanol and 1-hexanol, respectively.

Changing from a straight-chain alcohol to its highly branched isomer, as in going from 1-butanol to *tert*-butyl alcohol, causes an increase of specificity. A near quanti-

Table IV. C–C Insertions of Alcohols by Fe^+, Cr^+, and Mo^+

alcohols	ions formed	neutrals lost	% product distributn		
			Fe^+	Cr^+	Mo^+
CH_3OH	MCH_2O^+	H_2	...	...	...
C_2H_5OH	MOH^+	C_2H_5	4	...	...
C_3H_7OH	MCH_3OH^+	C_2H_4	2	...	...
	$MC_2H_5O^+$	CH_3	30	...	...
$i\text{-}C_3H_7OH$	...	...	...	...	...
C_4H_9OH	$MC_2H_4^+$	C_2H_6O	9	...	...
	$MC_3H_6^+$	CH_3OH	...	...	2
	$MC_3H_6O^+$	CH_4	...	80	...
$s\text{-}C_4H_9OH$	$MC_3H_6O^+$	CH_4	...	17	...
$t\text{-}C_4H_9OH$	$MC_3H_6^+$	CH_3OH	3	...	...
	$MC_3H_6O^+$	CH_4	...	16	...
$C_5H_{11}OH$	$MC_2H_4^+$	C_3H_8O	12	...	...
	$MC_3H_6^+$	C_2H_6O	16	...	2
	$MC_4H_8^+$	CH_3OH	...	...	15
	$MC_3H_6O^+$	C_2H_6	47	72	...
	$MC_4H_8O^+$	CH_4	...	7	...
$C_6H_{13}OH$	$MC_2H_4^+$	$C_4H_{10}O$	4	...	...
	$MC_3H_6^+$	C_3H_8O	17	...	...
	$MC_3H_6O^+$	C_3H_8	5	15	...
	$MC_4H_6^+$	C_2H_6O, H_2	17	21	...
	$MC_4H_8^+$	C_2H_6O	3	...	4
	$MC_3H_8O^+$	C_3H_6	...	5	...
	$MC_5H_6^+$	CH_3OH, $2H_2$	...	...	12
	$MC_5H_8^+$	CH_3OH, H_2	...	...	10
	$MC_5H_{10}^+$	CH_3OH	...	...	trace
	$MC_4H_8O^+$	C_2H_6	44	23	...
	$MC_4H_{10}O^+$	C_2H_4	...	16	...

tative yield of dehydration products is formed in the *tert*-butyl alcohol reaction as opposed to 54/37/9 reaction yields for dehydration, dehydrogenation, and C–C bond insertions, respectively, in the reaction with 1-butanol.

Changing the position of the hydroxyl group as in going from a primary to a secondary alcohol also causes an increased propensity for the Fe^+–alcohol adduct to dehydrate. Dehydration products occur in Fe^+ reactions with 2-propanol and 2-butanol to the extents of 98% and 93%, respectively, in contrast to 67% and 55% in the 1-propanol and 1-butanol reactions, respectively.

Discussion: Reaction Specificity. The above results indicate that the type of insertions that take place in gas-phase metal ion–organic reactions is a function of both the nature of the metal ion itself and the structure of the organic substrate.

The Cr^+ reaction specificity is generally high, and the nature of the reaction is determined by the chain length and type of branching. Reactions with straight-chain alcohols of four or more carbons all favor C–C bond insertion, whereas these insertions do not occur with smaller alcohols. If the alkyl chain is branched or the hydroxyl group is changed from the primary to secondary position, predominant dehydration occurs. The specificity of Mo^+ is particularly high for the short-chain primary alcohols and decreases as the chain length increases. Further decreases of specificity are seen when the alkyl chain is branched or the hydroxyl group is moved from a primary to a secondary position. The specificity of Fe^+ is high only when the alcohols are highly branched or when they are not primary. As chain length increases, C–C insertions become the predominant pathway.

The specificity of the reactions of Cr^+ and Fe^+ is largely controlled by thermodynamics. The more exothermic reactions are generally favored. For example, internal C–C bonds are preferentially attacked compared to terminal C–C bonds because bond dissociation energies of internal C–C bonds are lower (see Table I). Specificity for internal C–C bonds may also be controlled by the amounts of energy released upon making metal–alkyl bonds as has been suggested by Radecki and Allison.[29] These interpretations,

which hold for Fe^+ and Cr^+, are consistent with the increasing amounts of C–C bond insertion in the Mo^+ reactions with 1-pentanol and 1-hexanol.

Since the C–O bond strength of primary, secondary, and tertiary alcohols are approximately the same and usually greater than C–C bonds (Table I), the preference for insertion into the C–O bond in secondary and tertiary alcohols by Cr^+, Fe^+, and Mo^+ must be ascribed to the formation of more stable intermediates or products than those formed by C–C bond insertion (note that $D(M^+-OH)$ is usually larger than $D(M^+-CH_3)$).[21,30] Moreover, the subsequent loss of H_2O is usually a more thermodynamically favored pathway than the loss of alkanes following C–C bond insertions. For example, dehydrations are favored over C–C bond insertion followed by CH_4 eliminations by 11.05 and 12.42 kcal/mol for 2- and *t*-butyl alcohol respectively.[26,27] It is worth noting that although D-(M^+-OH) is larger than $D(M^+-CH_3)$, primary alcohols still prefer to undergo C–C bond insertion. It is likely that $D(M^+-t\text{-}Bu)$ is larger than $D(M^+-n\text{-}Bu)$ and that the polarization stabilization by the *t*-Bu is larger than that for *n*-Bu. Any combination of these factors will contribute to stabilization of the intermediate. The importance of polarization stabilization by the ligand of the highly acidic metal centers was reported previously.[21]

Fe^+ is the most reactive of the metal ions toward larger alcohols, and its high reactivity can be understood on the basis of electronic configuration. The ability for Fe^+ to insert into C–O bonds in short-chain alcohols is ascribed to the ions high reactivity. If, however, internal C–C bonds become available (i.e., in longer chain alcohols), Fe^+ will preferentially insert into these more energetically accessible bonds.

Dehydrogenation by both Cr^+ and Fe^+ only accounts for a small percentage of the reaction with alcohols having four or more carbons (see Tables II–IV) because, in part, the C–H bond strength is usually higher than that of C–C

(29) Radecki, B. D.; Allison, J., submitted for publication in *Organometallics*.

(30) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* 1984, *106*, 6176.

bonds (see Table I). In addition, the stability of the adduct formed by C–H insertion is less than those formed via C–O and C–C insertions. This is because $D(M^+$–H) is usually smaller than $D(M^+$–CH$_3$) or $D(M^+$–R)[21] where R is the alkyl group. It is intriguing that Cr$^+$ forms a large percentage of dehydrogenated products in its reactions with small alcohols in spite of its low reactivity. In a previous investigation,[3] it was found that Cr$^+$ prefers to form fragments with a high oxygen to carbon ratio. This may be an important factor in C–C bond insertion reactions (Table IV) in which the formation of CrC$_3$H$_6$O$^+$ appears very often and accounts for a high yield reaction channel.

The specificity exhibited by Mo$^+$ is not easily understood. While it is clear that Mo$^+$ is quite reactive, owing in part to its expanded-size d orbitals, it is unclear why it has such a large propensity for C–H insertion. These C–H insertions are the most energy demanding of the metal ion insertions, yet Mo$^+$ exclusively undergoes dehydrogenation and multiple dehydrogenations with alcohols having up to four carbons. This high specificity is surprising for such a reactive metal ion species. The formation of conjugated π-systems by multiple dehydrogenation has been postulated as a driving force for catalytic dehydrogenation in solution.[31] Interaction of Mo$^+$ with the multiple double bonds may lower the transition state energies for fragmentation of the initially formed adduct and channel most of the reactions along a dehydrogenation pathway. C–H activation followed by multiple dehydrogenation leading to stable aromatic ligands also occurs for reactions of molybdenum atoms.[32]

An interesting difference between Mo$^+$ and Cr$^+$ is that Mo$^+$ eliminates H$_2$ from methanol and Cr$^+$ does not. This may imply that Mo$^+$ inserts into the O–H bond, whereas the other metal ions do not. The loss of the first molecule of H$_2$ would then lead to formation of a C=O bond.

Conclusions

In conclusion, Fe$^+$ is the most reactive and least selective toward aliphatic alcohols having four or more carbon atoms. The chemistry of Cr$^+$ and alcohols having five or more carbons is quite similar to that of Fe$^+$ despite their different electronic configurations. Cr$^+$ is the least reactive species, and its reactions with alcohols that have four carbons or less are quite selective. Mo$^+$, on the other hand, is very reactive and specific in dehydrogenation or multidehydrogenation reactions. Dehydration and C–C bond insertion reactions appear as alternative reaction channels only when alcohols are branched or chain length is increased. It is important to note that although Mo$^+$ and Cr$^+$ have the same valance electronic configuration, their principal reactivities are distinctive.

The foci of this study are reactivity and reaction specificity. Only wide-ranging conclusions are possible at this stage. For example, reactivity and specificity may be discussed in terms of the energies of the bonds that need to be broken upon insertion, the energy released by bonding between the metal ion and its two ligands after insertion has occurred, and the stability of the product ions formed. The latter two factors affect the transition-state energies for decomposition reactions of the initially formed adduct. Specific details of reactions mechanisms must await studies of isotopic labeling and of comparisons of collisionally activated decomposition (CAD) spectra of product ions and reference compounds. We expect the CAD spectra to reveal, for example, whether Cr$^+$ simply attaches dissociatively to alcohols so that its d^5 electronic configuration is still retained despite its reactivity. These studies are underway.

(31) For a recent review, see: Crabtree, R. H. *Chem. Rev.* 1985, *85*, 245.
(32) Dam, E. M. V.; Brent, W. N.; Silvon, M. P.; Skell, P. S. *J. Am. Chem. Soc.* 1975, *98*, 465.

Reduction of Organic Carbonyl Compounds by the Cationic Dihydrido Carbonyl Species (Cp$_2$Ta(CO)H$_2$)$^+$. Synthesis of Alkoxy Tantalum(III) Derivatives

Jean-François Reynoud, Jean-François Leboeuf, Jean-Claude Leblanc, and Claude Moïse*

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences Gabriel, 21100 Dijon, France

The reaction of the monohydrides (η^5-C$_5$H$_4$R)$_2$Ta(CO)H (1, R = H; 1′, R = CMe$_3$) with HCl followed by treatment with NH$_4$PF$_6$ yields white salts ((η^5-C$_5$H$_4$R)$_2$Ta(CO)H$_2$)$^+$PF$_6^-$ (2, R = H; 2′, R = CMe$_3$) by protonation of the metal. Compound 2 reacts with carbonyl derivatives to give ((η^5-C$_5$H$_5$)$_2$Ta(CO)HOCHRR′)$^+$PF$_6^-$ (3a, 3b, and 3c, respectively, with acetone, 2-butanone, and propanal). In basic medium these salts are deprotonated leading to (η^5-C$_5$H$_5$)$_2$Ta(CO)(OCHRR′) (4a, 4b, and 4c, respectively). Spectroscopic characterization of the complexes have included measurement of their ^{1}H NMR, IR, and mass spectra.

The dihydrides Cp$_2$MH$_2$ (M = Mo, W) possess well-known basic properties owing to an electron lone pair situated in a low-lying molecular orbital. In acidic medium, the dihydrides can be protonated, yielding (Cp$_2$MH$_3$)$^+$, and can react with Lewis acids such as BF$_3$ and AlR$_3$[1] or with

unsaturated organometallic fragments leading to donor-acceptor bimetallic systems.[2] An electronic similarity

(1) Muetterties, E. L. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971; p 152.