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from our studies that these systems would show similar activity for the reduction of nitrogen.

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Reactions of Al^+ and Mg^+ with Alcohols and Organic Halides in the Gas Phase

Jack S. Uppal and Ralph H. Staley[*1]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received May 6, 1981*

Abstract: The chemistry of Al^+ and Mg^+ with alkyl halides and alcohols is studied by ion cyclotron resonance spectroscopy. Alkyl chlorides react with Al^+ and Mg^+ by chloride transfer when this is exothermic. In addition, Mg^+ induces the dehydrochlorination of alkyl chlorides to produce Mg^+–alkene complexes. Displacement of the alkene by the alkyl chloride is followed by a second elimination–displacement sequence resulting in $Mg(RCl)_2^+$. Both Al^+ and Mg^+ induce the dehydration of alcohols to give $Al(H_2O)^+$ and $Mg(H_2O)^+$. Ligand displacement reactions result in $Al(ligand)^+$ and $Mg(ligand)_2^+$ as the final product species. In the presence of strong proton bases, proton transfer from the $M(H_2O)^+$ intermediates is also observed, establishing upper limits on the metal hydroxide proton affinities, $PA(MOH) \equiv D(MOH{-}H^+)$; $PA(AlOH) \leq 220.4$ kcal/mol and $PA(MgOH) \leq 224.3$ kcal/mol.

Relative gas-phase binding energies of organic molecules, L, to metal cation species, M^+, have recently been determined by measuring the equilibrium constant for ligand exchange, reaction 1, using ion cyclotron resonance (ICR) techniques. The results

$$ML_1^+ + L_2 \rightleftarrows ML_2^+ + L_1 \qquad (1)$$

of a series of measurements can be combined to establish a scale of ligand binding energies, $D(M^+{-}L)$. Lithium cation, Li^+, generated by a thermoionic source has been studied utilizing the dehydrohalogenation reactions 2 and 3 with alkyl halides to

$$Li^+ + (CH_3)_2CHCl \rightarrow Li(C_3H_6)^+ + HCl \qquad (2)$$

$$Li^+ + (CH_3)_2CHCl \rightarrow Li(HCl)^+ + C_3H_6 \qquad (3)$$

produce the initial metal–ligand species.[2,3] Electron-impact ionization of CpNi(NO) ($Cp \equiv \eta^5\text{-}C_5H_5$, cyclopentadienyl radical) has been used to study ligands bound to $CpNi^+$ where the parent ion $CpNi(NO)^+$ is utilized directly as the initial metal–ligand species.[4,5] Data sets for Li^+ and $CpNi^+$ with over 30 ligands were obtained in these studies. Comparison of these results with each other and with the existing data set for proton affinities PA(B) $\equiv D(B{-}H^+)$ has provided useful quantitative insight into the interaction of metal ion species with organic molecules.

Attempts to utilize other volatile organometallics as precursors for studies of ligand binding energies have been less successful. Qualitative ordering of relative ligand binding energies was established for $TiCl_3^+$, $CpCo(CO)^+$, and $CpCo^+$ utilizing the parent ions of $TiCl_4$ and $CpCo(CO)_2$ and the fragment ion $CpCo(CO)^+$ from $CpCo(CO)_2$ as the initial metal–ligand species, respectively.[6,7] Extensive quantitative results were *not* obtained in these systems. With $TiCl_4$, reactions of the neutral $TiCl_4$ with organic molecules severely limited the set of molecules which could be studied.[6] With $CpCo(CO)_2$, condensation with $CpCo(CO)_2$ to give cluster species containing two or more cobalt atoms consumed the $CpCo(L)^+$ and $CpCo(CO)(L)^+$ species before the ligand-exchange reactions could approach equilibrium.[7] This problem was also noted with CpNi(NO) but was less severe.[4,5]

The thermionic source used to generate Li^+ is limited to alkali and other metals with low ionization potentials. However, a universal source of atomic metal cations for ICR studies has recently been developed.[8-11] This employs a pulsed YAG laser to volatilize/ionize metal targets inside the ICR cell. B, C, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Rh, and Ag cations have been generated and studied in our labatory with this source. Results of studies of reactions of Cu^+ and Ti^+ with organic halides have been reported.[9,10]

A requirement for use of atomic metal cations as ionic precursors in ligand binding energy studies is that a reaction suitable for the generation of initial metal–ligand species be available. Direct condensation of ligands with the metal cation has been observed for strongly bound ligands.[2,3,10,11] This is not suitable for ligand binding energy studies because it is usually too slow at the low pressures needed to trap the ions for times long enough for the ligand exchange reaction to approach equilibrium. Also, it is not effective with weakly bound molecules. The preferred reaction should be fast at low pressures and result in a product with a relatively low binding energy. Since the initial product will be readily displaced by the precursor neutral if the precursor is a stronger ligand, the precursor neutral should also be a weak ligand. Suitable precursor molecules and reactions to give the initial metal–ligand species may vary considerably from one metal cation to another.

The present paper reports studies of the chemistry of Mg and Al cations with alcohols and organic halides. Aspects of the

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(1) Address correspondence to this author at Central Research Department, Experimental Station, DuPont Co. E356, Wilmington, Del. 19898.

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reaction pathways and thermochemistry of these systems which bear on the choice of a suitable neutral reagent for ligand binding energy studies are investigated and discussed. Several aliphatic alcohols are identified as suitable precursor neutral reagents for ligand binding energy studies with Al^+. In the following paper relative binding energies of 30 organic molecules to Al^+ are reported.[12]

Experimental Section

Experiments were carried out using an ICR spectrometer and techniques which have been previously described.[10,11] Atomic metal cations are produced by focusing the output of a pulsed YAG laser onto a target mounted in the end plate of the ICR cell. The end plate is aluminum with an array of 14 holes drilled through it in which are mounted samples of various metals in the form of wires or chunks. These protrude into the cell up to about 0.5 cm. The laser beam is directed to a particular target on the end plate by adjusting a mirror outside the ICR cell.

The mass spectrum of the Al^+ or Mg^+ source with no added gas shows only the atomic metal cations; no cluster ions or multiply charged ions are observed. Three isotopes of Mg^+ are observed in relative abundances of 90.6, 4.4, and 5.0% for masses 24, 25, and 26, respectively, compared to the 78.6, 10.1, and 11.3% expected from their natural abundance.

Chemicals were obtained from commerical sources and used after repeated freeze–pump–thaw cycles. The relative accuracy of rate constants and product ratios is ±20% or better; absolute accuracy of rate constants is limited to a factor of 2 by pressure measurements. All experiments were carried out at ambient temperature which is typically 25 °C in our laboratory.

Results

Reactions with Halides. Atomic aluminum cation, Al^+, does not induce HX elimination with any of the organic halides studied in this work. Halide transfer, reaction 4, does occur in several

$$Al^+ + RX \rightarrow R^+ + AlX \quad (4)$$

cases where it is thermodynamically favored. Thus, CCl_3^+ is produced rapidly by chloride transfer from CCl_4, $k = 5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and by fluoride transfer from $CFCl_3$, $k = 5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. CF_2Cl_2 reacts by fluoride transfer. $CHCl_3$, CH_3Cl, and CH_3F are unreactive. Isopropyl, *n*-propyl ($k = 8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), isobutyl, and *n*-butyl chlorides react exclusively by chloride transfer.

Ethyl chloride, bromide, and iodide all show no reaction with Al^+. Other organic chlorides with relatively high chloride affinities, such as C_2H_3Cl, C_2HCl_3, C_2Cl_4, and C_6H_5Cl, are also unreactive. Direct condensation might be expected for chlorobenzene, since this has been observed for other atomic metal cations with aromatics,[11,13] but neither chlorobenzene nor benzene itself show any condensation product with Al^+ after 200 ms at 2×10^{-6} Torr. The only organic halide that was studied which shows a reaction other than simple halide transfer is CH_2ClCH_2Cl; this oxidizes Al^+ to $AlCl_2^+$, reaction 5. Chloride transfer follows,

$$Al^+ + CH_2ClCH_2Cl \rightarrow AlCl_2^+ + C_2H_4 \quad (5)$$

reaction 6, giving $C_2H_4Cl^+$ as the final product; double resonance

$$AlCl_2^+ + CH_2ClCH_2Cl \rightarrow C_2H_4Cl^+ + AlCl_3 \quad (6)$$

shows that at least 87% of this comes from $AlCl_2^+$, indicating that little or no direct chloride transfer to Al^+ occurs.

Atomic magnesium cation, Mg^+, reacts with *n*-propyl and isopropyl chlorides by both chloride transfer and induced HCl elimination, reactions 7 and 8. Chloride transfer is about 16%

$$Mg^+ + C_3H_7Cl \rightarrow C_3H_7^+ + MgCl \quad (7)$$

$$Mg^+ + C_3H_7Cl \rightarrow Mg(C_3H_6)^+ + HCl \quad (8)$$

in *n*-propyl chloride and 13% in isopropyl chloride. Retention of C_3H_6 but not HCl by Mg^+ is observed in the elimination reaction. This is followed by displacement, reaction 9, another elimination,

$$Mg(C_3H_6)^+ + C_3H_7Cl \rightarrow Mg(C_3H_7Cl)^+ + C_3H_6 \quad (9)$$

reactions 10 and 11, and another displacement, reactions 12 and

$$Mg(C_3H_7Cl)^+ + C_3H_7Cl \rightarrow Mg(C_3H_7Cl)(C_3H_6)^+ + HCl \quad (10)$$

$$Mg(C_3H_7Cl)^+ + C_3H_7Cl \rightarrow Mg(C_3H_7Cl)(HCl)^+ + C_3H_6 \quad (11)$$

$$Mg(C_3H_7Cl)(C_3H_6)^+ + C_3H_7Cl \rightarrow Mg(C_3H_7Cl)_2^+ + C_3H_6 \quad (12)$$

13, giving $Mg(C_3H_7Cl)_2^+$ as the final product. Retentions of C_3H_6 and of HCl are about equal in the second elimination.

$$Mg(C_3H_7Cl)(HCl)^+ + C_3H_7Cl \rightarrow Mg(C_3H_7Cl)_2 + HCl \quad (13)$$

Similar chemistry is seen with isobutyl chloride, reactions 14–16.

$$Mg^+ + C_4H_9Cl \xrightarrow{88\%} C_4H_9^+ + MgCl \quad (14)$$

$$Mg^+ + C_4H_9Cl \xrightarrow{12\%} Mg(C_4H_8)^+ + HCl \quad (15)$$

$$Mg(C_4H_8)^+ + C_4H_9Cl \rightarrow Mg(C_4H_9Cl)^+ + C_4H_8 \quad (16)$$

The relatively small size of the elimination channel makes it difficult to convincingly follow the chemistry beyond the first displacement product, $Mg(C_4H_9Cl)^+$, but this does appear to react further. EtCl reacts slowly, $k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, by HCl elimination and displacement, reactions 17 and 18. Again, further slow reaction of the displacement product occurs.

$$Mg^+ + C_2H_5Cl \rightarrow Mg(C_2H_4)^+ + HCl \quad (17)$$

$$Mg(C_2H_4)^+ + C_2H_5Cl \rightarrow Mg(C_2H_5Cl)^+ + C_2H_4 \quad (18)$$

Oxidation processes dominate the chemistry of Mg^+ with the other organic chlorides studied. CCl_4 and CH_2ClCH_2Cl both yield $MgCl_2$ neutral and a carbocation product, reactions 19 and 20.

$$Mg^+ + CCl_4 \rightarrow CCl_2^+ + MgCl_2 \quad (19)$$

$$Mg^+ + CH_2ClCH_2Cl \rightarrow C_2H_4^+ + MgCl_2 \quad (20)$$

Similarly, $CFCl_3$ gives MgClF and CCl_2^+, reaction 21. These

$$Mg^+ + CFCl_3 \rightarrow CCl_2^+ + MgFCl \quad (21)$$

reactions appear to be direct; no intermediates could be detected in the double resonance or mass spectra. With $CHCl_3$, however, the oxidation clearly proceeds in a two-step process through a $MgCl^+$ intermediate, reactions 22 and 23. CH_3Cl, C_2H_3Cl,

$$Mg^+ + CHCl_3 \rightarrow MgCl^+ + CHCl_2 \quad (22)$$

$$MgCl^+ + CHCl_3 \rightarrow CHCl_2^+ + MgCl_2 \quad (23)$$

C_2HCl_3, and C_2Cl_4 are unreactive with Mg^+. In the latter two systems, small amounts of products are produced shortly after the laser pulse by energetic ions; these amount to less than 10% of the total ionization and do not increase further with time.

Reactions with Alcohols. Atomic aluminum cation, Al^+, reacts with alcohols, ROH, by hydroxide transfer, reaction 24, and by

$$Al^+ + ROH \rightarrow R^+ + AlOH \quad (24)$$

dehydration, reaction 25. H_2O is always retained by Al^+ in the

$$Al^+ + ROH \rightarrow Al(H_2O)^+ + \text{alkene} \quad (25)$$

dehydration; $Al(\text{alkene})^+$ is never observed. Dehydration is followed by displacement, reaction 26, B = ROH, to give $Al(B)^+$

$$Al(H_2O)^+ + B \rightarrow Al(B)^+ + H_2O \quad (26)$$

as the final product. Variation of ion abundance with time for Al^+ in the presence of 6×10^{-6} Torr of EtOH is shown in Figure 1. Hydroxide transfer to give Et^+ is only 5% of total reaction in this system and is not shown. Dehydration is rapidly followed by displacement to give $Al(EtOH)^+$. This decreases slowly as ions are lost from the cell by diffusion. The total reaction rate for Al^+,

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[12] Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.*, following paper in this issue.

[13] Uppal, J. S.; Staley, R. H., unpublished results.

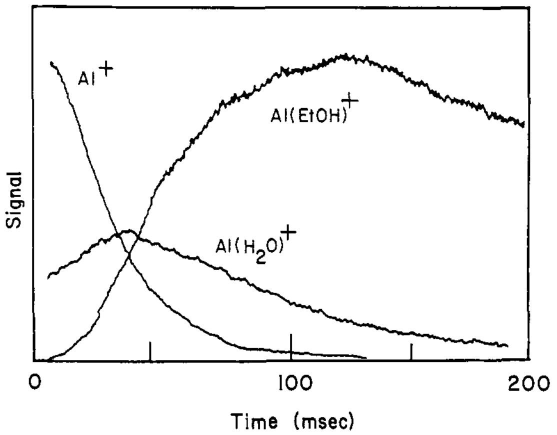


Figure 1. Variation of ion abundance with time following production of Al^+ by a pulsed laser ion source in the presence of 6×10^{-6} Torr of EtOH. Dehydration of EtOH followed by displacement of H_2O from $Al(H_2O)^+$ gives $Al(EtOH)^+$ which does not react further in this system. The $Al(EtOH)^+$ signal decreases slowly after 130 ms as ions are lost from the cell by diffusion. A small amount (5%) of Al^+ reacts by hydroxide transfer to give Et^+ (not shown).

reactions 24 and 25, is 2×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Reactions of all of the saturated three- and four-carbon alcohols with Al^+ are the same as for EtOH except that hydroxide transfer is a larger fraction of total reaction: *n*-PrOH (21%), *i*-PrOH (10%), *n*-BuOH (39%), *sec*-BuOH (13%), *i*-BuOH (84%), *t*-BuOH(100%). Al^+ does not react with MeOH.

The Al $(H_2O)^+$ produced in reaction 25 may be viewed as an Al^+ with an H_2O molecule bound to it. The expected reaction with a base stronger than H_2O in this case is displacement of the H_2O, reaction 26, as observed with the alcohols. The $Al(H_2O)^+$ may also be viewed as protonated aluminum hydroxide, $(AlOH)H^+$. In this case the expected reaction with a stronger proton base than AlOH is proton transfer, reaction 27. Pyridine

$$Al(H_2O)^+ + B \rightarrow BH^+ + AlOH \qquad (27)$$

and Me_3N react with $Al(H_2O)^+$ principally by proton transfer. Only reaction 26 could be detected for other molecules having lower proton affinities, such as Et_2O and $(n\text{-}Pr)_2O$ (see below).

In a binary mixture of alcohols, the two alcohols can compete for the binding site on Al^+ by the displacement reaction 28. When

$$Al(ROH)^+ + R'OH \rightleftarrows Al(R'OH)^+ + ROH \qquad (28)$$

the equilibrium constant for this reaction is large, the reaction is observed to proceed only in one direction, establishing a relative order of ligand binding energies, $D(Al^+\text{–}R'OH) > D(Al^+\text{–}ROH)$. When the equilibrium constant is small enough, the ratio of the products $Al(ROH)^+$ and $Al(R'OH)^+$ is observed to approach a constant equilibrium value at long times, Figure 2. A value for the equilibrium constant can be calculated from this ratio and the measured ratio of partial pressures of the two alcohols. From the preferred direction of ligand displacement and equilibrium constants measured in the present work, binding energies of alcohols to Al^+ are found to increase in the order: EtOH < *n*-PrOH < *n*-BuOH < *i*-PrOH < *i*-BuOH < *sec*-BuOH < *t*-BuOH. Additional direct and indirect determinations of the relative binding energies of alcohols to Al^+ are given in the following paper where the details of these experiments are also given.

Atomic magnesium cation, Mg^+, is unreactive with MeOH and EtOH. With *n*-PrOH and *n*-BuOH, direct condensation occurs to give $Mg(ROH)^+$, reaction 29. this is followed by a second

$$Mg^+ + ROH \rightarrow Mg(ROH)^+ \qquad (29)$$

direct condensation at a slower rate, reaction 30, giving $Mg(ROH)_2^+$ as the final product. Apparent rate constant for *n*-BuOH at 4×10^{-6} Torr are 7×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the

$$Mg(ROH)^+ + ROH \rightarrow Mg(ROH)_2^+ \qquad (30)$$

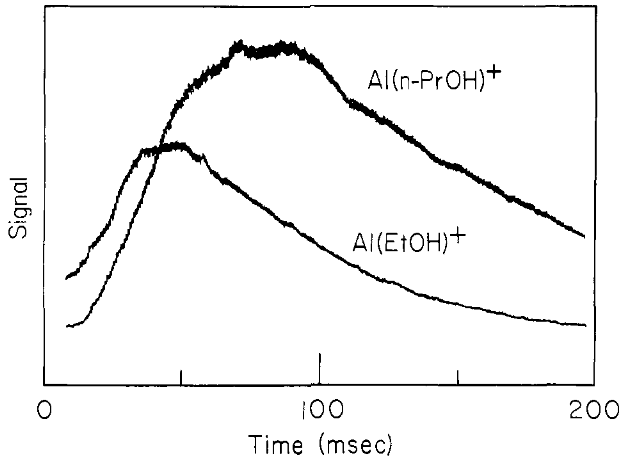


Figure 2. Variation of ion abundance with time for Al^+ with a 4.5:1 mixture of EtOH and *n*-PrOH at a total pressure of 9×10^{-6} Torr. After initial dehydration–displacement reactions the ligand displacement reaction $Al(EtOH)^+ + n\text{-PrOH} \rightleftarrows Al(n\text{-PrOH})^+ + EtOH$ approaches equilibrium; the equilibrium constant for an average of four determinations is $K = 11.4 \pm 1.1$. Only the product species are shown. These both decrease with time after 100 ms as ions are lost from the cell by diffusion.

first condensation and 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the second. Double resonance spectra show no evidence of a $Mg(H_2O)^+$ or $Mg(alkene)^+$ intermediate in reaction 29 for *n*-PrOH and *n*-BuOH. However, *i*-PrOH, *sec*-BuOH, *i*-BuOH, and *t*-BuOH do all react to give $Mg(ROH)^+$ via a two-step sequence with a $Mg(H_2O)^+$ intermediate, reactions 31 and 32. For *i*-PrOH the

$$Mg^+ + ROH \rightarrow Mg(H_2O)^+ + \text{alkene} \qquad (31)$$

$$Mg(H_2O)^+ + ROH \rightarrow Mg(ROH)^+ + H_2O \qquad (32)$$

rate constant for the first step is 6×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. The $Mg(ROH)^+$ products of reaction 32 slowly condense with a second alcohol molecule by reaction 30.

The $Mg(H_2O)^+$ produced in reaction 31 proton transfers to Me_3N, but even in this case displacement of H_2O to give $Mg(Me_3N)^+$ is the predominant reaction. With other bases studied only displacement was observed.

In binary mixtures of alcohols with Mg^+, displacement reactions occur for both the $Mg(ROH)^+$ and $Mg(ROH)_2^+$ species, reactions 33–35. Figure 3 shows the variation of ion abundance with time

$$Mg(ROH)^+ + R'OH \rightleftarrows Mg(R'OH)^+ + ROH \qquad (33)$$

$$Mg(ROH)_2^+ + R'OH \rightleftarrows Mg(R'OH)(ROH)^+ + ROH \qquad (34)$$

$$Mg(R'OH)(ROH)^+ + R'OH \rightleftarrows Mg(R'OH)_2^+ + ROH \qquad (35)$$

for a 3:1 mixture of *n*-PrOH and *n*-BuOH. Double resonance spectra show that all of the reactions 33–35 are proceeding to a significant extent in both directions during the observed 200-ms time period, but approach to equilibrium is too slow for a reliable equilibrium constant to be determined. From the preferred direction and approximate equilibrium constants of these reactions, binding energies to Mg^+ are found to increase in the order *n*-PrOH < *n*-BuOH < *i*-PrOH < *i*-BuOH < *sec*-BuOH < *t*-BuOH. The order is the same for $Mg(ROH)^+$ and $Mg(ROH)_2^+$.

Other Reactions of Al^+. Most of the ethers, aldehydes, ketones, esters, nitriles, sulfides, and aromatics studied with Al^+ showed no direct reactions. Methyl acetate and ethyl ether are exceptions. The principal reaction of Al^+ with $MeCO_2Me$ is ketene elimination to give $Al(MeOH)^+$, reaction 36; some CH_3CO^+ is also produced,

$$Al^+ + CH_3CO_2CH_3 \xrightarrow{90\%} Al(CH_3OH)^+ + CH_2CO \qquad (36)$$

reaction 37. Both products react further with $MeCO_2Me$: MeOH

$$Al^+ + CH_3CO_2CH_3 \xrightarrow{10\%} AlOCH_3 + CH_3CO^+ \qquad (37)$$

is displaced from $Al(MeOH)^+$ to give $Al(MeCO_2Me)^+$, and CH_3CO^+ proton transfers to give $MeCO_2MeH^+$. The latter

Table I. Chloride Affinities, Hydroxide Affinities, and Associated Heats of Formation for Cations Studied in This Work[a]

R	$\Delta H_{f_0}(R^+)$	$\Delta H_{f_{300}}(RCl)$	$\Delta H_{f_{300}}(ROH)$	$D(R^+-Cl^-)$[j]	$D(R^+-OH^-)$[k]
Me	262[b]	−19.6[h]	−48.0[h]	227.0	277.2
Et	219[b]	−26.7[h]	−56.2[h]	191.1	242.4
n-Pr	207[b]	−31.0 ± 0.2[i]	−61.2 ± 0.3[i]	183.4	235.4
i-Pr	191[b]	−33.6 ± 1.0[i]	−65.1 ± 0.1[i]	170.0 ± 1	223.3
n-Bu	200[b]	−35.1 ± 2.0[i]	−66.0 ± 0.1[i]	180.5 ± 2	233.2
i-Bu	198[b]	−38.1 ± 2.0[i]	−67.8 ± 0.2[i]	181.5 ± 2	233.0
sec-Bu	183[b]	−38.6 ± 2.0[i]	−70.0 ± 0.2[i]	167.0 ± 2	220.2
t-Bu	167[b]	−43.7 ± 0.6[i]	−74.7 ± 0.2[i]	156.1	208.9
CH_2Cl	228.8 ± 0.4[c]	−22.8[h]		197.0	
$CHCl_2$	211.8 ± 0.4[c,d]	−24.6[h]		181.8	
CCl_3	192[e]	−22.9[h]		160.3	
$CFCl_2$	155 ± 5[e]	−69.0 ± 1.5[g]		169.4 ± 5	
Al	215.5[b]	−11.2[h]	−43 ± 3[g]	172.1	226 ± 3
AlCl	204.5 ± 10[f]	−67 ± 5[f]		217 ± 11	
$AlCl_2$	113.6 ± 18[f]	−139.7[h]		199 ± 18	
Mg	211.3[b]	−10 ± 10[h]	−39.4 ± 9[f]	167 ± 10	218 ± 9
MgCl	156 ± 20[g]	−95.5 ± 2[h]		197 ± 20	

[a] All data in kcal/mol for gas-phase species. [b] Reference 20. [c] Werner, A. S.; Tsai, B. P.; Baer, T. *J. Chem. Phys.* 1974, *60*, 3650. [d] Lossing, F. P. *Bull. Soc. Chim. Belg.* 1972, *81*, 125. [e] Lais, S. G.; Ausloos, P. *Intl. J. Mass Spectrom. Ion Phys.* 1977, *23*, 273. [f] Reference 21. [g] Reference 22. [h] Reference 23. [i] Reference 24. [j] Calculated using $\Delta H_{f_0}(Cl^-) = -54.6$ kcal/mol.[20] [k] Calculated using $\Delta H_{f_0}(OH^-) = -32.8$ kcal/mol.[20]

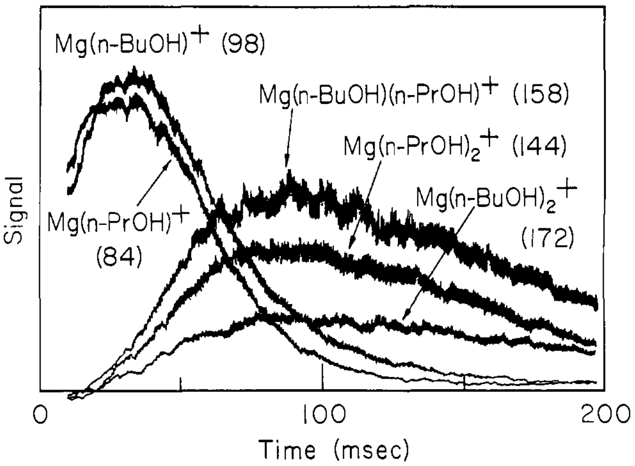


Figure 3. Variation of ion abundance with time for Mg^+ with a 3:1 mixture of *n*-BuOH and *n*-PrOH at a total pressure of 16×10^{-6} Torr. Double resonance spectra show that ligand displacement reactions are occuring in both directions for both the $Mg(ROH)^+$ and $Mg(ROH)_2^+$ species, but the approach to equilibrium is too slow for a reliable equilibrium constant to be determined. The *m/e* value for the isotopic peak which was followed for each ion is given in parentheses. The intitial Mg^+ and $Mg(H_2O)^+$ species are not shown.

reaction is expected since CH_2CO and $MeCO_2Me$ have comparable proton affinities.[14] The ion chemistry of $EtCO_2Et$ with Al^+ is similar to that of $MeCO_2Me$.

Al^+ reacts with Et_2O by eliminating ethylene to give $Al(EtOH)^+$, reaction 38, $k = 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This

$$Al^+ + Et_2O \rightarrow Al(EtOH)^+ + C_2H_4 \tag{38}$$

reacts again with Et_2O by displacement, reaction 39, or by elim-

$$Al(EtOH)^+ + Et_2O \xrightarrow{16\%} Al(Et_2O)^+ + EtOH \tag{39}$$

inating two or three ethylenes, reactions 40 and 41. The Al-

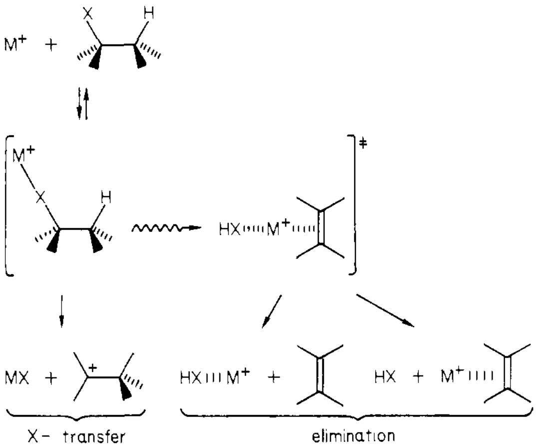
$$Al(EtOH)^+ + Et_2O \xrightarrow{75\%} Al(EtOH)(H_2O)^+ + 2C_2H_4 \tag{40}$$

$$Al(EtOH)^+ + Et_2O \xrightarrow{9\%} Al(H_2O)_2^+ + 3C_2H_4 \tag{41}$$

$(Et_2O)^+$ product of reaction 39 does not react further. The product of reaction 41, $Al(H_2O)_2^+$, reacts by displacement, reaction 42.

$$Al(H_2O)_2^+ + Et_2O \rightarrow Al(Et_2O)(H_2O)^+ + H_2O \tag{42}$$

Scheme I



The product of reaction 40, $Al(EtOH)(H_2O)^+$ reacts by displacement of either H_2O or EtOH, reactions 43 and 44; two other

$$Al(EtOH)(H_2O)^+ + Et_2O \xrightarrow{49\%} Al(Et_2O)(EtOH)^+ + H_2O \tag{43}$$

$$Al(EtOH)(H_2O)^+ + Et_2O \xrightarrow{20\%} Al(Et_2O)(H_2O)^+ + EtOH \tag{44}$$

products are observed at *m/e* 133 (18%) and *m/e* 163 (13%), but the structures of these species cannot be unambiguously assigned. All four of these products react further by condensing with another Et_2O. The resulting species do not react further with Et_2O. Al^+ does not react with Me_2O, *t*-BuOMe, or $MeOC_2H_3$.

Discussion

Most of the chemistry of Al^+ and Mg^+ with alcohols and alkyl halides can be understood in terms of the mechanism of Scheme I. This mechanism was originally proposed to explain the chemistry of Li^+[15] and has since been found to occur in the chemistry of a number of other atomic metal cations[10,16,17] and NO^+[18] with alcohols, alkyl halides, and phenyl halides.[11,19] Initial

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Table II. Enthalpies for Elimination of HCl and HOH from Alkyl Chlorides and Alcohols HYX → HX[a]

HY	ΔH_f(Y)	ΔH_{elim}^{HCl} [g]	ΔH_{elim}^{HOH} [h]
Et	12.5[b]	17.2	10.9
n-Pr	4.9[b]	13.9	8.3
i-Pr	4.9[b]	16.5 ± 1	12.2
n-Bu	−0.2 ± 0.1[c]	12.9 ± 2	7.8
i-Bu	−4.3 ± 0.2[c]	11.8 ± 2	5.8
sec-Bu	−3.0 ± 0.2[c,d]	13.6 ± 2[d]	9.2[d]
sec-Bu	−1.9 ± 0.2[c,e]	14.7 ± 2[e]	10.3[e]
sec-Bu	−0.2 ± 0.1[c,f]	16.4 ± 2[f]	12.0[f]
t-Bu	−4.3 ± 0.2[c]	17.4 ± 1	12.7

[a] All data in kcal/mol for gas-phase species. [b] Reference 23. [c] Reference 24. [d] *trans*-2-Butene product. [e] *cis*-2-Butene product. [f] 1-Butene product. [g] Calculated using $\Delta H_f(HCl) = 22.0$ kcal/mol[23] and $\Delta H_{f_0}(Cl^-) = -54.6$ kcal/mol.[20] [h] Calculated using $\Delta H_f(HOH) = -57.8$ kcal/mol[23] and $\Delta H_{f_0}(OH^-) = -32.8$ kcal/mol.[20]

association of the metal cation, M^+, with the neutral reactant HYX, leads to transfer of X^- if this is exothermic, or internal rearrangement of the complex, elimination of HX, to give HX and Y both bound to M^+. This dissociates to either $M(HX)^+$ and Y or $M(Y)^+$ and HX.

Transfer Reactions. Al^+ reacts by chloride transfer with CCl_4 and *i*-PrCl but not EtCl and MeCl. This is as expected from the known chloride affinity, $D(R^+–Cl^-)$, values for these species (Table I); $D(Al^+–Cl^-)$ is higher than $D(R^+–Cl^-)$ for CCl_4 and *i*-PrCl and lower than $D(R^+–Cl^-)$ for EtCl and MeCl. Al^+ also reacts, however, with *n*-PrCl, *n*-BuCl, and *i*-BuCl by chloride transfer. This is not as expected from the data in Table I since these alkyl chlorides all have chloride affinities *above* the reported value for Al^+. This behavior is not unique with Al^+ since $CHCl_2^+$ reacts rapidly and completely with *n*-PrCl by chloride transfer[13] even though the data in Table I show that this reaction should also be endothermic. A likely explanation of this behavior is that the primary carbonium ion products in these reactions, *n*-Pr^+, *n*-Bu^+, and *i*-Bu^+, rearrange to *i*-Pr^+, *sec*-Bu^+, and *t*-Bu^+, respectively, releasing the rearrangement energy to the reaction complex before the product AlCl or $CHCl_3$ dissociates. Including the rearrangement energy in calculating the chloride affinities of *n*-PrCl, *n*-BuCl, and *i*-BuCl gives values of 167.4, 163.5 ± 2, and 150.5 ± 2 kcal/mol, respectively.[25] The observed reactions with Al^+ and $CHCl_2^+$ are then found to be exothermic.

The observed fluoride transfer reactions from $CFCl_3$ and CF_2Cl_2 to Al^+ are in agreement with expectations based on the relative fluoride affinities $D(Al^+–F^-) = 219 \pm 1$ kcal/mol, $D(CCl_3^+–F^-) = 201 \pm 2$ kcal/mol, and $D(CFCl_2^+–F^-) = 210 \pm 5$ kcal/mol.[26]

Chloride and fluoride transfer results for Al^+ with MeCl, EtCl, *i*-PrCl, CCl_4, $CFCl_3$, and CF_2Cl_2 in the present work are the same as those obtained at low energies by Hodges, Armentrout, and Beauchamp in a beam study.[16]

Atomic magnesium cation, Mg^+, is unreactive with MeCl and EtCl as expected from relative chloride affinities (Table II). The observed reaction with *i*-BuCl is expected if the rearrangement energy is included in calculating the effective chloride affinity. The observed reaction with *i*-PrCl establishes a new lower limit for $D(Mg^+–Cl^-)$ of 170 ± 1 kcal/mol which is the value for $D(i\text{-}Pr^+–Cl^-)$. This is within the error limits of, but above the value of, the previous result, $D(Mg^+–Cl^-) = 167 \pm 10$ kcal/mol.[22] A new upper limit on $\Delta H_f(MgCl)$ of −13.3 ± 1 kcal/mol is implied.

Hydroxide transfer from alcohols to Al^+ occurs for *i*-PrOH, *sec*-BuOH, and *t*-BuOH but not for MeOH, as expected (Table I). Utilization of rearrangement energy must again be invoked to explain the observed hydroxide transfer reactions with *n*-PrOH, *n*-BuOH, and *i*-BuOH. These reactions are predicted to be exothermic when hydroxide affinities are recalculated to include rearrangement energies, giving values of 219.4, 216.2, and 202.0 kcal/mol, respectively. The small amount of hydroxide transfer observed from EtOH to Al^+ (5%) is likely due to reaction by kinetically hot ions. Failure of the majority of the Al^+ ions to react supports this interpretation. The reaction is endothermic by 16 kcal/mol (Table I).

No hydroxide transfer from alcohols to Mg^+ is observed. This is as expected (Table I) except for *t*-BuOH where hydroxide transfer to Mg^+ should be exothermic by 9 kcal/mol. Competition by the more favorable elimination reaction is probably responsible for supressing hydroxide transfer below observable levels in this case.

Oxidation Reactions. The several oxidation processes which are seen with Al^+ and Mg^+ are not included in the chemistry described in Scheme I. Oxidation of Al^+ to $AlCl_2^+$ by CH_2ClCH_2Cl was reported in the beam study of Hodges, Armentrout, and Beauchamp.[16] This reaction is exothermic by 57 kcal/mol[27] and is found to proceed rapidly to completion in the present ICR study, reaction 5. Oxidation of Al^+ to $AlCl^+$ by chlorine abstraction is not observed since $D(Al^+–Cl) = 40 \pm 10$ kcal/mol is much less than typical carbon–chlorine bond dissociation energies in the organic chlorides studied, for example, $D(i\text{-}Pr–Cl) = 80 \pm 1$ kcal/mol.[28] While processes involving oxidation of Al(I) to Al(III) might be expectd to commonly occur,[16] it is noteworthy that the only example of this in the present work or the previous beam study is reaction 5. No cases of oxidation by oxygen species were noted. More recent results have shown that the aluminum oxide–cation bond dissociation energy is rather low, between 25 and 40 kcal/mole.[29]

With Mg^+ the energetics for oxidation by chlorine transfer to give $MgCl^+$ become more favorable since $D(Mg^+–Cl) = 84 \pm 20$ kcal/mol.[30] This process is observed with $CHCl_3$, reaction 22. With other reactants formation of neutral Mg(II) products is favored. For example CCl_4 and CH_2ClCH_2Cl react to give $MgCl_2$, reactions 19 and 20. The calculated enthalpies for these reactions are $\Delta H = -19 \pm 2$ and 3 ± 2 kcal/mol, respectively.[31] Observation of reaction 20 even though it is calculated to be slightly endothermic suggests that ΔH_f for one or both of the products is lower than the reported values, $\Delta H_f(MgCl_2) = -95.5 \pm 2$ kcal/mol and $\Delta H_f(CCl_2^+) = 287$ kcal/mol.

Metal Hydroxide Proton Affinities. Observation of proton transfer from a protonated metal oxide, MOH_2^+, to a base, B, establishes an upper limit on the proton affinity, $PA(B) \equiv D(B–H^+)$, of the metal oxide: $PA(MOH) \leq PA(B)$. Thus, observation of reaction 27 for $AlOH_2^+$ with pyridine and Me_3N establishes the limits $PA(AlOH) \leq 220.4$ and ≤ 224.3 kcal/mol, respectively.[32] The observation of proton transfer from $MgOH_2^+$ to Me_3N establishes the limit $PA(MgOH) \leq 224.3$ kcal/mol.[32] Other molecules were studied with $AlOH_2^+$ and $MgOH_2$ in an unsuccessful attempt to establish better limits for the proton affinities. Displacement of H_2O, reaction 26, competes in these studies with proton transfer, reaction 27.

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(26) Calculated from data in Table I and $\Delta H_{f0}(F^-) = -60.0$ kcal/mol from ref 20.

(27) Calculated from data in Table I and $\Delta H_f(CH_2ClCH_2Cl) = -30.7 \pm 0.4$ kcal/mol from ref 24.

(28) Calculated from data in Table I and $\Delta H_f(Cl) = 28.9$ kcal/mol and $\Delta H_f(i\text{-}Pr\cdot) = 17.6$ kcal/mol from ref 23.

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(30) Calculated from data in Table I and $\Delta H_f(Cl) = 28.9$ kcal/mol from ref 23.

(31) Calculated from data in Table I and $\Delta H_f(CH_2ClCH_2Cl) = -30.7 \pm 0.4$ kcal/mol,[24] $\Delta H_f(C_2H_4^+) = 257$ kcal/mol,[20] and $\Delta H_f(CCl_2^+) = 287$ kcal/mol from $\Delta H_{f0}(CCl_2) = 56.7 \pm 5$ kcal/mol,[22] and $IP(CCl_2) = 9.76$ eV.[20]

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Elimination Reactions. Examples of induced 1,2-eliminations of HX from HYX molecules by metal cations to give $M(HX)^+$ or $M(Y)^+$ products are now commonplace.[2,10,11,17,19] The present study adds several new examples. Al^+ and Mg^+ induce HOH elimination from various aliphatic alcohols, and Mg^+ induces HCl elimination from alkyl chlorides.

One noteworthy feature of the thermochemistry of these processes is that their observation implies a lower limit on the ligand binding energy $D(M^+–L)$ for the fragment retained by the metal, L = HX or Y. The elimination is usually endothermic, requiring a net energy $\Delta H_{elim}^{HX}(HYX)$, the enthalpy for the process HYX $\rightarrow$ Y + HX. Thus, for the overall induced elimination process to be exothermic requires that $\Delta H_{elim}^{HX} < D(M^+–L)$ where L = HX or Y, whichever is retained by the metal cation. Values for $\Delta H_{elim}^{HCl}(RCl)$ and $\Delta H_{elim}^{HOH}(ROH)$ for the alcohols and alkyl chlorides used in this work are given in Table II.

Lower limits on various metal–ligand binding energies are thus established by the occurrence of the elimination reactions observed in this work. The occurrence of reaction 25 for Al^+ with *i*-PrOH implies $D(Al^+–H_2O) \geq 12.2$ kcal/mol (Table II). Also, from the HCl eliminations induced by Mg^+ with *i*-PrCl, *i*-BuCl, and EtCl, reactions 8, 15, and 17, we infer the limits $D(Mg^+–C_3H_6) \geq 16.5 \pm 1$ kcal/mol, $D(Mg^+–i\text{-}C_4H_8) \geq 11.8 \pm 2$ kcal/mol, and $D(Mg^+–C_2H_4) \geq 17.2$ kcal/mol, respectively. These limits are useful in providing bounds for the range of the relative ligand binding energy scale derived in the following paper.

Reactions 11 and 12 are eliminations induced by the metal–ligand species $Mg(PrCl)^+$. Even with one ligand already attached, magnesium cation can induce another elimination. The solvation energy provided by attaching the *second* ligand is also greater than ΔH_{elim}^{HCl}, e.g., $D(Mg(i\text{-}PrCl)^+–L) \geq 16.5 \pm 1$ kcal/mol for L = HCl or C_3H_6.

Two other Al^+-induced elimination processes are observed in this work. Ketene is eliminated from $MeCO_2Me$, reaction 36, with retention of MeOH by Al^+. The free elimination process is endothermic by 38.6 kcal/mol,[33] implying a limit from observation of the induced elimination reaction of $D(Al^+–MeOH) \geq 38.6$ kcal/mol. Ethylene is eliminated from Et_2O, reaction 38, with retention of EtOH. The free elimination is endothermic by 16.6 kcal/mol in this case.[34] Elimination of two and three ethylenes in reactions with Et_2O is also observed (reactions 40 and 41). The limits on ligand binding energies established by these observations are not particularly useful, however, because of the complexity of the species involved and the relatively low endothermicity of free ethylene elimination.

Elimination of HCl induced by Al^+ was noted as one of several product channels for EtCl and $C_3H_6Cl_2$ in the beam study of Al^+ chemistry by Hodges, Armentrout, and Beauchamp.[16] The collision energy dependence of these reactions observed in that study did not show whether they would be expected to occur at thermal energies. Studies of Al^+ with EtCl in the present work show no evidence of the occurrence of elimination reaction.

Ligand-Exchange Studies. The alkene elimination reaction of Al^+ with alcohols, reaction 25, is well suited to produce an initial Al^+–ligand species for ligand-exchange studies. In particular, with EtOH, this reaction proceeds rapidly to completion and constitutes 95% of total reaction; hydroxide transfer is only 5%. Studies of ligand-exchange reactions with mixtures of alcohols show that ligand exchange proceeds rapidly and approaches equilibrium faster than ions are lost form the ICR cell by diffusion. Indeed, Al^+ with EtOH as an initiator reagent has proven to be a favorable system for quantitative ligand binding energy studies. The results of such studies are described in detail in the following paper.[12]

With Mg^+ the situation is less favorable. The slow addition of a second ligand interferes with ligand-exchange studies of one-ligand species since these are reacting away to two-ligand species. But the two-ligand species are generated too slowly for ligand exchange to reach equilibrium after they are produced. However, ligand-exchange studies of the two-ligand species might be accessible with an ICR instrument having a higher magnetic field, and thus better trapping, than the 11 kG our electromagnet provides.

The ligand-exchange studies carred out in the present work establish a relative order of ligand binding energies for the alcohols. It is identical for the $Al(L)^+$, $Mg(L)^+$, and $Mg(L)_2^+$ species studied: *n*-PrOH < *n*-BuOH < *i*-PrOH < *i*-BuOH < *sec*-BuOH < *t*-BuOH; with Al^+ EtOH is also accessible to study and ranks below *n*-PrOH. This same order is observed for proton affinity of a functional group as the alkyl substituent is varied. This has been shown with primary amines, for example.[32] Further analysis of ligand binding energies accompanies the complete quantitative results for $Al(L)^+$ in the following paper.

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Registry No. MeCl, 74-87-3; EtCl, 75-00-3; *n*-PrCl, 540-54-5; *i*-PrCl, 75-29-6; *n*-BuCl, 109-69-3; *i*-BuCl, 513-36-0; *sec*-BuCl, 78-86-4; *t*-BuCl, 507-20-0; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; CCl_4, 56-23-5; $CFCl_3$, 75-69-4; AlCl, 13595-81-8; $AlCl_2$, 16603-84-2; $AlCl_3$, 7446-70-0; MgCl, 14989-29-8; $MgCl_2$, 7786-30-3; MeOH, 67-56-1; EtOH, 64-17-5; *n*-PrOH, 71-23-8; *i*-PrOH, 67-63-0; *n*-BuOH, 71-36-3; *i*-BuOH, 78-83-1; *sec*-BuOH, 78-92-2; *t*-BuOH, 75-65-0; AlOH, 20768-67-6; MgOH, 12141-11-6; Al^+, 14903-36-7; Mg^+, 14581-92-1.

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(33) Calculated from data in Table I and $\Delta H_f(MeCO_2Me) = -98.0$ kcal/mol and $\Delta H_f(CH_2CO) = -11.4$ kcal/mol from ref 23.

(34) Calculated from data in Tables I and II and $\Delta H_f(Et_2O) = -60.3 \pm 0.2$ kcal/mol.[24]