this anomaly occurs in other related systems such as butatriene or butatrienone, and we hope to report further on this in the future.

The failure of structural theory for this class of compound also extends to calculations by the method of molecular mechanics[18] and to ab initio molecular orbital calculations at the SCF level,[2] but at least in the case of propadienenone, and probably more generally, molecular orbital calculations including electron correlation[5] are consistent with the observed quasi-symmetry.

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Registry No. 1, 59078-44-3.

Supplementary Material Available: A listing of frequencies and uncertainties for all measured transitions used in this work (3 pages). Ordering information is given on any current masthead page.

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The Chemistry of First-Row Transition-Metal Ions with Primary Amines in the Gas Phase: Correlations of Reactivity with Electronic Structure

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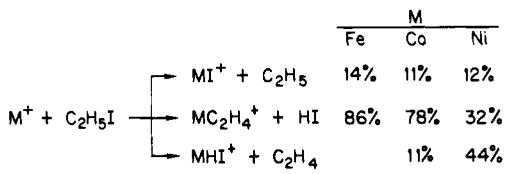
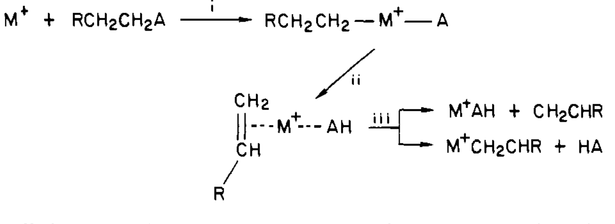
Abstract: In the past several years, an extensive body of literature has appeared in the area of gas-phase organometallic ion/molecule reactions. Most of the observed reactions can be explained by assuming that the first step of the interaction is a metal ion insertion into a bond of the organic molecule. Presented here are reactions of first-row transition-metal ions with a primary amine. They parallel the literature in that, for other types of organic molecules as well, Fe^+ typically inserts into many types of bonds, Ni^+ is very selective in this regard, Co^+ is intermediate between Fe^+ and Ni^+, and Mn^+ is frequently unreactive. An explanation of the reactivity trends of the first-row transition-metal ions is suggested, based on a consideration of the thermodynamics of the metal insertion process. The explanation uses the concept of promotion energy, the energy required to achieve a metal ion configuration conducive to the formation of two σ-bonds. Available data on excited states of these metal ions leads to an ordering in terms of these promotion energies, which appear to correlate with reactivity in terms of ability to insert into various bonds in organic molecules.

In the past several years a substantial amount of work has been published concerning the gas-phase chemistry of transition-metal ions with organic molecules.[1]

In 1979, Allison and Ridge[2] reported the bimolecular ion/molecule chemistry of Fe^+, Co^+, and Ni^+ with alkyl halides and alcohols. With the polar compounds studied, these three metal ions exhibited essentially the same chemistry, e.g.



While the product distributions varied, all three ions reacted by a common mechanism involving a (i) metal insertion/(ii) β-H atom shift/(iii) competitive ligand loss mechanism[3] (shown here for the reaction of M^+ with a polar compound, RCH_2CH_2A):



(1)

All three transition-metal ions appeared to insert into C–I, C–Cl, and C–OH bonds.[2] In subsequent years, studies of other transition-metal ions with polar compounds such as alkyl halides appeared, with similar results. Also, subsequent papers showed that the metal insertion/β-H shift mechanism was a common one. For example, Co^+ also reacts with thiols,[4] alkanes,[5] alkenes,[6] nitroalkanes,[7] ketones,[4] acids,[4] and amines[8] via this general mechanism, involving metal insertion into a variety of polar and nonpolar bonds.

One type of organic molecule for which the most extensive studies have been reported with the most metal ions is alkanes. From such data, differences in the reactivity of first-row transition-metal ions became more apparent. It has been pointed out that, with alkanes, Fe^+ is "indescriminate" in inserting into C–H and C–C bonds, Ni^+ is more selective, Co^+ is intermediate in reactivity between these two, while Mn^+ and Cr^+ are unreactive.[9]

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(1) Recent publications representative of the groups currently active in this area include the following: (a) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403. (b) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623. (d) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883. (e) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065.

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Table I. Reactions of First-Row Transition-Metal Ions with *n*-Propylamine; Product Distributions,[a] Electronic Configurations, Promotion Energies

reaction	M = Cr	Mn	Fe	Co[b]	Ni	Cu	Zn
$M^+ + n\text{-}C_3H_7NH_2 \rightarrow MNH_3^+ + C_3H_6$			17%				
$\rightarrow MC_3H_6^+ + NH_3$			3%				
$\rightarrow MC_2H_5N^+ + CH_4$			5%				
$\rightarrow MCH_5N^+ + C_2H_4$		NR[c]	63%	68%	100%		NR[c]
$\rightarrow MC_3H_7N^+ + H_2$	100%		8%	16%		100%	
$\rightarrow MC_2H_5NH_2^+ + CH_2$			4%				
$\rightarrow MC_3H_5N^+ + 2H_2$				16%			
M^+ ground-state configuration[d]	$3d^5$	$3d^54s^1$	$3d^64s^1$	$3d^8$	$3d^9$	$3d^{10}$	$3d^{10}4s^1$
$PE(s^1d^n)$[e]	34.2	0	0	9.6	24.0	62.7	0
$PE(s^1p^1d^n)$[f]	<380.4[h]	238.0	155.8	229.6	<418.6[i]	308.6	296.4
$PE(s^2d^n)$[g]	148.5	153.6	65.3	113.9	<418.6[i]	195.2	175.6

[a] Metal-containing ionic products only. [b] Data taken from ref 8. [c] NR, no reaction products were observed. [d] Data taken from ref 13. [e] Promotion energy (kcal/mol) required to reach the atomic ion's lowest s^1d^n configuration. [f] Promotion energy (kcal/mol) required to reach the atomic ion's lowest $s^1p^1d^n$ configuration. [g] Promotion energy (kcal/mol) required to reach the atomic ion's lowest s^2d^n configuration. [h] Based on the Cr(III) limit, 133 060 cm^{-1}. [i] Based on the Ni(III) limit, 146 408 cm^{-1}.

No studies of the chemistry of Zn^+ have been reported to date. In this area of research, the term "reactivity" usually refers to the *number* of different products formed, since this is usually indicative of the number of different bonds in an organic molecule into which a given metal will insert.

The past 10 years have produced a sizable amount of descriptive chemistry from which many mechanisms have been proposed and some reaction trends noted. In addition to largely mechanistic studies, a number of thermodynamic determinations of ionic and neutral heats of formation and metal-ligand bond strengths have appeared. In studies reporting M^+–H and M^+–CH_3 bond strengths, Armentrout and Beauchamp[9] noted a correlation between $D°(M^+–CH_3)$ and the "promotion energy" required to obtain a $3d^n4s^1$ configuration, $PE(s^1d^n)$, of the first-row transition-metal ion, M^+ (The same correlation holds for $D°(M^+–H)$). These promotion energies are given in Table I. This correlation led to the proposal that the ground state of molecular species such as $Co^+–CH_3$ does *not* correlate to the ground-state fragments $[Co^+(3d^8) + CH_3]$ but rather to $[Co^+(3d^74s^1) + CH_3]$. That is, for the first-row transition-metal ions, a metal s electron is required for the formation of the first σ-bond; and when considering the thermodynamics of this bond formation, one must be aware of the promotion energy required to achieve a $3d^n4s^1$ configuration. The results suggest that while $D°(Co^+(3d^n4s^1) - CH_3)$ and $D°(Fe^+(3d^n4s^1) - CH_3)$ are approximately equal,[9] the "observed" bond strengths (relative to the fragments in their ground states) differ due to the difference in promotion energies. These concepts explain the bond-strength trends, but these alone do not predict the observed *reactivity* trends since reactions which involve metal *insertion* require the formation of an intermediate in which *two* σ-bonds are formed to the transition-metal ion.

We present here an ordering of transition-metal ions based on the concept of promotion energies, considering the energies required to obtain a metal ion electronic configuration conducive to the formation of two bonds. We will use the reactions of the first-row transition-metal ions with *n*-propylamine as additional support for proposed "reactivity" trends.

Experimental Section

All experiments were performed with an ion cyclotron resonance (ICR) spectrometer of conventional design, which has been described elsewhere.[8] The instrument was used in the drift mode. First-row transition-metal ions were formed by electron impact on volatile metal compounds. Chromium hexacarbonyl, dimanganese decacarbonyl, nickel tetracarbonyl, and diethylzinc were obtained from the Alfa Chemical Co. Iron pentacarbonyl was obtained from the Aldrich Chemical Co. These compounds were used as supplied, subjected to several freeze/pump/thaw cycles before use. $Cu(CF_3COCH_2COCF_3)_2$ was obtained from Research Organic/Inorganic Chemicals Inc. The anhydrous form of copper bis-hexafluoroacetylacetonate was obtained by slow dehydration of the dihydrate in vacuo over fuming sulfuric acid in a desiccant container.

In a typical experiment, low-pressure electron impact (EI) spectra of each compound used were recorded to determine purity. Higher pressure spectra were obtained and ion/molecule reactions which occur were identified and their precursors determined by ion cyclotron double resonance. Then spectra were obtained of 1:1 mixtures of the metal compound:*n*-propylamine at total pressures up to 1.5×10^{-5} torr. Ion/molecule reaction products in the mixture were identified and precursors determined. The observed reactions for Cr^+, Mn^+, Fe^+, Ni^+, Cu^+, and Zn^+ with *n*-propylamine are listed in Table I (with the prevously reported results[8] for the cobalt ion).

Results and Discussion

First consider the fact that the reactions of these transition-metal ions generally follow the proposed reactivity trends. The iron ion forms the largest variety of products, Cr^+ and Ni^+ form one product each, Co^+ is intermediate in its reactivity, Mn^+ is unreactive, etc. After a discussion of the proposed correlation between metal ion reactivity and electronic structure, some specific reactions in Table I will be discussed.

The first step of gas-phase organotransition-metal ion chemistry is usually metal ion insertion into a bond. Insertion requires the formation of *two* bonds. Presumably energy is required for M^+ to achieve a configuration conductive to 2-bond formation, M^{+*}. In reaction 1, if metal insertion into the R–A bond is to be an exothermic process, the following must hold:

$$D(M^{+*}–R) + D(RM^{+*}–A) > D(R–A) + PE(M^+ \rightarrow M^{+*})$$

If the values on the left side of the equation are approximately independent of M (M = first-row transition metal), then there may be cases where an insertion may occur only for metals with low PE's. This would be the case if $D(R–A)$ was very strong, or one of the bonds formed to the metal was very weak. That is PE's may control reactivity—a metal ion with a low PE could insert into more types of bonds than one with a higher PE.

Can the first-row transition-metal ions be ordered in terms of $PE(M^+ \rightarrow M^{+*})$? Ab initio calculations suggest[10,11] that the first-row transition-metal dihydrides and dihalides are linear, the bonding being due to sp-hybridized orbitals. It is not unreasonable to assume that this would also be the case for the analogous monopositive ions. The 4s and 4p orbitals have a much larger radial extent than the 3d orbitals, thus it is more energetically favorable to bond in this way than to form bonds with 3d orbitals.[11] While extensive theoretical work has not been done on *ionic* transition-metal-containing species, the work done to date does show that analogous species such as $MnCH_2$ and $MnCH_2^+$ have

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similar orbitals.[12] These calculations may then suggest that the promotion energy to achieve a $3d^n4s^14p^1$ configuration, PE($s^1p^1d^n$), should correlate with a metal's "ability" to insert. These are listed in Table I. Values for Cr^+ and Ni^+ are not available; however, consideration of the energies required to promote a d electron to an s orbital or a p orbital separately suggests that PE($s^1p^1d^n$) values for Cr^+ and Ni^+ would be similar, and fall between the values for Co^+ and Cu^+.[13]

A generalized valence bond (GVB) approach[14] may suggest that the promotion energy to achieve a $3d^n4s^2$ configuration, PE(s^2d^n), would correlate with metal ion reactivity with regard to insertion. The sp hybrid orbitals used in forming, e.g., MH_2 are of the type ($s + \lambda p$). These orbitals are predominantly of s character ($\lambda < 0.20$). Thus PE(s^2d^n) may be more useful for correlation with reactivity.

Both sets of PE values given in Table I indicate that PE($M^+ \rightarrow M^{+*}$) should follow the order:

$$Fe^+ < Co^+ < Ni^+ \approx Cr^+ < Mn^+ < Zn^+ < Cu^+$$

We believe that this ordering correlates with reactivity in processes involving metal insertion as the first mechanistic step. Ions with the lowest PE's insert into more types of bonds; for ions with higher PE's, the number of bonds into which insertion is an exothermic process decreases. Note that this promotion energy ordering is different from that associated with single bond formation.[9] The two proposed PE's correlate with each other and suggest that the important concept involves promotion of the metal ion to a state in which 2 electrons are *not* in d orbitals.

The copper ion should, perhaps, not be included in this discussion, since Freiser et al.[15] has suggested that this metal ion does not react by metal-insertion mechanisms, but rather by dissociative attachment. The usually high promotion energy may dictate this as the only mechanism for reaction, since insertion into any bond in an organic molecule would be energetically prohibited.

The chemistry of first-row transition-metal ions with *n*-propylamine was chosen to further test the promotion energy correlation with reactivity. It has recently been suggested that Co^+ does not insert into the C–N bond of primary amines, possibly due to a thermodynamically inaccessible insertion intermediate, due to a weak $RCo^+–NH_2$ bond.[8] Consider the formation of this metal-insertion intermediate:

$$M^+ + C_3H_7NH_2 \rightarrow (C_3H_7–M^+–NH_2)$$

If ($M^{+*}–C_3H_7$) and ($C_3H_7M^{+*}–NH_2$) are each approximately independent of M, *no* ion with a PE less than PE(Co^+) would be expected to insert into the C–N bond (if the reaction does not occur for Co^+ due to a thermodynamic "bottleneck" at the insertion step). The only possible candidate for insertion into this bond would be Fe^+, based on the proposed ordering. The $M^+(C_3H_6)$ and $M^+(NH_3)$ products formed via reaction 1 indicate that only Fe^+ inserts into this bond. The reactivity of M^+, in terms of number and types of bonds subject to attack, does follow the proposed trend. Ions with relatively high PE's are much more "selective" of the bonds into which insertion occurs (in an exothermic process), while ions with relatively low PE's insert into many types of bonds.

Without considering promotion energies leading to states of the metal ions with 2 electrons out of d orbitals, we may have taken the approach of considering bond strengths such as $D°(M^+–CH_3)$ as indicative of reactivity. That is, Mn^+, Fe^+, and Zn^+ form stronger bonds to CH_3 than does Co^+. Therefore, these may all have been selected as metal ions which are more likely to insert into the C–NH_2 bond than Co^+. However, excitation of a d electron out of the stable half-filled d shell of Mn^+ [9] (or out of the stable filled d shell of Zn^+) requires a considerable amount of energy, leaving only Fe^+ with a promotion energy leading to a state conducive to 2-bond formation less than that of Co^+.

Thus, metal ion insertion into the C–N bond of primary amines is very sensitive to PE differences. The promotion energies discussed here cannot literally be interpreted as the energies required to achieve an M^+ configuration conducive to insertion (in contrast to the role played by the s^1d^n configuration on single-bond formation); however, they do indicate the *ordering* of energies involved in rearranging electrons when a transition-metal ion interacts with an organic molecule in the gas phase to achieve a metal insertion.

A few aspects of the chemistry reported in Table I deserve comment. The mechanisms by which, e.g., CH_4 elimination occurs have been reported previously.[8] We note that the major reaction product for the iron, cobalt, and nickel ions corresponds to loss of ethylene. For the less reactive nickel ion, this is the only product. However, the only product for Cr^+ is formed by elimination of H_2. We suggest two possible explanations for this. One is that Cr^+ may react with amines as Cu^+ presumably does,[15] by dissociative attachment, since they both form the same product. An alternate explanation is excited-state chemistry. Of the compounds used in this study, to date only electron impact on $Cr(CO)_6$ has been shown to form both ground-state and excited-state metal ions.[16,17] It may be that the ground-state chromium ions are unreactive (they could well be from their position in the PE ordering), and the long-lived excited state(s) reacts by a mechanism leading to the elimination of H_2.

Another "unusual" process is the elimination of methylene from propylamine by Fe^+. Due to the relatively high heat of formation of CH_2, reactions of this type are usually endothermic. For a reaction of the type

$$Fe^+ + A \rightarrow Fe^+\text{-}B + CH_2:$$

to be exothermic, one possible explanation would be the formation of a very stable FeB^+ species. This would be the case if $D(Fe^+–B)$ is very large. This may well be the case here. Presumably B here is ethylamine. It has been suggested that metal ion–ligand bond strengths parallel the ligands proton affinities.[18,19] Amines are at the upper end of the proton affinity scale, suggesting that $D(Fe^+–C_2H_5NH_2)$ should be relatively high, presumably high enough to make methylene elimination an exothermic process. Methylene elimination in similar reactions has been observed in the chemistry of Co^+ with acetic acid[4] and small nitroalkanes.[7]

Conclusions

The first-row transition-metal ions can be ordered in terms of the promotion energy required to achieve a configuration in which two electrons are not in d orbitals. This is apparently the configuration which is achieved as two σ-bonds are formed—the situation which exists when a metal ion inserts into a single bond of an organic molecule. First-row transition-metal ions with high promotion energies are unreactive or insert into a limited number of bonds, while ions with low promotion energies appear to be more reactive, inserting into a wider variety of bonds. Primary amines are a good test of this concept, since the exothermicity of the insertion process into the C–NH_2 bond appears to be dependent on this promotion energy.

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Registry No. $C_3H_7NH_2$, 107-10-8; Cr^+, 14067-03-9; Mn^+, 14127-69-6; Fe^+, 14067-02-8; Ni^+, 14903-34-5; Cu^+, 17493-86-6; Zn^+, 23713-49-7.

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