Gas-Phase Reactions of Sc^+ , Y^+ , and Lu^+ with Alcohols. Effects of the Class and Chain Length of Alcohols on the Nature of Primary Products

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The primary gas-phase reactions between methanol, ethanol, propan-1-ol, propan-2-ol, and 2-methylpropan-2-ol and the isovalent rare earth metal ions Sc^+ , Y^+ , and Lu^+ generated by laser desorption-ionization of metal targets have been investigated by using a Fourier transform ion cyclotron resonance mass spectrometer. The three metal ions react exothermically with all the alcohols. The overall reactivity is controlled by the high oxophilicity of these metals, and the primary metallated ions obtained are principally oxygenated species. However, the number and the nature of these primary products depends on the electronic configuration of the metal ions as well as on the class and the principal chain length of alcohols. The order of reactivity is $\text{Y}^+ > \text{Sc}^+ > \text{Lu}^+$. The Y^+ and Sc^+ ions principally react via C—O and O—H insertions, whereas Lu^+ reacts by direct abstraction or via various five-center electrocyclic mechanisms as a function of the class and the alcohol chain length. 1996 American Society for Mass Spectrometry (*J Am Soc Mass Spectrom* 1996, 7, 1151–1160)

In recent years, studies that concern the chemical, structural, and applied aspects of alkoxo and aryloxo chemistry of lanthanides, yttrium, and scandium have been greatly boosted [1], not only because of the exploitation of these metal alkoxides or aryloxides in new synthetic reactions [2], but also because of their application in high-tech materials, which often use gas-phase processes [3]. Moreover, it is recognized that gas-phase studies of the reactions of metal ions with organic molecules can provide valuable hints about the mechanisms operative in the condensed phase [4–6]. Therefore, attempts have been made recently to prepare dialkoxo-metal ions and neutral metal alkoxides in the gas phase from reactions of Sc, Y, and lanthanides or their monopositive ions with alcohols or other oxygenated precursors [7–9].

Thus, in a previous work that used Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR), we demonstrated that methanol, which is known to be relatively unreactive with bare metal ions, as are other C_1 compounds (ref 6 and references cited therein), exhibits an impressive gas-phase reactivity with Sc^+ , Y^+ , and Lu^+ , due in part to the strong oxophilicity of these metals [9a]. All the primary ions obtained (MO^+ ,

MOH^+ , MOCH_2^+ , and MOCH_3^+) undergo subsequent reactions with methanol, and the final product is always the dialkoxo-metal species solvated with alcohol molecules $[\text{M}(\text{OCH}_3)_2(\text{CH}_3\text{OH})_n]^+$ ($n = 0\text{--}3$). Now, it appears from the literature data that concern gas-phase reactions of several metal ions (M^+) with various alcohols that gas-phase chemistry becomes much more varied, even for the same class of alcohols, when the chain length increases, because of the increase of the possibilities of bond activations [5–8, 10–28]. For instance, 12 types of primary reactions, which include “remote functionalization” [24], can be identified from propan-1-ol and various metal ions [14, 15, 17–19, 24]. Therefore, the aim of the work performed in our laboratory was to study the structural effects of the alcohols on the primary reactions of the three metal ions Sc^+ , Y^+ , and Lu^+ , and to demonstrate whether the formation of dialkoxo-metal ions $[\text{M}(\text{OR})_2]^+$ ($\text{M} = \text{Sc}^+$, Y^+ , and Lu^+) from the subsequent reactions of primary ions can be generalized whatever the nature of the alcohols. However, taking into account the impressive reactivity of these metal ions with alcohols and for the sake of clarity, the present paper is devoted only to the effects of the class and aliphatic chain length of alcohols on the primary reactions of metal ions with methanol, ethanol, propan-1-ol (C_1 , C_2 , and C_3 primary alcohols), propan-2-ol (secondary alcohol), and 2-methylpropan-2-ol (tertiary alcohol).

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Experimental

The experiments were performed on an FT-ICR mass spectrometer constructed in part in our laboratory at the University of Nice–Sophia Antipolis [29]. A complete description of the apparatus and experimental procedures is given elsewhere [9a, 29].

Scandium, yttrium, and lutetium ions were generated by laser desorption–laser ionization [30] by focusing the beam of a nitrogen pulsed laser (model VSL 337ND, Laser Science Inc., Newton, MA) onto a pure metal target (> 99%, from Alfa Johnson Matthey, Karlsruhe, Germany) placed close to the cell.

For the general procedure, the reactant ions were isolated selectively by double-resonance ejection pulse [31] and/or frequency sweep excitation–ejection [32] to remove all other ions in the ion cyclotron resonance (ICR) cell. The widths and the intensities of ejection and excitation pulses were optimized to minimize the translation activation of reactant ions [33]. The reactants ions were then stored in the cell and allowed to react with the chosen alcohol. Reaction times were varied by a programmable delay event from a minimum of 0.0014 s to a maximum of 8 s prior to ion detection, which allows both primary and sequential reaction products to be observed. The kinetic analysis of the exponential fall of ions under investigation (from the metal ion to the final product) was performed to determine their decay rates. These decay rate constants were determined from the slope of a semilog plot of the decay of the reactant ion of interest over time and the pressure of the neutral substrate. However, this general procedure does not exclude any possible reaction of electronically excited metal ions, which could be produced by the laser ablation process. Indeed, because all transitions between metal ion states in Table 1 [34] are parity forbidden, the radiation life-

times of the excited states are on the order of seconds long [35, 36].

Thus, a second series of experiments was performed with each metal to verify that the reaction products observed from the general procedure are obtained from the ground states of metal ions. In this procedure, the partial pressure of the neutral reactant is maintained in the range $(1\text{--}1.5) \times 10^{-6}$ Pa. The laser-generated metal ions are stored for 5 s in the cell prior to isolation by using a double ejection pulse. The isolated metal ions are then allowed to react with the alcohol. Of course, in comparison with the general procedure, this particular procedure which uses very low partial pressures of the neutral reactant, needs long reaction times to obtain the reaction products. It appears that there is no difference between the nature of products obtained with the general and particular procedures, and that the rate constants obtained for each metal ion from the two procedures are identical within the limit of experimental error, so we can conclude that the reactivity seen from the general procedure is due to the ground state of the metal ions. Furthermore, the reproducibility of the reaction kinetics as well as the very good linearity of the semilog decays of the normalized ion intensities versus time (nonoccurrence of an upward curvature in the decay that results from a translational deexcitation of the reactant ion in nonreactive collisions followed by rapid reaction in subsequent encounters) are highly valuable indications of the thermalization of reactant ions [37–39].

Reaction sequences were confirmed with standard double-resonance techniques [40] in which suppression of the daughter ion is sought by ejection of the supposed parent ion.

Labeling experiments were carried out with CD_3OH , CH_3OD , $\text{CH}_3\text{CD}_2\text{OH}$, $\text{CD}_3\text{CH}_2\text{OH}$, $\text{CD}_3(\text{CH}_2)_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CD}_2\text{OH}$, $(\text{CH}_3)_2\text{CDOH}$, $(\text{CD}_3)_2\text{CHOH}$, and

Table 1. The first electronic states and the total energy cost (promotion energies plus exchange energies lost when two single bonds are formed) of Sc^+ , Y^+ , and Lu^+

Metal ions	State	Electron config.	Energy ^a (eV)	Exchange ^b + promotional ^c costs (eV)
Sc^+	a^3D	$4s3d$	0.013	0.16
	a^1D	$4s3d$	0.315	
	a^3F	$3d^2$	0.608	
	b^1D	$3d^2$	1.357	
Y^+	a^1S	$5s^2$	0.000	0.38
	a^3D	$5s4d$	0.148	
	a^1D	$5s4d$	0.409	
	a^3F	$4d^2$	1.045	
Lu^+	a^3P	$4d^2$	1.742	1.90
	a^1S	$6s^2$	0.000	
	a^3D	$6s5d$	1.628	
	a^1D	$6s5d$	2.149	

^aEnergies are a statistical average over the J levels. Values from ref 34.

^bEnergy lost upon forming two single bonds (insertion) from the first d^1s^1 configuration of metal ions. Values from refs 35 and 36.

^cEnergy required for the promotion from the ground state of metal ions to the first d^1s^1 state [34].

(CD₃)₃COH to unravel the mechanistic pathways. No unexplained scrambling occurs in these experiments. Labeled alcohols CD₃OH (99% D), CH₃OD (99.5% D), CH₃CD₂OH (98% D), and CD₃CH₂OH (99% D) were obtained commercially from Aldrich Chemical Co. (Milwaukee, WI). (CH₃)₂CDOH (98% D), (CD₃)₂CHOH (98% D), and (CD₃)₃COH (98% D) were obtained commercially from Cambridge Isotope Laboratories, Inc. (Andover, MA). Purified samples (> 98% D) of isotopomers CD₃(CH₂)₂OH and CH₃CH₂C₂OH were a gift from Professor H. Schwarz [24].

Collision-induced dissociation (CID) experiments [30a] were used with argon target gas to probe the structures of some ions. The collision energy was varied between 0 and 150 eV (E_{lab} scale).

The relevant thermodynamic values used in the discussion are obtained from refs 4 and 41–44.

Results and Discussion

Overall Reactivity of Sc⁺, Y⁺, and Lu⁺

The generally accepted assumption is that gas-phase ion-molecule reactions often occur with little or no activation barrier because of the long range ion-dipole and ion-induced dipole attraction [45]. The consequence of this long range interaction is that ion-molecule are several orders of magnitude faster than reactions in solution and that observation of a gas-phase ion-molecule reaction proceeding at roughly 1/10 or greater the diffusion-controlled collision rate is likely to be exothermic [46]. Thus, the high kinetic efficiencies [47] for disappearance of the three bare metal ions reported in Table 2 show that these metal ions react exothermically with the alcohols, which confirms our earlier results obtained with methanol [9a]. As expected, the overall reactivity of the three rare earth metal ions is controlled by the high oxophilicity of metals and, whatever the class and the chain length of alcohols studied here, the three Group 3 metal ions exhibit an impressive reactivity compared with the isovalent Group 13 metal ions [22]. Qualitatively these different behaviors can be linked to the large difference of oxophilicity of these metals as depicted by the bond dissociation energies for the metal-oxygen [43]

Figure 1. Overall reactivity of Sc⁺, Y⁺, and Lu⁺ with alcohols.

or metal ion-oxygen bonds [41, 44] via the equation $D^{\circ}[M^{+}-O] = D^{\circ}[M-O] + IE[M] - IE[MO]$.

The overall reactivity of the three metal ions as a function of the structure of alcohols is schematized in Figure 1. It increases from methanol to ethanol and propan-1-ol (primary alcohols) to propan-2-ol (secondary alcohol), and decreases for 2-methylpropan-2-ol, probably because there is steric hindrance around the functional group. This reactivity efficiency depends on the nature of the metal ions, and it appears that the order of reactivity globally is $Y^{+} > Sc^{+} > Lu^{+}$, whatever the class of alcohols. However, although the overall reactivity of propan-1-ol falls in the reactivity order of the alcohol class effect, a discrepancy clearly appears for this alcohol in the reactivity order of metal ions ($Y^{+} \approx Sc^{+} \approx Lu^{+}$ for propan-1-ol), which shows that the reactivity of these metal ions also is dependent on the alcohol chain length.

Primary Products as a Function of the Metal Ion and of the Alcohol

The branching ratios, calculated by allowing for the subsequent reactions for the three metal ions Sc⁺, Y⁺, and Lu⁺, are reported in Table 3.

Table 2. Rates k^a (cm³ molecule⁻¹ s⁻¹) and efficiencies^b (Eff.) for the disappearance of Sc⁺, Y⁺, and Lu⁺ that react with alcohols

Alcohols	Metal ions					
	Sc ⁺		Y ⁺		Lu ⁺	
	k ($\times 10^{10}$)	Eff.	k ($\times 10^{10}$)	Eff.	k ($\times 10^{10}$)	Eff.
CH ₃ OH	8.6	0.46	8.2	0.50	5.9	0.38
C ₂ H ₅ OH	12.5	0.66	11.7	0.71	7.8	0.52
<i>n</i> -C ₃ H ₇ OH	12.5	0.64	10.6	0.64	9.5	0.64
<i>i</i> -C ₃ H ₇ OH	17.8	0.91	16.2	0.98	12.1	0.82
<i>t</i> -C ₄ H ₉ OH	15.5	0.79	14.5	0.87	9.8	0.66

^aRates are estimated to be accurate to $\pm 15\%$.

^bEfficiency = k/k_{ADO} ; k_{ADO} = collision rates [47].

Whatever the nature of alcohols ($C_xH_{2x+1}OH$) or metals, some typical reactions, such as the formation of the complex $M(C_xH_{2x+1}OH)^+$ (eq 1) and of the $C_xH_{2x+1}^+$ ion (eq 2) or the loss of water (eq 3), observed as primary reactions from many metal ions [14, 15, 17-19, 24] do not occur here.

Depending on the nature of metal ions and on the class and chain length of alcohols, 10 primary reactions are identified here (eqs 4-13).

Table 3. Primary ion-molecule reaction products of Sc^+ , Y^+ , and Lu^+ with alcohols

Alcohols	Ions formed	Neutrals lost	% Product distribution from		
			Sc^+	Y^+	Lu^+
CH_3OH	MH_2^+	$HCHO$	—	12	—
	MO^+	CH_4	14	12	—
	MOH^+	CH_3	40	36	60
	$MOCH_2^+$	H_2	32	17	—
	$MOCH_3^+$	H	14	23	40
C_2H_5OH	MH_2^+	CH_3CHO	—	6	—
	MO^+	CH_3CH_3	44	19	—
	MOH^+	CH_3CH_2	42	53	33
	MOH_2^+	CH_2CH_2	3	4	47
	$MOCH_2^+$	CH_4	4	—	—
	$MOCH_3^+$	CH_3	3	4	13
	$MOC_2H_4^+$	H_2	1	2	—
	$MOC_2H_5^+$	H	3	12	7
$n - C_3H_7OH$	MO^+	$CH_3CH_2CH_3$	42	26	6
	MOH^+	$CH_3CH_2CH_2$	34	47	21
	MOH_2^+	CH_3CHCH_2	8	8	42
	$MOCH_2^+$	CH_3CH_3	6	5	—
	$MOCH_3^+$	CH_2CH_2	4	3	20
	$MOC_3H_4^+$	$2H_2$	6	5	6
	$MOC_3H_7^+$	H	—	6	5
$i - C_3H_7OH$	MO^+	$CH_3CH_2CH_3$	37	14	—
	MOH^+	CH_3CHCH_3	46	72	42
	MOH_2^+	CH_3CHCH_2	14	12	53
	$MOC_3H_4^+$	$2H_2$	3	2	5
$t - C_4H_9OH$	MO^+	$(CH_3)_3CH$	32	12	—
	MOH^+	$(CH_3)_3C$	47	73	46
	MOH_2^+	$(CH_3)_2CCH_2$	14	12	40
	$MOC_3H_4^+$	$CH_4 + H_2$	7	3	14

Table 4. Enthalpies of reaction 5 calculated from the relevant thermodynamic values

Oxides	Alcohols; $\Delta_r H_5$ (kJ mol ⁻¹)				
	CH ₃ OH	C ₂ H ₅ OH	<i>n</i> - C ₃ H ₇ OH	<i>i</i> - C ₃ H ₇ OH	<i>t</i> - C ₄ H ₉ OH
ScO ⁺	-312	-288	-289	-271	-261
YO ⁺	-376	-352	-353	-335	-325
LuO ⁺	-183	-159	-160	-142	-132

Except for production of the metal dihydride ion MH_2^+ (eq 4), which is observed only for $M = Y$, all the metallated ions are oxygenated species, probably with the oxophilic metal linked to oxygen. It clearly appears from Tables 2 and 3 that the formation of these oxygenated species depends not only on the class and on the alcohol chain length, but also on the metal ion. The behavior of Sc^+ and Y^+ differs from that of Lu^+ , so for the sake of clarity, each proposed process will be discussed and schematized separately for Sc^+ and Y^+ , and for Lu^+ .

The first primary product for which the formation is a function of the alcohol chain length is the metal oxide ion $[MO]^+$ (eq 5). Indeed, this ion is observed for all the alcohols only when $M = Sc$ and Y , and for all three metals only when propan-1-ol is used (Table 3). Assuming that only exothermic ion-molecule reactions can occur [48], we note that the metal oxide ion formation from the five alcohols with Sc^+ and Y^+ is in agreement with the large negative values of $\Delta_r H$ for reaction 5 (denoted as $\Delta_r H_5$, Table 4). However, the formation of LuO^+ is observed only with propan-1-ol, although $\Delta_r H_5$ is largely negative for the five alcohols. Assuming that the formation of metal oxide ions requires that the M^+ insert into the C—O bond of alcohols (path a, Scheme I) followed by the loss of

C_xH_{2x+2} that occurs via a four-center mechanism [9] (path a₁, Scheme I), the difference in behaviors observed here for Sc^+ and Y^+ , and for Lu^+ on the other hand, can be explained for all the alcohols with the exception of propan-1-ol. This explanation is based on a model that has been applied successfully to the reactivity of *d* transition metal ions with hydrocarbons [49–53] and also to the reactions of lanthanides with alkanes, alkenes, and arenes [39, 54, 55]. According to this model, a $d^{n-1}s^1$ configuration is necessary for an ion to be able to insert itself into a C—H or C—C bond and form two σ bonds: the reactivity is then controlled by the energy required to promote the metal ion from the ground state to the appropriate $d^{n-1}s^1$ state and by the exchange energy (high-spin coupling) lost upon bond formation. Applying this model to a C—O insertion, it appears from data reported in Table 1 that, in contrast to Sc^+ , Y^+ , the closed-shell stability of the Lu^+ ($1S, 6s^2$) ground state makes the insertion reaction difficult. Indeed, the electrostatic potential well for the M^+ —alcohol adduct is not deep enough to lower the barrier for the insertion reaction sufficiently below the energy of the reactants, Lu^+ and alcohol, to lead to the metal oxide ion formation (Figure 2).

Now, the question is why does propan-1-ol lead to LuO^+ , whereas alcohols with one or two atoms of

Scheme I

Figure 2. Schematic of a general potential energy surface for reaction 5 when a C—O insertion is invoked for $M = \text{Lu}$. The initial electrostatic potential well (E^*) is not deep enough to lower the barrier (E_a) to reaction 5 below the energy of the reactants ($E_a < E^*$).

carbon on the principal chain do not? The interpretation of this result cannot be based on the increase of the size and polarizability of the neutral reactant: larger alcohols deepen the electrostatic potential well for the M^+ —alcohol adduct, which binds the alcohol more strongly to M^+ and provides more energy for chemical activation ($E_a < E^*$ in Figure 2). Indeed, propan-2-ol and 2-methylpropan-2-ol with higher polarizabilities than propan-1-ol should lead to formation of LuO^+ , but they do not. However, it can be resorted that this interpretation must apply to the same class of alcohols and that an alcohol class effect could explain the nonoccurrence of LuO^+ for propan-2-ol and 2-methylpropan-2-ol. However, if deepening the initial electrostatic well lowers the barrier to insertion reaction below the energy of the reactants (when they are Lu^+ and propan-1-ol), then to observe the metal oxide ion formation, the same process must occur for the three metal ions. Consequently, the overall reaction efficiencies for the three metal ions must increase and the trend between the three metals must be the same from methanol to ethanol and from ethanol to propan-1-ol. This hypothesis disagrees with the experimentally observed trends. The results of Table 2 show that the overall reaction efficiency of M^+ increases from Lu^+ to Sc^+ and Y^+ , and from methanol to ethanol in agreement with the increase of alcohol polarizabilities, yet it increases only for $M = \text{Lu}$ from ethanol to propan-1-ol.

The fact that the formation of LuO^+ is observed only with propan-1-ol must be related to another observation. Indeed, we can observe in Table 3 that the $[\text{MOCH}_4]^+$ species is formed only from propan-1-ol (eq 12) and that the proportion of this product is large only for $M = \text{Lu}^+$. The labeling experiments performed with $\text{CD}_3(\text{CH}_2)_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CD}_2\text{OH}$

show that the $[\text{MOCHD}_3]^+$ and $[\text{MOCH}_4]^+$ ions are formed (no scrambling observed), respectively, which thus shows that the actual structure of $[\text{MOCH}_4]^+$ is $[\text{CH}_3 - \text{M} - \text{OH}]^+$. For the reasons explained in the foregoing text, it is clear that the formation of the metal oxide ion with $M = \text{Lu}$ when the alcohol chain length is greater than two carbons must imply a mechanism in which the C—O insertion is not required, and we suggest that the formation of LuO^+ and that of $[\text{CH}_3\text{LuOH}]^+$ are closely related. We propose a five-center electrocyclic mechanism (path a, Scheme II) that explains the formation of the hydroxide-methyl-metal ion $[\text{CH}_3\text{MOH}]^+$ and MO^+ , and that would be effective only when the exchange and promotional costs for a C—O insertion are excessive (i.e., $M = \text{Lu}$). This mechanism leads first to the formation of the vibrationally excited $[\text{CH}_3\text{LuOH}]^+$ species. The nascent product of reaction 12 has enough energy for a second intramolecular elimination reaction (eq 14), which results in the metal oxide ion LuO^+ (path a₁, Scheme II).

Stabilization of the product of reaction 12 leads to the hydroxide-methyl-metal ion (path a₂, Scheme II). In contrast to $[\text{CH}_3\text{LuOH}]^+$, the relative proportions of the hydroxide-methyl-metal ions $[\text{CH}_3\text{MOH}]^+$ when $M = \text{Sc}$ and Y are very low. This result can be interpreted by the fact that the previous five-center mechanism is not very effective when a C—O insertion is thermodynamically feasible, where the formation of the hydroxide-methyl-metal ion from the insertion into the C—O bond of propan-1-ol (path a₂, $R = \text{CH}_3$, Scheme I) is a side reaction of the principal processes that lead to the metal-oxide ion MO^+ from the loss of alkane (path a₁, Scheme I) and to the hydroxide-metal ions MOH^+ from the loss of an alkyl group (eq 6, path a₃, Scheme I).

It is noteworthy that the formation of $[\text{CH}_3\text{MOH}]^+$ from propan-1-ol closely parallels that of the $[\text{HMOH}]^+$ species from alcohols that bear a hydrogen on the β -carbon (eq 7). Indeed, the proportion of $[\text{HLuOH}]^+$ is relatively large for all these alcohols compared with its scandium and yttrium homologs (Table 3). The formation of the $[\text{HMOH}]^+$ species (eq 7) does not require an insertion mechanism, and this ion can be obtained either by a preliminary insertion of the metal into the C—O bond followed by a four-center elimination of alkene (path a₂', Scheme I) or by a five-center mechanism as can be seen in Scheme II (path b). Thus, Sc^+ and Y^+ give $[\text{HMOH}]^+$ principally via the intermediate $[\text{C}_x\text{H}_{2x+1} - \text{M} - \text{OH}]^+$, and Lu^+ probably from a direct five-center electrocyclic elimination of alkene. The proposed mechanisms are supported by the labeling experiments with $\text{CH}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CD}_2\text{OH}$, $\text{CD}_3(\text{CH}_2)_2\text{OH}$, and $(\text{CH}_3)_2\text{CDOH}$, which show that $[\text{HMOH}]^+$ is formed, and with $\text{CD}_3\text{CH}_2\text{OH}$, $(\text{CD}_3)_2\text{CHOH}$, and $(\text{CD}_3)_3\text{COH}$, which show that $[\text{DMOH}]^+$ forms. Moreover, these labeling experi-

Scheme II

ments allow the assumption that the hydride-hydroxide-metal ion could coexist in an equilibrium mixture with the ion-dipole complex $[M^+ \cdots OH_2]$. Indeed, the reaction of the $[MOH_2]^+$ species with the alcohols leads to dihydroxide-metal ions $[HOMOH]^+$, and the deuterated species $[MOHD]^+$ obtained from β -deuterated alcohols leads to the expected product $[HOMOH]^+$ as well as the deuterated ion $[HOMOD]^+$, which is obtained in lower proportion. This difference of proportions can be interpreted by the displacement of equilibrium $[D-M-OH]^+ \rightleftharpoons [M \cdots OH_2]^+ \rightleftharpoons [H-M-OD]^+$ toward the $[D-M-OH]^+$ form due to an isotopic effect.

Comparison of the similarity between the mechanisms for the formation of $[HMOH]^+$ and $[CH_3MOH]^+$ species can be extended to the behavior of the nascent products, and now the question is why does the nascent $[HLuOH]^+$ species not undergo an intramolecular elimination like $[CH_3LuOH]^+$ does to give $[LuO]^+$ (eq 15).

However, the experiments show that although $[HLuOH]^+$ is produced (path b₂, Scheme II) from ethanol, propan-2-ol, and 2-methylpropan-2-ol for which the reaction in eq 14 cannot occur, the formation of $[LuO]^+$ is not observed. This result is difficult to explain. Nevertheless, we note that reaction 14 is approximately 33 kJ mol⁻¹ more exothermic than reaction 15. Thus, it seems energetically more favorable to lose a methane molecule than to lose a dihydrogen molecule from the metallated species. In addition,

methane has a stronger electrostatic interaction than dihydrogen with Lu^+ due to its greater polarizability. Thus, losing methane rather than dihydrogen should give rise to a deeper potential energy in the exit channel. This situation may also lower the energy of the transition state for this elimination process. These effects conspire to make the loss of methane more favorable than the loss of dihydrogen.

Note that the proposed five-center electrocyclic mechanisms for $[CH_3LuOH]^+$ and $[HLuOH]^+$ formation (paths a and b, Scheme II) are reminiscent of the "remote functionalization" of alcohols previously described by Schwarz and co-workers [23, 24]. However, in the present case we postulated that the insertion of the "anchored" metal ion into the terminal C-H or C-C bond cannot occur because the exchange and promotional costs for an insertion are too great for the metal ion under study.

The primary reaction (eq 6) that leads to the formation of the hydroxide-metal species $[MOH]^+$ is common to the three metals and the five alcohols. For $M = Sc$, this result agrees very well with the large value of the bond dissociation energy (BDE) for Sc^+-OH [44]. For $M = Y$ and Lu , the lower limit of BDEs for M^+-OH is higher than the BDE for CH_3-OH [42]: $D^0[M^+-OH] > 385 \text{ kJ mol}^{-1}$. As for the $[MO]^+$, $[HMOH]^+$, and $[CH_3MOH]^+$ species, the formation of the $[MOH]^+$ ions is observed in relatively high proportion whatever the alcohol chain length and can be obtained either by a preliminary insertion of the metal ion into the C-O bond followed by the loss of the alkyl group (path a₃ for $M = Sc$ and Y , Scheme I) or by a "direct reaction" with the loss of the alkyl group (path c₁ for $M = Lu$, Scheme II). Similarly, the

$[\text{MOC}_x\text{H}_{2x+1}]^+$ ion observed for methanol, ethanol, and propan-1-ol (eq 10) can be formed either by preliminary insertion of the metal ion in the O—H bond ($\text{M} = \text{Sc}$ and Y) via the intermediate $[\text{C}_x\text{H}_{2x+1}\text{O} - \text{M} - \text{H}]^+$ (path b_1 , Scheme I) or by a "direct" reaction ($\text{M} = \text{Lu}$) with loss of H (path c_2 , Scheme II). Loss of H is a high endothermic process, and the formation of $[\text{MOC}_x\text{H}_{2x+1}]^+$ instead of MH^+ is driven by strong BDEs of $[\text{M}^+ - \text{OR}]$ and low BDEs of $[\text{M}^+ - \text{H}]$ [4]. The inability to observe the $[\text{MOC}_x\text{H}_{2x+1}]^+$ ion for the secondary and tertiary alcohols is indicative of the effect of the class of alcohols on the reactivity. Lower and upper limits of BDEs for $[\text{M}^+ - \text{OR}]$ can be estimated from these results and the relevant thermodynamic values [4, 41]: $D^\circ[\text{M}^+ - \text{OCH}_3] > 439 \text{ kJ mol}^{-1}$ and $D^\circ[\text{M}^+ - \text{OC}_2\text{H}_5] > 436 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Sc}$, Y , and Lu ; $D^\circ[\text{Sc}^+ - \text{O}(n - \text{C}_3\text{H}_7)] < 432 \text{ kJ mol}^{-1}$; $D^\circ[\text{M}^+ - \text{O}(n - \text{C}_3\text{H}_7)] > 432 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Y}$ and Lu ; $D^\circ[\text{M}^+ - \text{O}(i - \text{C}_3\text{H}_7)] < 438 \text{ kJ mol}^{-1}$ and $D^\circ[\text{M}^+ - \text{O}(t - \text{C}_4\text{H}_9)] < 440 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Sc}$, Y , and Lu .

The structure of the $[\text{MOH}]^+$ and $[\text{MOCH}_3]^+$ ions obtained from methanol has been discussed previously in terms of electronic, thermodynamic, and mechanistic arguments, and we concluded that the metal-hydroxide and metal-methoxide structures are the most likely structures for $[\text{MOH}]^+$ and $[\text{MOCH}_3]^+$, respectively [9a]. The same arguments applied to the $[\text{MOH}]^+$ and $[\text{MOC}_x\text{H}_{2x+1}]^+$ species obtained from ethanol and propan-1-ol, as well as the results of CID experiments, plead in favor of the metal-hydroxide $[\text{M} - \text{OH}]^+$ and metal-alkoxide $[\text{M} - \text{OC}_x\text{H}_{2x+1}]^+$ structures for these species.

Monodehydrogenation and formation of the metal ion-carbonyl compound complex $[\text{MOC}_x\text{H}_{2x}]^+$ (eq 9) also depend on the class and alcohol chain length and on the nature of metal ions. Only methanol and ethanol lead to the metal ion-aldehyde complex with Sc^+ and Y^+ . This reaction must be explained from insertion mechanisms, and Lu^+ is not expected to react via these mechanisms. For alcohols $\text{C}_x\text{H}_{2x+1}\text{OH}$ ($x \geq 2$), three insertion mechanisms have been proposed in the literature to explain the dehydrogenation reaction. Jones and Staley [15] and Huang et al. [19] proposed dehydrogenation via insertion into the H—OR bond, whereas Weil and Wilkins [18] suggested a mechanism that involves metal cation insertion into a $\text{C}_\alpha\text{—H}$ bond followed by a β -hydrogen atom transfer. The "remote functionalization" mechanism, which was described more recently by Prüsse et al. [27], requires the insertion of the metal ion into a terminal C—H bond of long-chain alcohols. In the present case, we must consider that the highest proportions of $[\text{MOC}_x\text{H}_{2x}]^+$ ions are obtained with methanol for which the "remote functionalization" mechanism cannot proceed, and taking into account the oxophilicity of the metal ions under study, we conclude that their interaction with the O—H bond is more likely than their interaction with a C—H bond. Thus, we retain only the O—H

insertion followed by a β -hydrogen atom transfer and loss of dihydrogen as the principal mechanism to explain the formation of the $[\text{MOC}_x\text{H}_{2x}]^+$ species when M is Sc or Y (path b_2 , Scheme I).

In the same way, the formation of the metal ion-formaldehyde complex $[\text{MOCH}_2]^+$ (eq 8) from ethanol and propan-1-ol when $\text{M} = \text{Sc}$ and Y can be explained from the same O—H insertion, which is now followed by a methyl or ethyl group transfer and elimination of methane or ethane for ethanol and propan-1-ol, respectively (path b_3 , Scheme I). The reactions with $\text{CD}_3\text{CH}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{CH}_2\text{OH}$ give results that agree with the proposed mechanisms in eqs 8 and 9. It is noteworthy that a five-center mechanism could take place with Lu^+ and lead to the formation of the $[\text{LuOC}_x\text{H}_{2x}]^+$ or $[\text{LuOCH}_2]^+$ species (paths d_1 and d_2 , Scheme II). However, the species are never observed regardless of the alcohol chain length. The weakness of the Lu^+ -aldehyde bond could explain the nonobservation of these species. Indeed, the exothermicity of the reaction in eq 8 requires that the BDE of $\text{M}^+ \cdots \text{OCH}_2$ be higher than 51 and 62 kJ mol^{-1} for ethanol and propan-1-ol, respectively, and that of the reaction in eq 9 requires that the BDE of $\text{M}^+ \cdots \text{OC}_x\text{H}_{2x}$ be higher than 93, 69, and 67 kJ mol^{-1} for methanol, ethanol, and propan-1-ol, respectively. On the other hand, we can observe that ethanol leads to the $[\text{MOCH}_3]^+$ species (eq 11) in addition to the normal metal-alkoxide ion $[\text{MOC}_2\text{H}_5]^+$.

The relative proportion of the $[\text{MOCH}_3]^+$ ions formed from ethanol is larger for $\text{M} = \text{Lu}$ than for $\text{M} = \text{Sc}$ and Y . Whatever the metal used, labeling experiments give $[\text{MOCD}_2\text{H}]^+$ and $[\text{MOCH}_3]^+$ from $\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$, respectively. Thus, except for methanol for which the methoxy-metal species is the normal product issued from eq 10, the $[\text{MOCH}_3]^+$ is specific to ethanol, and the mechanisms for its formation seem to depend on the nature of the metal ion. These mechanisms closely parallel those proposed to explain the formation of the $[\text{MOC}_x\text{H}_{2x}]^+$ and $[\text{MOCH}_2]^+$ species. Thus, the first step that leads to the $[\text{ScOCH}_3]^+$ and $[\text{YOCH}_3]^+$ species is the insertion into the O—H bond of ethanol. This insertion is followed by a β -methyl group transfer, and the ion-dipole complex $[\text{CH}_2\text{O} \cdots ^+\text{MHCH}_3]$ coexists in equilibrium with the $[\text{CH}_3\text{OMCH}_3]^+$ intermediate. The latter loses a methyl group to give the $[\text{MOCH}_3]^+$ ion (path b_4 , Scheme I). Concerning the $[\text{LuOCH}_3]^+$ species from ethanol, the five-center mechanism previously discussed for the possible formation of the $[\text{LuOC}_x\text{H}_{2x}]^+$ or $[\text{LuOCH}_2]^+$ species leads to the ion-dipole complex $[\text{CH}_2\text{O} \cdots ^+\text{LuHCH}_3]$, which then evolves like the scandium and yttrium homologs toward the metal-methoxy ion (path d_3 , Scheme II). Note that the lower limit of the BDE of $\text{M}^+ - \text{OCH}_3$ required to obtain the exothermicity for reaction 11 ($D^\circ > 396 \text{ kJ mol}^{-1}$) easily is exceeded because it was demonstrated previously that $D^\circ[\text{M}^+ - \text{OCH}_3] > 439 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Sc}$, Y , or Lu [9a].

In contrast to methanol and ethanol, propan-1-ol does not lead to the $[\text{MOC}_x\text{H}_{2x}]^+$ ions nor to $[\text{MOCH}_3]^+$ and $[\text{MOC}_2\text{H}_5]^+$, whereas the formation of the $[\text{MOC}_3\text{H}_4]^+$ species is observed (eq 13). In the same way, the primary ion $[\text{MOC}_3\text{H}_4]^+$ is obtained from propan-2-ol and 2-methylpropan-2-ol in reactions with the three metal ions, whereas the monodehydrogenated or demethanated species $[\text{MOC}_3\text{H}_6]^+$ are not observed for these alcohols. Labeling experiments performed with $\text{CH}_3\text{CH}_2\text{CD}_2\text{OH}$ principally lead to $[\text{MOC}_3\text{H}_3\text{D}]^+$ with traces of $[\text{MOC}_3\text{H}_2\text{D}_2]^+$. The $[\text{MOC}_3\text{H}_2\text{D}_2]^+$ ion is the only product obtained from $\text{CD}_3\text{CH}_2\text{CH}_2\text{OH}$. Moreover, the MO^+ ion is the only fragment observed from the CID spectra of the $[\text{MOC}_3\text{H}_4]^+$ species regardless of the alcohols from which it is formed. These results associated with possible scrambling do not allow unambiguous validation or invalidation of one of the three structures (a)–(c) for the $[\text{MOC}_3\text{H}_4]^+$ ions from propan-1-ol and propan-2-ol nor of the two structures (a) and (b) for the species from 2-methylpropan-2-ol (Scheme III). This double dehydrogenation reaction (for propan-1-ol and propan-2-ol) or the dehydrogenation–demethanation (for 2-methylpropan-2-ol) for which we are unable to propose a mechanism at this time, may explain why the $[\text{MOC}_3\text{H}_6]^+$ species expected from path b_2 of Scheme I or from path d_1 of Scheme II are not observed for these alcohols. There are examples in the literature of gas-phase metal ion–alcohol reactions for which products of double and triple dehydrogenations are observed while monodehydrogenated product is not [19]. For instance, the reactions between Mo^+ and propan-1-ol or propan-2-ol give $[\text{MoOC}_3\text{H}_4]^+$ and $[\text{MoOC}_3\text{H}_2]^+$, whereas the product of monodehydrogenation is not obtained [19]. On the other hand, the formation of $[\text{MOC}_3\text{H}_4]^+$ from 2-methylpropan-2-ol, for which the losses of dihydrogen and methane are required, is not observed with Mo^+ [19], whereas it is with $\text{M} = \text{Sc}, \text{Y}, \text{and Lu}$.

The metal dihydride-ion MH_2^+ (eq 4) is observed only for $\text{M} = \text{Y}$ with methanol and ethanol. It is the result of competitive aldehyde–dihydrogen ligand losses from a $[\text{H}_2\text{MOC}_x\text{H}_{2x}]^+$ intermediate that may be formed from an O–H insertion mechanism (path b_5 , Scheme I). The different behaviors of Sc^+ , Lu^+ , and Y^+ are not surprising because the values for $\Delta_f H_4$ [derived from $\Delta_f H_4 = 2 \Delta_f H(\text{H}) - D^\circ[\text{M}^+ - \text{H}] - D^\circ[\text{HM}^+ - \text{H}] + \Delta_f H(\text{C}_x\text{H}_{2x}\text{O}) - \Delta_f H(\text{C}_x\text{H}_{2x+1}\text{OH})$] are +46 and +22 kJ mol^{-1} for Sc^+ , +118 and +94 kJ mol^{-1} for Lu^+ , and –4 and –28 kJ mol^{-1} for Y^+ , with methanol and ethanol, respectively.

Scheme III

Conclusion

The three isovalent rare earth metal ions Sc^+ , Y^+ , and Lu^+ react exothermically with methanol, primary, secondary, and tertiary alcohols. The overall reactivity is controlled by the high oxophilicity of these metals, and the primary metallated ions obtained are principally oxygenated species. However, the number and the nature of these primary products depend on the electronic configuration of the metal ions as well as on the class and the chain length of alcohols. The reactions with Sc^+ and Y^+ are directed by insertions into the C–O and O–H bonds, whereas the closed-shell stability of the Lu^+ ($^1S, 6s^2$) ground state forbids the insertions. Lu^+ reacts by direct abstraction and electrocyclic mechanisms. Thus, among the major primary products $[\text{MO}]^+$, $[\text{MOH}]^+$, and $[\text{HMOH}]^+$, only one is common to the three metals and the five alcohols—the hydroxide–metal $[\text{MOH}]^+$ ion. The formation of MO^+ from alcohols with less than three carbon atoms in the principal chain (i.e., methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol) requires an insertion mechanism and is observed only with $\text{M} = \text{Sc}$ and Y , whereas $[\text{LuO}]^+$ is formed from propan-1-ol by using an electrocyclic mechanism. The $[\text{HMOH}]^+$ species is obtained only from alcohols that bear a hydrogen on the β -carbon and principally when $\text{M} = \text{Lu}$. The formation of other species, such as $[\text{MOCH}_2]^+$, $[\text{MOC}_x\text{H}_{2x+1}]^+$, $[\text{HOMCH}_3]^+$, or $[\text{MOC}_3\text{H}_4]^+$, depends on the class of alcohols $\text{C}_x\text{H}_{2x+1}\text{OH}$ and on their chain length. Thus, the $[\text{MOC}_x\text{H}_{2x+1}]^+$ species is obtained only with methanol and primary alcohols, and lower and upper limits for BDEs of $[\text{M}^+ - \text{OR}]$ can be estimated: $D^\circ[\text{M}^+ - \text{OCH}_3] > 439 \text{ kJ mol}^{-1}$ and $D^\circ[\text{M}^+ - \text{OC}_2\text{H}_5] > 436 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Sc}, \text{Y}, \text{and Lu}$; $D^\circ[\text{Sc}^+ - \text{O}(n - \text{C}_3\text{H}_7)] < 432 \text{ kJ mol}^{-1}$; $D^\circ[\text{M}^+ - \text{O}(n - \text{C}_3\text{H}_7)] > 432 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Y}$ and Lu ; $D^\circ[\text{M}^+ - \text{O}(i - \text{C}_3\text{H}_7)] < 438 \text{ kJ mol}^{-1}$ and $D^\circ[\text{M}^+ - \text{O}(t - \text{C}_4\text{H}_9)] < 440 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Sc}, \text{Y}, \text{and Lu}$.

In our next article, we will examine whether the formation of dialkoxy–metal ions $[\text{M}(\text{OR})_2]^+$, observed with methanol from the subsequent reactions of primary ions [9a], can be generalized for the subsequent reactions of principal primary ions obtained with ethanol, propan-1-ol, propan-2-ol, and 2-methylpropan-2-ol.

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