Gas-Phase Ion Chemistry of Zinc Atoms and Ions

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There has been considerable recent interest in the gas-phase chemistry of metal ions, due to the remarkable reactivity observed for such unsolvated species. Direct insertion into C-C and C-H bonds and catalytic transfer of groups have been observed, and quantitative ligand-binding energies have been measured. Much of this work has focused on the mid transition metals, with relatively little attention paid to other metals, however. Similarly, while there have been numerous studies dealing with transient species produced by radiolysis,6 much of this work has been focused on the mid transition metals, with relatively little attention paid to other metals, however. Similarly, while there have been numerous investigations of the gas-phase chemistry of metal atoms with neutral organic molecules,4 there are only a few reports of the gas-phase chemistry of neutral metal atoms reacting with ionic species. In this work, we report some gas-phase chemistry of zinc atoms reacting with a variety of ionic species by proton transfer, as well as some reactions of Zn+. This oxidation state of zinc, while not unknown in solution, has chemistry primarily dealing with transient species produced by radiolysis.5

Experimental Section

The ion cyclotron resonance spectrometer used for this work has been previously described.1 Zinc atoms were volatilized by passing ca. 3-4 A of direct current through a brass filament (33% Zn, 67% Cu) adjacent to the ICR cell. No zinc signals were obtained when a pure zinc filament was substituted for the brass filament. Inspection of the surface of the brass filament after several weeks of intermittent operation revealed the surface to be pitted and no longer shiny. We believe that the zinc atoms are volatilized thermally from the surface of this filament, and then undergo ionization in the electron beam. The lack of a Zn+ signal when the electron energy is less than 9.4 eV rules out ion production via surface ionization on the hot rhenium filament that generates the electron beam.8 When other chemicals were present in the spectrometer, the largest Zn+ signals were obtained when the ionizing electron beam was operated at an electron energy of 14 eV. This is presumably due to the relative cross sections for ionization of the zinc atoms and the polyatomic molecules used in these experiments. Only very small signals, normally buried in the base line noise but brought out by extensive signal averaging, could be detected in the normal quenched-mode operation. On the basis of the slow rise time for these signals and the ionization cross section for zinc,10 we estimate the number density of zinc atoms in the cell to be on the order of 10^14 cm^-3 (10^11 torr). The necessity of operating in unquenched mode unfortunately rules out measurement of any kinetic parameters but allows certain inferences to be made concerning the chemical pathways of zinc atoms or ions reacting with any other chemical species admitted into the spectrometer. If a primary electron impact ion of some species reacts away rapidly (e.g., in less than 100 collisions) with its own neutral species, then that ion will not persist long enough to react with a zinc atom. Only those ions that are the end products of an ion/molecule reaction sequence will be present for a sufficient time under unquenched conditions to react with the very low concentration of zinc atoms present.

Other chemicals were obtained commercially and subjected to the usual freeze-pump-thaw cycles before being admitted to the ICR spectrometer.

Results

A spectrum obtained at a background pressure of 10^-7 torr is shown in Figure 1. The peak ratios are within 0.5% of the natural isotope abundance,11 which is on the order of the accuracy of the detection electronics used in our instrumentation. Various gases were admitted to the vacuum system to further probe the reactivity of these ions and their precursor neutrals.

Alkanes. When 2 × 10^-7 torr of methane is present in the spectrometer, both Zn+ and ZnH+ are observed under typical conditions. The protonated ion has 10-20% of the intensity of the atomic ion, depending on the exact experimental conditions. Double-resonance techniques indicate that the ion ZnH+ arises from CHS+ and not from C2H5+, in agreement with the work of Porter and coworkers.2 Such placing the basicity of Zn between 128.2 and 163 kcal/mol.12 Double resonance techniques indicate that the ion ZnH+ arises from CHS+ and not from C2H5+, in agreement with the work of Porter and coworkers.2 Such placing the basicity of Zn between 128.2 and 163 kcal/mol.12


arises from Zn\(^+\) and not from NF\(_3^+\) or NF\(_2^+\). This places the double resonance to the N\(_2\)O, then N\(_2\)O\(^+\) becomes a prominent ion in the spectrum, and ZnH\(^+\) also appears. Double resonance indicates that the protonated nitrous oxide is the source of the protonated ion that also appears. This places a lower limit on the PA(Zn) of 139 kJ/mol.\(^{12}\)

Nitrous Oxide. When nitrous oxide is present at 2 \times 10^{-7} torr in the spectrometer, the only zinc-containing peaks are Zn\(^+\) and ZnO\(^+\). The latter is a product of Zn\(^+\), and not N\(_2\)O\(^+\), NO\(^+\), or O\(^+\), by double resonance. Zn\(^+\) is not derived from any other ion in the spectrum by double resonance. We note that reproducibility problems exist with observing ZnO\(^+\); its production is a sensitive function of electron energy, filament current, plate voltages, detection rf level, and sweep rate of the rf. If reaction 2 is the source of the ZnO\(^+\) signal and is

\[
\text{Zn}^+ + \text{N}_2\text{O} \rightarrow \text{ZnO}^+ + \text{N}_2
\]  

exothermic, the Zn--O bond strength must be greater than that of N\(_2\)O at 39 kJ/mol.\(^{13}\) This is in direct contrast to the work of Kappes and Staley,\(^ {14}\) where Zn\(^+\) ions created in an ICR spectrometer by laser desorption/ionization from a cold metal surface were not reactive with N\(_2\)O. If 2 \times 10^{-8} torr of methane is admitted to the spectrometer in addition to the N\(_2\)O, then N\(_2\)O\(^+\) becomes a prominent ion in the spectrum, and ZnH\(^+\) also appears. Double resonance indicates that the protonated nitrous oxide is the source of the protonated zinc, placing a lower bound on the proton affinity (PA) of zinc of 135.6 kJ/mol.\(^ {15}\)

Carbon Monoxide. With 2 \times 10^{-7} torr of CO present, no ZnO\(^+\), ZnCO\(^+\), or ZnC\(^+\) ions are observed, although Zn\(^+\) is present. Added methane results in a large HCO\(^+\) signal, which by double resonance is shown to be the precursor to the ZnH\(^+\) ion that also appears. This places a lower limit on the PA(Zn) of 139 kJ/mol.\(^ {15}\)

Nitrogen Trifluoride. With 2 \times 10^{-7} torr of NF\(_3\) present, NF\(_3^+\) and NF\(_2^+\) are the principal primary ions. Both Zn\(^+\) and ZnF\(^+\) are observed; double resonance indicates that the latter arises from Zn\(^+\) and not from NF\(_3^+\) or NF\(_2^+\). This places the Zn--F bond strength at \geq 59 kJ/mol.\(^ {15}\) The appearance of ZnF\(^+\) is not dependent on electron energy, occurring at all energies where Zn\(^+\) is observed. With 2 \times 10^{-8} torr of added methane, HNF\(_3^+\) becomes an appreciable ion in the spectrum and by double resonance gives rise to the ZnH\(^+\) signal also observed. Unfortunately, the PA of NF\(_3\) is at present only bracketed as 147 ± 4 kJ/mol by the PA sequence\(^ {16}\) CO < NF\(_3^+\) < CH\(_3\)F < C\(_2\)H\(_2\) so that this allows only a rough increase in the lower limit for PA(Zn).

Other Gases. No zinc-containing ions are formed when Zn\(^+\) is in the presence of CO\(_2\), OCS, CS\(_2\), elemental sulfur, SO\(_2\), or 2-chloropropane. The last species is used as a standard derivatizing reagent for gas-phase metal ions, as in reactions 3 and 4,\(^ {1,17}\) Under the uncondensed conditions, the possible precursor ions to any zinc-containing ions arising from Zn\(^0\) are the self-chemical ionization products of 2-chloropropane, isopropyl cation and the disisopropylchloronium ion. Both charge exchange and proton transfer (see below) to zinc from the isopropyl cation are calculated to be endothermic, by 42 and 30 kcal/mol, respectively.\(^ {15}\) For disisopropylchloronium ion, taking the binding strength of isopropyl cation to chloromethane\(^ {18}\) as that for isopropyl bound to 2-chloropropane, dissociative proton transfer to Zn\(^0\) to give propene, 2-chloropropene, and ZnH\(^+\) is calculated to be ca. 48 kcal/mol endothermic, and dissociative electron transfer, 70 kcal/mol endothermic. The lack of zinc atom reactions under our conditions with these species is therefore not surprising. If the nonobservation of reaction 2 or 3 is taken as a thermochemical threshold, the bond strength of Zn\(^+\) bound to HCl or propene is <18 kcal/mol.\(^ {15}\)

Discussion

Proton Affinity of Zn. There are several previous values for PA(Zn). The report by Porter and co-workers\(^ {5}\) involves an experimental bracketing of PA(Zn) between that of CH\(_4\) (current best value 128.2 kJ/mol)\(^ {19}\) and that of CH\(_2\)=CH\(_2\) (PA = 162.6 ± 0.5 kJ/mol);\(^ {16}\) using high-pressure mass spectrometry. This yields a direct experimental value of PA(Zn) = 145.7 ± 17.0 kJ/mol. They also derive a value for PA(Zn) of 6.8 ± 0.2 eV (156.8 ± 4.6 kcal/mol) from the spectroscopic bond strength for Zn\(^+\)-H of 2.5 eV given by Herzberg,\(^ {19}\) plus the appropriate ionization potentials of Zn and H. An uncertainty of 0.2 eV is placed on this PA, presumably from the upper experimental bound involving no Zn+ transfer from C\(_2\)H\(_5\) to Zn, with no rationale for the same lower limit. No explicit uncertainty is given by Herzberg for the original spectroscopic bond strength, though generically 9 times the last decimal place is stated as a probable bound.\(^ {15}\) A value of 164 ± 10 kcal/mol can be derived for PA(Zn) from the appearance potential, with no kinetic shift correction, for ZnH\(^+\) formed from Zn(CH\(_3\))\(_2\) in an electron-impact mass

\[
\text{M}^+ + \text{(CH}_3\text{HCl)}^+ \rightarrow \text{CH}_2\text{CH}=\text{CH}_2 + \text{HCl}
\]

\[
\text{M}^+ + \text{(CIH}_3\text{HCl)}^+ \rightarrow \text{CH}_2\text{CH}=\text{CH}_2 + \text{HCl}
\]
A molecular orbital calculation has given the $\text{Zn}^{+}\text{H}$ bond strength as 35 kcal/mol.20

The present work experimentally brackets PA(Zn) between those of NF$_3$ at 147 ± 5 kcal/mol,15 and hexafluoroacetone at 160.4 ± 0.7 kcal/mol16 for an average of 154.2 ± 2 kcal/mol. This places the Zn$^+$-H bond strength at 57±2 kcal/mol, compared to the spectroscopic value of 58 kcal/mol. A $\Delta H^\circ(\text{ZnH}^+) = 242.8\pm 1/2$ kcal/mol similarly derived. It would be desirable to have more bases in this region to enable a more precise bracketing of the PA; however, there are relatively few known. AsF$_3$ and CH$_3$F both have basicities between those of NF$_3$ and (CF$_3$)$_2$CO.16 The protonated species of these, HAsF$_3^+$ and HFC$_2$CH$_2^+$, react away in their neutral vapors, so that the protonated base is not available under unquenched conditions to react with zinc. The Zn$^+$-H bond is stronger than the Zn-H bond of 20 ± 2 kcal/mol.19 This bond strength increase upon ionization is due to the presence of a total of three $s$ electrons from Zn and H, with the third having to occupy an antibonding orbital in ZnH; ionization of ZnH results in the stronger two electron bond. ZnO$^+$. There is a striking contrast between the results of the present work, that zinc ions will abstract oxygen from nitrous oxide, and the corresponding lack of reaction of N$_2$O with laser-generated Zn$^+$.14 One possible explanation is the presence of an electronically excited state of Zn$^+$; the first excited state of Zn$^+$ is at 15.4 eV above Zn$^0$,22 near where the best Zn$^+$ signals are observed. Such excited species have been invoked in other transition-metal ion/molecule chemistry to explain apparently endothermic reactions.12,13,19,23 The instances cited in the literature, however, all involve excited states of multiplicity different from that of the ground state, so that relaxation will be slow, relative to the collision rate. The radiative lifetime of the (Zn$^+$)$^+$ state at 15.4 eV is ca. 3 ns, since the excited and ground states are both doublets.23 This is far too fast for chemistry to be attributed to a free (Zn$^+$)$^+$ in the ICR spectrometer. A preferable explanation is based on chemistry observed by Beauchamp and co-workers, who have measured the excess translational energy needed to drive reactions 5 and 6, using

\begin{align}
\text{M}^+ + \text{O}_2 & \rightarrow \text{M}^+\text{O} + \text{O} \quad (5) \\
\text{M}^+ + \text{N}_2 & \rightarrow \text{M}^+\text{O} + \text{N}_2 \quad (6)
\end{align}

an ion beam apparatus, for a number of transition-metal ions.24 They find that a kinetic barrier exists for exothermic oxygen transfer to the metal ions from nitrous oxide, compared to an endothermic, but barrier-free, transfer from oxygen. This is ascribed to multiplicity differences: oxygen dissociating from MO$^+$ correlates with the triplet state, while dissociation from N$_2$O correlates with the singlet state. The resulting singlet-triplet crossing on one of the potential surfaces results in a barrier to oxygen transfer at the thermochemical onset. A similar reduction in rate constant for Zn$^+$ reacting with N$_2$O is observed in aqueous solution, relative to Zn$^+$ reacting with other species.25 The appearance of ZnO$^+$ in our spectrometer, as noted above, is not easily reproducible. This is interpreted as due to the nature of the unquenched mode and the intermediate-passage method in ICR spectrometry. Detection of Zn$^+$ in the ICR spectrometer is due to translational excitation, and since Zn$^+$ is not removed from the cell after detection (as is usual in pulsed ICR spectrometry) but allowed to remain, it may undergo endothermic reactions. If the balance of rf level, power absorption, ion loss by diffusion, and N$_2$O pressure are just right, the oxygen transfer is facilitated by the excess energy of the Zn$^+$. The ZnO$^+$ so formed is detected on the next frequency scan. Thus, lack of thermal reactivity with N$_2$O cannot be taken as an upper thermochemical limit in assigning bond strengths here, due to possible kinetic problems. Even the use of CO$_2$ and COS as upper limits to oxygen transfer cannot be taken as necessarily valid since a similar singlet-triplet correlation problem exists there.23

Charge Transfer. No charge transfer to zinc is detected by double resonance by any of the cations present; all zinc ions are observed to arise by primary electron impact. For atomic ions, this is consistent with the lack of a rotational or vibrational sink for the excess energy, if the charge transfer is not a resonant process and if the collision complex is weakly coupled translationally due to long-range electron transfer. None of the atomic ions that arise from the nonmetallic species used have recombination energies closer to the ionization potential of zinc than 2 eV.25 For diatomic and larger cations, nonresonant charge transfer could occur due to rotational and vibrational coupling in the long-lived collision complex, and as due to translational disposal of energy.25 For the di-, tri-, and tetratomics used here, such transfer is in general not observed. The only case where such a transfer might have occurred is with the S$^+$ ions, $n = 2$–8, which have recombination energies within 0.5 eV of the IP of zinc at 9.394 eV.25 These ions are depleted from the S$_8$ spectrum when zinc atoms are present, and a much larger than usual Zn$^+$ signal is observed. Of the usual sulfur ions, only S$^+$ is present. The lack of signals for these S$_n^+$ ions precludes double-resonance detection of this possible charge transfer.

Other Thermochemistry. It is risky to infer thermochemical stability from a lack of reaction, save when dealing with a homologous series where the reacting sites are constant. For ion/molecule reactions, kinetic barriers, as noted above for N$_2$O, can result in reactions that proceed at much less than collision rate even though they are thermochemically favored.24 With this caveat, several upper bounds on bond strengths will be derived here for some zinc-containing species. The lack of sulfur transfer from CS$_2$, elemental sulfur, or OCS to Zn$^+$ implies a Zn$^+$-S bond strength of less than 34 kcal/mol. A hard-soft acid-base analysis predicts a weaker Zn$^+$-S bond than Zn$^+$-O, but the lack of good data for the latter precludes further evaluation. The lack of chlorine transfer from 2-chloropropane to Zn$^+$ implies that the Zn$^+$-Cl bond strength is less than 83 kcal/mol, in agreement with DH(Zn$^+$-Cl) = 54 ± 6 kcal/mol based on the appearance potential of ZnCl$^+$ from Cl$_2$.26

In no case were any transfers of cationic species from other ions to Zn$^0$ observed, other than proton transfer. On the basis of a reasonable range for the Zn$^+$-O bond strength of 30–70 kcal/mol and the ionization potentials of Zn and O, O$^+$ transfer from XO$^+$ to Zn$^0$ should be endothermic for all the oxide cations used in this work save for N$_2$O$^+$. In that case, O$^+$ transfer should be exothermic by >75 kcal/mol. Since this reaction is not observed, there must be a kinetic barrier. Such a rate reduction is not a result of different collision rates since, due to polarizability differences, Zn$^0$ should collide with N$_2$O$^+$ at a 24% greater rate than for Zn$^+$ colliding with N$_2$O.27 The lack of reaction may be due to a multiplicity argument as given for N$_2$O above: N$_2$O$^+$ is a doublet, and correlates

Vanadium(II) Pair Excitations in CsMg1-xVxCl3

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Mixed crystals CsMg1-xVxCl3 with x between 1% and 15% were prepared by the Bridgman technique. Single and double excitations to the "E", "F" and "T" states of V2Cl9" dimers were studied by optical absorption and Zeeman spectroscopy. The ground-state exchange parameter is $2J = -187 \pm 5$ cm⁻¹. From an analysis of singly excited "E" pair states the following orbital exchange parameters were derived: $2J_{e_1} = -570$ cm⁻¹, $2J_{e_2} = -193$ cm⁻¹. $J_{e_1}$ is the dominant antiferromagnetic pathway as expected on the basis of overlap arguments.

1. Introduction

The exchange in the quasi-one-dimensional (1D) antiferromagnets CsVX₃ (X = Cl, Br, I) is unusually strong. In the chloride bond, but the bonding may involve p orbitals, so that the promotion-energy correlation is not applicable. The chlorode fluoride bond strengths for Zn²⁺ parallel the general order DH(M²⁺-Cl) < DH(M²⁺-F) observed for the first-row transition metals. For the 2B elements Zn, Cd, and Hg, the uncertainties in the M²⁺-H bond strengths are large, but the order Cd²⁺-H < Zn²⁺-H < Hg²⁺-H can be taken to be a mixture of electronegativity change and the lanthanide contraction. This order is not reflected in the neutral ordering Zn-H > Cd-H > Hg-H, where the unpaired antibonding electron affects the stability. Similarly, the groups capable of sharing one electron in a bond, such as H and C, have neutral Zn-X bonds weaker than their ionic counterparts, while oxygen, requiring a two-electron donation from the metal, has stronger neutral bonds, compared to the ionic analogues, for the 2B elements. On the basis of periodic trends, we predict that DH(Zn²⁺-O) should be ca. 30 kcal/mol.

Conclusions

Zinc atoms and ions are relatively unreactive, in terms of atom abstraction or oxidative insertion, compared to the first-row transition metals, in spite of Zn²⁺ having the strongest metal ion to one-electron-donor ligand bond strengths of the first long series. This is a reflection of the filled-d-shell nature of Zn and Zn²⁺, with the bonding being primarily due to the s electrons.

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Registry No. Zn, 7440-66-6; Zn²⁺, 15176-26-8; ZnH²⁺, 41336-21-4; CH₃, 1535-34-9; N₂O, 10024-97-2; ZnO²⁻, 60131-08-0; CH₄, 74-82-8; N₂OH-, 76412-54-9; CO, 630-08-0; HCO²⁻, 17036-74-9; NF₃, 7783-54-2; ZnF²⁻, 19624-01-2; HNF₃, 62700-73-8; (CF₃)₂CO, 684-16-2; (CF₃)₂COH⁺, 79999-78-3; F₂, 7782-41-4; S, 7704-34-9; Cl₂, 7782-50-5; O₂, 7782-44-7.

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