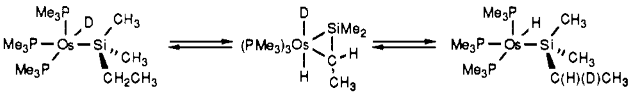
from the silyl ligand to yield $Os(PMe_3)_3(H)(D)(\eta^2\text{-}Me_2SiCHCH_3)$, a silene complex or silametallacycle. Subsequent migration of deuteride onto the silene ligand would effect isotopic exchange of an alkyl C–H position, as shown in eq 4. Further



reaction with C_6D_6 could result in incorporation of additional deuterium into the silane, eventually followed by exchange with free silane. Thus both Si–H and C–H deuteration would be initiated by a single intermolecular Si–H addition, and only those C–H positions adjacent to silicon (β to the metal) will be susceptible to exchange.

The β-hydrogen migration process is well-documented in the chemistry of transition-metal alkyls. This work provides the first evidence for β-hydrogen migration in metal silyls. Furthermore, the formation of transient silene complexes such as $(PMe_3)_3Os(H)_2(\eta^2\text{-}Me_2SiCH_2)$ formally represents the dehydrogenation of the silane within the osmium coordination sphere. In conjunction with subsequent reaction chemistry, this process could form the basis for other, more useful, catalytic transformations of organosilanes as well as synthetic routes to stable silene complexes. We are currently exploring this new mode of reactivity with such goals in mind.

Acknowledgment. We gratefully acknowledge the National Science Foundation and the University of Pennsylvania Research Fund for financial support. L.J.P. thanks the University of Pennsylvania School of Arts and Sciences for a Dean's Fellowship. We also thank Professor Tom Flood and Mark Deming at USC for helpful discussions and an independent sample of $(PMe_3)_4Os(H)(CH_2CMe_3)$.

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(10) Exchange between free silane and $(PMe_3)_3Os(D)(SiMe_3)$ could proceed through either Os(IV) or Os(0) intermediates (e.g., $P_3Os(H)(D)(SiMe_3)_2$ or P_3Os). On the basis of the extensive studies of Flood and co-workers, the former would appear most likely.[8]

Gas-Phase Water and Hydroxyl Binding Energies for Monopositive First-Row Transition-Metal Ions[1]

Thomas F. Magnera,* Donald E. David, and Josef Michl*

Center for Structure and Reactivity, Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712-1167

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We report the binding energies of a single water molecule and a single hydroxyl group to singly charged cations of the first-row transition metals, obtained with use of collision-induced dissociation in a triple-quadrupole mass spectrometer.[2] For Fe^+, Co^+, and Ni^+, the second hydration energies have been determined as well. As found recently[2] for Cu^+, they are larger than the first hydration energies.

Data of this type were previously available for covalent bonds in metal ion hydrides.[3] Successive gas-phase hydration energies of some main group metal ions are known,[4] but the only results published for bonds between transition-metal ions and simple ligands such as water are those for Cu^+[2,5] and Ag^+.[5] A few monopositive transition-metal ion hydroxyl bond strengths were previously determined by standard gas-phase methods.[6-9]

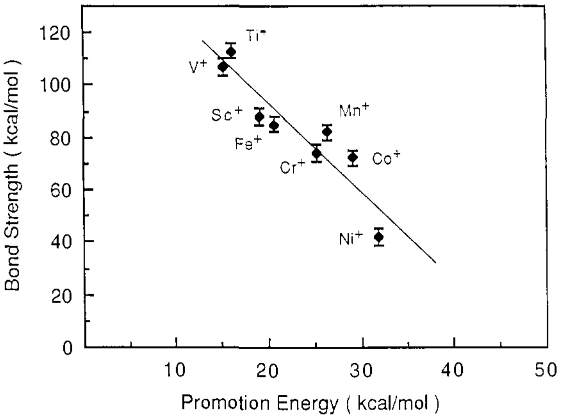

Figure 1. Transition-metal ion hydroxide bond strengths vs promotion energy.[13]

$M^+(H_2O)_2$ and $M^+OH(H_2O)$ ions were generated[2] by 6–10 keV Ar atom impact on cold frosted metal plates or hydrated metal salts under conditions where negligible quantities of protonated water clusters are formed, velocity selected in a retarding-stop analyzer, mass selected by a quadrupole mass filter, and after acceleration permitted to undergo a single collision with Ar or Xe (10^{-5}–10^{-4} Torr) in a second quadrupole which functioned as an ion guide. The product ions were analyzed in a third quadrupole. The excitation curves obtained by variation of the accelerating voltage were analyzed as described elsewhere.[2] The curve for the parent ion $M^+(H_2O)_n$ defines its velocity distribution, used to deconvolute the curves for the daughter ions $M^+(H_2O)_{n-1}$ and $M^+(H_2O)_{n-2}$. The differences of their thresholds define the successive binding energies of water molecules. A similar procedure starting with $M^+OH(H_2O)$ ions yields the hydroxyl binding energies (Table I). The accuracy of the results is believed[2] to be ±3 kcal/mol.

For three of the new values a comparison with literature data is possible. The agreement is excellent for $D(Cr^+\text{–}OH)$[8] and $D(Co^+\text{–}OH)$,[7,9] but our value for $D(Fe^+\text{–}OH)$[7,9] is 8–12 kcal/mol higher. Considering the combined error bars, a possible explanation of the difference might be that the Fe^+ product of collision-induced dissociation of $FeOH(H_2O)^+$ is produced in its quartet state, about 5 kcal/mol above the ground sextet state.[10] This would be a likely outcome if the ground state of $FeOH(H_2O)^+$ is a triplet.

Two obvious structures are possible for the ions: $H\text{—}M^+\text{=}O$ or $M^+\text{—}OH$ and $H\text{—}M^+\text{—}OH$ or $M^+\text{—}OH_2$. Assuming that bond energies are additive in a first rough approximation,[11] the energy $E(H\text{—}M^+\text{=}O)$ needed for removal of OH from $H\text{—}M^+\text{=}O$ can be estimated from known values of $D(M^+\text{—}H)$[3] and $D(M^+\text{=}O)$.[8] The results are listed in Table I and differ greatly from our measured OH binding energies, except in the case of Ti^+. We take this as evidence that our ions have the structure $M^+\text{—}OH$, with the possible exception of $H\text{—}Ti^+\text{=}O$.

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(11) The large difference between the first and second hydration energies of Fe^+ calls for caution in assuming bond energy additivity. We have relied only on large energy differences in drawing structural conclusions.

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Table I.[a] Thermochemical Data for First-Row Transition-Metal Hydrates, Hydroxides, Oxides, and Hydrides

M^+	$D(M^+{-}OH_2)$[b]	$D(M^+{-}OH)$[b]	E_p[c]	$D_0(M^+{=}O)$[d]	$D_0(M^+{-}H)$[e]	$E(H{-}M^+{-}OH)$[f]	$E(H{-}M^+{=}O)$[f]	$D(M^+O{-}H)$[f]
K^+	17.0[g]							
Ca^+	29.0[h]	106[i]		58[i]	45.9[d]	34	3	149
Sc^+	31.4	87.8	19.1	159	55.3	25	113	30
Ti^+	38.0	113	16.1	161	55.1	50	115	53
V^+	36.2	107	15.2	131	47.3	36	77	71
Cr^+	29.0	74.3, 73[j]	25.3	85	27.7	−16	12	90, 89
Mn^+	32.5	82	26.5	57	47.5	12	3	127
Fe^+	28.8	85.3, 76,[k] 77,[l] 73[m]	20.6	69	47.0	14, 5, 6, 2	15	117, 108, 109, 105
Co^+	37.1	72.2, 71[l]	29.2	64	45.5	0	8	109, 108
Ni^+	36.5	42.2	31.9	45	38.5	−37	−18	98
Cu^+	35.0				21.8			
Zn^+	39.0	30.4			53.3			

[a] All values in kcal/mol. [b] This work except where noted. Average standard deviation in about a dozen measurements for each ion, ±3 kcal/mol; this is also believed to be the accuracy of the method.[2] [c] The promotion energy.[13] [d] Reference 8, with ±3–7 kcal/mol uncertainty. [e] Reference 3, ±2–4 kcal/mol. [f] Assuming reformation of the O—H bond and using $D_0(H{-}OH) = 118$ kcal/mol and $D_0(O{-}H) = 101$ kcal/mol from *JANAF Thermochemical Tables*, 2nd ed.; NSRDS-NBS 37; National Bureau of Standards: Washington, DC, 1971. [g] Reference 4a. [h] Reference 4b. [i] Murad, E. *J. Chem. Phys.* **1981**, *75*, 4080. [j] Reference 8. [k] Reference 9, ±4.6 kcal/mol. [l] Reference 7, ±6 kcal/mol. [m] Reference 7, ±3 kcal/mol.

Having established the hydroxyl bond energies, we can estimate the energies $E(H{-}M^+{-}OH)$ needed for removal of H_2O from $H{-}M^+{-}OH$ ions for all M^+ except Ti^+ (Table I). These disagree strongly with our measured H_2O binding energies, except in the case of V^+ and possibly Ca^+ and Sc^+. We conclude that our ions have the structure $M^+{-}OH_2$, with the possible exceptions of $M^+ = Ca^+$ to V^+.

The hydroxyl binding energies of the transition-metal cations vary strongly and show a tendency to decrease for late transition metals. The water binding energies fall into two groups: the values for Sc^+, Cr^+, Mn^+, and Fe^+ are near 30 kcal/mol, the others near 37 kcal/mol; this is hard to attribute to variations in the ionic radius. Detailed understanding of the $D(M^+{-}OH)$ and $D(M^+{-}OH_2)$ values requires elaborate calculations similar to those published[12] for the $M^+{-}H$ bond. We merely note the existence of an approximate linear correlation between the $M^+{-}OH$ bond energies and promotion energies[13] (Figure 1). The correlation suggests that early transition-metal ions have a propensity to use their 3d orbitals, whereas the late ones prefer to utilize the 4s orbital for bonding, as demonstrated previously[12] for $M^+{-}H$ bonds.

Our value of the hydration energy $D(Fe^+{-}OH_2) = 28.8$ kcal/mol conflicts with the previous estimate[6a] $D_0(Fe^+{-}CO) = 37.6$ kcal/mol, since H_2O readily displaces CO in Fe^+CO at low pressure and room temperature.[14] The reported value of $D_0(Fe^+{-}C_2H_4) = 34 \pm 2$ kcal/mol[15] also contradicts the earlier estimate,[6a] since C_2D_4, too, displaces CO in Fe^+CO.[14]

The Cu^+ ion binds a second water molecule somewhat more strongly (39 kcal/mol) than the first one (35 kcal/mol).[2] We have now measured the second hydration energies also for Fe^+ (38 kcal/mol), Co^+ (45 kcal/mol), and Ni^+ (38 kcal/mol). These can be compared with the first hydration energies of 29, 37, and 37 kcal/mol, respectively. Monopositive ions of first-row transition metals thus may have a general tendency to attach a second water ligand at least as strongly as the first one. Along with the variation in the first hydration energies across the series, this is indicative of some degree of dative bonding, distinct from the presumably purely electrostatic bonding between water and alkali[4a] or alkaline earth[4b] cations. In these, the first hydration energy is dictated by the ionic radius, and the second hydration energy is several kcal/mol smaller than the first one as a result of unfavorable electrostatic ligand–ligand interactions.

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Registry No. Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; H_2O, 7732-18-5.

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(13) (i) For Sc^+—Cr^+, the energy required to promote the ground state free ion to the lowest $3d^n$ state plus a spin decoupling correction (Schilling, J. B.; Beauchamp, J. L. *Organometallics* **1988**, *7*, 194). (ii) For Mn^+—Cu^+, the promotion energy of the lowest $3d^{n-1}4s$ state plus the average of the d-electron and s-electron spin decoupling energies. The free ion energy states were derived from ref 10.

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Sequential Solvation of Atomic Transition-Metal Ions. The Second Solvent Molecule Can Bind More Strongly Than the First

Peter J. Marinelli and Robert R. Squires*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47906

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We wish to report the determination of sequential water and ammonia solvation energies for the series of first-row transition-metal atomic ions V^+, Cr^+, Mn^+, Fe^+, Co^+, and Ni^+. A remarkable trend is found wherein for most metals the second solvent binding energy significantly exceeds the first. This is a striking departure from the normal *decrease* in successive solvent binding energies of all other atomic ions for which data are available.[1]

Atomic transition-metal ions are generated by dissociative electron ionization and Penning ionization of volatile metal carbonyl complexes in the helium flow reactor of a flowing afterglow–triple quadrupole apparatus.[2] Termolecular association reactions of the metal ions with added H_2O or NH_3 vapor produce a kinetic mixture of thermalized $M^+(H_2O)_n$ ($n = 1$–3) and $M^+(NH_3)_n$ ($n = 1$–4) cluster ions. Unimolecular and bimolecular reactions of mass-selected cluster ions are carried out in the central quadrupole of the triple quadrupole analyzer, where both pressure and kinetic energy effects can be characterized.

The thermochemistry for sequential solvation of the atomic metal ions by H_2O and NH_3 can be estimated from the translational energy thresholds for collision-induced dissociation (CID) of the corresponding cluster ions with argon target gas.[3] Figure

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(3) $P(Ar) \leq 5 \times 10^{-5}$ Torr (single-collision conditions); reactant ion retarding potential analysis locates the energy origin and shows a typical kinetic energy distribution of 0.8–1.3 eV (fwhm, lab frame).