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Gas-Phase Reactions of Electrons, Halide Ions, and Radicals with Bis(2,4-pentanedionato)metal(II) Complexes in NF$_3$, CF$_2$Cl$_2$, and CF$_3$Br Plasmas

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The gas-phase negative ion chemistry of a series of bis(2,4-pentanedionato)metal(II) complexes (metal = Co, Ni, Cu, Zn) in NF$_3$, CF$_2$Cl$_2$, and CF$_3$Br plasmas has been examined by using the technique of negative chemical ionization (NCI) mass spectrometry. Ionization of the metal complexes occurs by resonance electron capture and competing reactions involving halide ions. Fluoride ions react with the metal complexes by nucleophilic addition, proton abstraction and nucleophilic ligand displacement. The less reactive chloride and bromide ions react by nucleophilic addition only. Reactions of radicals with the metal complexes occur prior to ionization in the NCI plasmas, and the products of these reactions are detected when they are ionized by either electron capture or ion/molecule processes to form negative ions. Halogen radicals react by ligand displacement, hydrogen atom abstraction, and homolytic substitution into the ligand, while halogenated methyl radicals undergo oxidative addition to the metal.

Introduction

Investigation of the chemistry of ions in the gas phase provides a fundamental insight into the intrinsic properties of these species in the absence of solvation effects. In a number of previous studies,[1-11] we have used the technique of negative chemical ionization (NCI) mass spectrometry to examine the gas-phase negative ion chemistry of transition-metal coordination compounds. Reactions of metal complexes with low-energy electrons have been a primary interest in this work.[2-6] More recently, the formation of negative ions from metal complexes as a result of radical/molecule reactions followed by electron capture has been examined.[7-10] A preliminary study of the ion/molecule reactions of bis(β-keto enolato)zinc(II) complexes with chloride ions has also been made.[11]

In this paper we present the results of a systematic study into the gas-phase negative ion chemistry of a series of bis(acetylacetonato)metal(II)[12] complexes (metal = Co, Ni, Cu, Zn) in NF$_3$, CF$_2$Cl$_2$, and CF$_3$Br NCI plasmas.[10] As a class, acetylacetonate complexes are relatively well characterized so that much complementary information on their structure and reactivity in solution is available,[13,14] and aspects of their gas-phase negative ion chemistry have been established.[2,3,5,9,11] Abundant fluoride, chloride, and bromide ions may be generated in the gas phase by subjecting NF$_3$,[15] CF$_2$Cl$_2$,[16] and CF$_3$Br,[10] respectively, to dissociative electron capture under NCI conditions. Plasmas of these reagent gases also contain populations of thermalized electrons, halogen atoms, and halogenated methyl radicals, which may react with metal complexes in competition with the halide ions.[11]

The present work was undertaken to identify the products and reaction channels for competing electron/molecule, ion/molecule, and free-radical/molecule processes, to assess the influence of the halogenated plasmas on negative ion abundances, and to define the stability of the +2 oxidation state of the metals with respect to both reduction and oxidation, the Lewis acidity of the complexes, and the Brønsted basicity of the halide ions.

Experimental Section

The bis(acetylacetonato)metal(II) complexes of cobalt, nickel, copper, and zinc were obtained from the ROC/RIC Chemical Corp., Sun Valley, CA, and were vacuum-sublimed prior to use. The reagent gases, NF$_3$ (Spectra Gases, Newark, NJ) and CF$_2$Cl$_2$ and CF$_3$Br (Pacific Chemical Industries, Sydney, Australia), were used as purchased. In the absence of added analyte molecules, these reagent gases gave very simple NCI mass spectra in which 99% of the negative ion current was carried by $[F]^-$, $[Cl]^-$, or $[Br]^-$, respectively.

Negative ion mass spectra were obtained on a VG MM-16F single-focusing mass spectrometer fitted with a dual EI/CI ion source under conditions described previously[11] or specified in Table I. The influence of the filament emission current on the NCI mass spectra was determined by recording spectra at filament emission currents of 100–1000 μA in order to identify ions arising from radical processes.[17-19] Ions arising from radical/molecule reactions prior to ionization were distinguished from ion/radical reaction products by varying the ion source repeller potential between 0 and −20 V at a pressure of $\leq$0.01 Torr.[9,10]

An isotopic cluster simulation program[20] was used to confirm the empirical formulas assigned to the ions observed and to calculate the relative abundances of overlapping ion clusters.

Standard enthalpies of formation for gas-phase ions[21] and molecules[22,23] were used in all thermochemical calculations.

Results and Discussion

Consideration of the physical processes taking place in the NF$_3$, CF$_2$Cl$_2$, and CF$_3$Br reagent gas plasmas is necessary to an understanding of the chemistry that proceeds when metal complexes are introduced into these plasmas. Moderation of the energetic (50–100 eV) primary electron (e_p^-) beam by the reagent gases occurs initially by ionization reactions that produce positive ions and energy-moderated secondary electrons (e_s^-).[24] In the halo-

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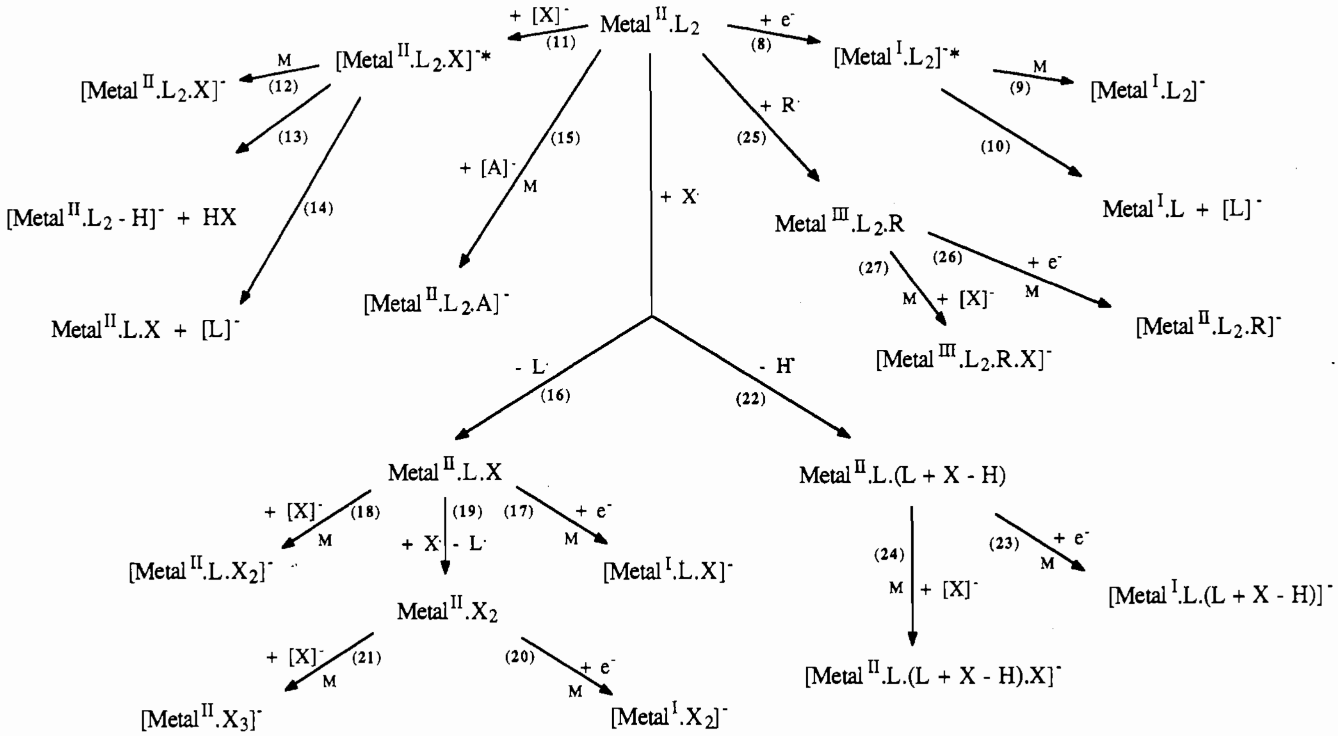
Scheme I



(M = stabilizing body)

genated reagent gases used in this study reactions 1–3 are significant.[25-27]

$$NF_3 + e_p^- \rightarrow [NF_2]^+ + F^\bullet + 2e_s^- \tag{1}$$

$$CF_2Cl_2 + e_p^- \rightarrow [CF_2Cl]^+ + Cl^\bullet + 2e_s^- \tag{2}$$

$$CF_3Br + e_p^- \rightarrow [CF_3]^+ + Br^\bullet + 2e_s^- \tag{3}$$

Electrons whose energy has been collisionally moderated to near-thermal values may undergo dissociative electron capture as shown in reactions 4–6.[28-32] These reactions are rapid: k_4

$$NF_3 + e_s^- \rightarrow [F]^- + {}^\bullet NF_2 \tag{4}$$

$$CF_2Cl_2 + e_s^- \rightarrow [Cl]^- + {}^\bullet CF_2Cl \tag{5}$$

$$CF_3Br + e_s^- \rightarrow [Br]^- + {}^\bullet CF_3 \tag{6}$$

$= 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} with thermal electrons[28] and 6×10^{-9} cm^3 molecule^{-1} s^{-1} with 1.3 eV;[29] $k_5 = 7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1};[28,30,31] $k_6 = 2 \times 10^{-8}$ cm^3 molecule^{-1} s^{-1}.[32]

Most of the charged particles formed initially in CI plasmas are consumed by loss mechanisms such as ion/electron and ion/ion recombination as well as collisions with the ion source surfaces.[33] In NF_3, CF_2Cl_2, and CF_3Br CI plasmas mutual ion/ion neutralization as generalized in reaction 7 may be expected to be a major loss mechanism, as such reactions typically have rate constants of 10^{-7}–10^{-8} cm^3 molecule^{-1} s^{-1}.[34,35] Radicals are

$$[A]^+ + [X]^- \rightarrow A^{\bullet *} + X^\bullet \tag{7}$$

NF_3: $A = NF_2$, $X = F$

CF_2Cl_2: $A = CF_2Cl$ and $CFCl_2$, $X = Cl$

CF_3Br: $A = CF_3$, $X = Br$

produced rapidly in each of the preceding reactions but, unlike charged particles, are destroyed only slowly once formed. The rate constant for recombination of two halogen atoms in the presence of a stabilizing molecule is of the order of 10^{-30}–10^{-34} cm^6 molecule^{-2} s^{-1} [36] and is therefore of negligible importance at 0.1 Torr pressure. Recombination reactions involving halogenated radicals such as $^\bullet NF_2$, $^\bullet CF_2Cl$, and $^\bullet CF_3$ are also relatively slow with rate constants of the order of 10^{-11} cm^3 molecule^{-1} s^{-1}.[36] Moreover, whereas every collision of a charged particle with an ion source surface leads to destruction of the charged particle,[33] only 0.01–1% of radical/surface collisions lead to loss of the radical.[37,38] From these considerations it may be concluded that the radical populations within CI plasmas of the halogenated reagent gases will be several orders of magnitude greater than the charged particle populations.[18]

NCI Mass Spectra of the Metal Complexes. Introduction of the bis(acetylacetonato)metal(II) complexes into the reagent gas plasmas leads to the formation of a considerable variety of metal-containing ions, many of which contain one or more halogen atoms. Table I lists the assignments and relative abundances of

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Table I. Percentage of Total Ion Current (TIC) Carried by Ions in the NF_3, CF_2Cl_2, and CF_3Br Negative Chemical Ionization Mass Spectra of the Bis(acetylacetonato)metal(II) Complexes[a-d]

	NF_3				CF_2Cl_2				CF_3Br			
ion	Co	Ni	Cu	Zn	Co	Ni	Cu	Zn	Co	Ni	Cu	Zn
$[\text{Metal}^{II}{}_x\cdot L_y\cdot X_z]^-$ [e]							0.5	2	0.1			1
$[\text{Metal}^{II}\cdot L_2\cdot A]^-$ [f]	9	3	0.7	13	0.3	0.1	0.1	1	2	2	1	1
$[\text{Metal}^{II}\cdot L_2\cdot X_2 - H]^-$					2	2	0.5	0.3	10	8	2	0.3
$[\text{Metal}^{III}\cdot L_2\cdot X\cdot R]^-$ [g]					0.3				10			
$[\text{Metal}^{II}\cdot L_2\cdot X]^-$	12	2	0.9	7	82	81	18	56	53	54	7	88
$[\text{Metal}^{II}\cdot L_2\cdot X - H]^-$					0.6	0.2	0.5					
$[\text{Metal}^{II}\cdot L_2\cdot R]^-$ [g]					0.1				1			
$[\text{Metal}^{I}\cdot L_2]^-$	0.1	2	7		0.9	6	25			0.2	52	
$[\text{Metal}^{II}\cdot L_2 - H]^-$	12	9	21	56	0.4	0.6	0.3	0.4	0.3	0.6	0.8	0.2
$[\text{Metal}^{II}\cdot L\cdot X_2]^-$	0.2	0.5		1	2	6	7	27	5	20	1	7
$[\text{Metal}^{I}\cdot L\cdot X]^-$					0.9	1	23		0.6		9	
$[\text{Metal}^{II}\cdot X_3]^-$					2	0.4	1	8	4	10		0.5
$[\text{Metal}^{I}\cdot X_2]^-$					0.5	0.4	22				9	
$[L + A']^-$ [h]	8	7	7	2	1	0.1	0.3	0.2	4	2	12	0.6
$[L + X - H]^-$	6	15	27	0.1	2	0.5	0.5	4	2	0.2	2	0.1
$[L]^-$	45	44	23	17	4	1	0.6	1	2	2	4	1
ligand fragments[i]	7	17	13	3	0.3	0.2	0.1	0.1	0.4	0.4	0.1	0.1
$[X]^-/\text{TIC}$ [j]	0.30	0.84	0.71	0.33	3.1	1.8	0.95	0.89	2.7	3.3	2.3	1.0
temp, °C	115	160	120	90	105	165	145	100	120	155	140	90

[a] Ion source pressure 0.1 Torr; filament emission current 500 μA; primary electron energy 50 eV; ion accelerating voltage −4 kV; ion source repeller voltage 0 to −1 V. [b] All isotopes of all atoms are included in the relative abundance of each ion. [c] $L = CH_3COCHCOCH_3$. [d] X = F, Cl, and Br, respectively, in the NF_3, CF_2Cl_2, and CF_3Br NCI mass spectra. [e] Cluster ions where $x = 2$ or 3 and $y + z = 2x + 1$. [f] A = L and ligand-related species such as (L + X − H); also includes HF_2 and CN in NF_3 mass spectra as well as F in CF_2Cl_2 and CF_3Br mass spectra. [g] R = CF_2Cl in CF_2Cl_2 mass spectra and CF_3 in CF_3Br mass spectra. [h] $A' = HX, X_2$. [i] Mainly $[L - H]^-$ and $[L - CH_3]^-$. [j] Ratio of the halide ion current to the total ion current arising from the metal complex.

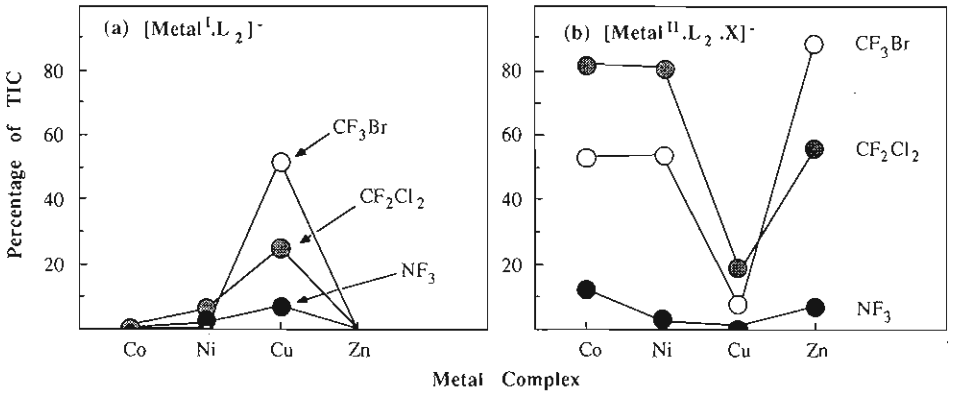

Figure 1. Percentage of total ion current (TIC) carried by (a) $[\text{Metal}^{I}\cdot L_2]^-$ and (b) $[\text{Metal}^{II}\cdot L_2\cdot X]^-$ in the NF_3, CF_2Cl_2, and CF_3Br NCI mass spectra of the bis(acetylacetonato)metal(II) complexes.

the ions identified in the NF_3, CF_2Cl_2, and CF_3Br NCI mass spectra of the metal complexes. Scheme I details the principal reaction pathways that are proposed to account for the observed negative ions. It is noteworthy that ion formation under the experimental conditions used may be attributed to three classes of bimolecular process, viz., electron/molecule and ion/molecule reactions as well as free-radical/molecule reactions followed by electron/molecule or ion/molecule ionization of the neutral products. As the ions formed by electron/molecule and ion/molecule encounters are likely to be excited due to the exothermicity of charge–polar interactions and bond formation, it is envisaged that collisional deactivation of the excited ions is necessary in each case to prevent decomposition of the ions by fragmentation or electron autodetachment.

(a) Electron/Molecule Reactions. Formation of the molecular ion, $[\text{Metal}^{I}\cdot L_2]^-$, occurs by the resonance electron capture/collisional deactivation sequence represented in reactions 8 and 9, Scheme I, where a thermalized electron is captured into a metal-based orbital, thereby effecting a one-electron reduction of the metal. This is a well-recognized gas-phase process with metal complexes[1] and has previously been noted to occur with the nickel[2,5,9] and copper[3,9] acetylacetonate complexes. The relative abundance of the respective $[\text{Metal}^{I}\cdot L_2]^-$ ions in each of the reagent gases suggests that the cross section for the resonance electron capture process decreases in the order Cu > Ni > Co and is negligible for the zinc complex (Figure 1a). Under NCI ion source conditions where methane was used as the electron energy moderation and collisional stabilization gas, a similar decrease in the molecular ion current generated with these complexes was noted.[9] Hence, it seems probable that the electron affinity of these complexes decreases in the same order and reflects the stability of the +2 oxidation state of each metal with respect to reduction to the +1 state.

(b) Ion/Molecule Reactions. Each of the mass spectra contains a halide adduct ion, $[\text{Metal}^{II}\cdot L_2\cdot X]^-$. These adducts are the most abundant ions in the CF_2Cl_2 and CF_3Br NCI mass spectra of the cobalt, nickel, and zinc complexes. As the metal complexes are coordinatively unsaturated and exhibit well-established Lewis acid properties in solution,[13,14] it is probable that the adduct ions are five-coordinate species formed by addition of a halide ion to a vacant coordination site at the metal followed by collisional stabilization (reactions 11 and 12). Compared to resonance electron capture, addition of a halide ion to the acetylacetonate complexes is significantly less dependent upon the nature of the metal, since, with the exception of the copper complex, the relative abundances of the $[\text{Metal}^{II}\cdot L_2\cdot X]^-$ ions for a given halide are similar (Figure 1b). Although the relative abundance of the halide adduct ion is comparatively low in each of the spectra of the copper complex,

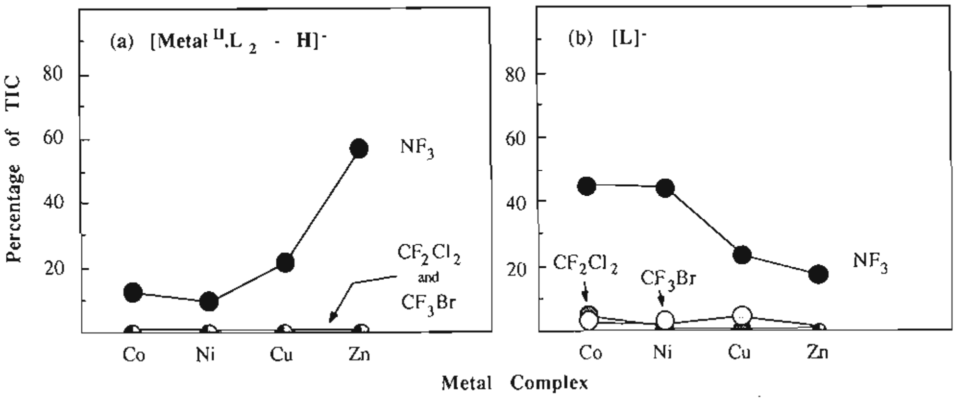

Figure 2. Percentage of total ion current (TIC) carried by (a) $[\text{Metal}^{II}\cdot L_2 - H]^-$ and (b) $[L]^-$ in the NF_3, CF_2Cl_2, and CF_3Br NCI mass spectra of the bis(acetylacetonato)metal(II) complexes.

this may be attributed largely to the high relative abundance of the molecular ion in these spectra and cannot be taken as an indication that the copper complex has a lower affinity for halide ions than the other complexes. The similarity in the halide ion affinities of the complexes is of interest in view of the differing structures of the metal complexes[39] and suggests that structure does not have a major difference on the halide ion affinities.

Although the fluoride ion binds to most molecules more tightly than the other halide ions,[44-47] the abundances of the $[\text{Metal}^{II}\cdot L_2\cdot F]^-$ ions are low compared with those of the corresponding chloride and bromide adduct ions. This is associated with the comparatively high relative abundances of the $[\text{Metal}^{II}\cdot L_2 - H]^-$ and $[L]^-$ ions in the NF_3 mass spectra (Figure 2). It is evident that the excited fluoride adduct formed in reaction 11, $[\text{Metal}^{II}\cdot L_2\cdot F]^{-*}$, has two fragmentation channels available, reactions 13 and 14, which are closed to the excited chloride and bromide adduct ions.

In competition with collisional stabilization, $[\text{Metal}^{II}\cdot L_2\cdot F]^{-*}$ may dispose of its excess energy by elimination of a molecule of HF to produce $[\text{Metal}^{II}\cdot L_2 - H]^-$ (reaction 13). A metastable peak arising from this elimination was particularly prominent in the NF_3 mass spectrum of the cobalt complex. Abstraction of a methyl proton from the metal complexes in this manner may be likened to removal of a methyl proton from acetone since in both cases, the negative charge produced upon deprotonation is stabilized by the neighboring carbonyl group. Of the halide ions, only the fluoride ion is a Brønsted base sufficiently strong to abstract a proton exothermically from acetone in the gas phase.[21] Similar thermochemistry may be expected with proton abstraction from the acetylacetonate complexes and is therefore consistent with the high relative abundance of the $[\text{Metal}^{II}\cdot L_2 - H]^-$ ion in the NF_3 NCI mass spectra.

Alternatively, $[\text{Metal}^{II}\cdot L_2\cdot F]^{-*}$ may eliminate a $\text{Metal}^{II}\cdot L\cdot F$ molecule to produce $[L]^-$ (reaction 14). By an approximation of the heat of formation of the respective $\text{Metal}^{II}\cdot L\cdot X$ complexes as $\Delta H_f^\circ(\text{Metal}^{II}\cdot L\cdot X) = [\Delta H_f^\circ(\text{Metal}^{II}\cdot L_2) + \Delta H_f^\circ(\text{Metal}^{II}\cdot X_2)]/2$, it is estimated that nucleophilic ligand displacement of $[L]^-$ by $[F]^-$ is exothermic or nearly thermoneutral with each of the complexes when X = F, with enthalpies in the range +1.2 to −9.9 kcal mol^{-1}.[21,23] In contrast, the analogous reactions of the other halides are substantially endothermic, with estimated enthalpies in the ranges +16.5 to +25.5 kcal mol^{-1} for the chloride ion and +21.1 to +31.3 kcal mol^{-1} for the bromide ion.[21,23]

Since the enthalpy of proton abstraction involving a methyl proton remote from the metal may be expected to be less dependent on the metal than nucleophilic ligand substitution at the metal, it may be expected that the $[L]^-/[\text{Metal}^{II}\cdot L_2 - H]^-$ ion ratios in the NF_3 mass spectra should increase as the exothermicity of the ligand displacement reaction increases, i.e. Ni > Co > Zn > Cu. Although the order for Cu and Zn is reversed, this is in reasonable agreement with the $[L]^-/[\text{Metal}^{II}\cdot L_2 - H]^-$ ion ratios observed: Ni, 4.9 > Co, 3.8 > Cu, 1.1 > Zn, 0.3.

(c) Radical/Molecule Reactions. Ions attributed to radical/molecule reactions prior to ionization are a particularly noteworthy feature of the NCI mass spectra. A number of previous studies have demonstrated that, in CI plasmas generated from hydrocarbon reagent gases such as methane or isobutane, some molecules may react with radicals at a rate that is competitive with the rate of ionization, whereupon the CI mass spectra may contain "anomalous" ions arising from subsequent ionization of the radical/molecule reaction products.[7-9,17-19] Such ions form because CI plasmas contain radical concentrations that are orders of magnitude higher than the ion and electron concentrations.[18] Fortunately, ions arising from radical reactions may be identified readily by changing the primary electron current, since the relative abundance of such ions increases with the flux of primary electrons projected into the ion source.[17,18] Radical/molecule and ion/radical processes may be distinguished by varying the ion source repeller potential at reduced pressure.[9]

Formation of the ions $[\text{Metal}^{I}\cdot L\cdot X]^-$, $[\text{Metal}^{II}\cdot L\cdot X_2]^-$, $[\text{Metal}^{I}\cdot X_2]^-$, and $[\text{Metal}^{II}\cdot X_3]^-$ is attributed to halogen radical/molecule displacement reactions.[11] These ions are most prominent in the CF_2Cl_2 and CF_3Br NCI spectra and have abundances that increase markedly relative to those of $[\text{Metal}^{I}\cdot L_2]^-$ and $[\text{Metal}^{II}\cdot L_2\cdot X]^-$ as the primary electron current is increased.[11] Since the relative abundances of the ions are not influenced by the voltage applied to the ion source repeller plate, it is concluded that radical/molecule reactions rather than ion/radical processes are involved. Reactions 16–21 are proposed to account for the formation of the observed ions. Prior to ionization, a proportion of the metal complex molecules may react with halogen radicals, leading to displacement of $L^\bullet$ and production of the mixed-ligand complex $\text{Metal}^{II}\cdot L\cdot X$ (reaction 16). It is estimated that for X = Cl, reaction 16 is exothermic with each of the metal complexes with enthalpies in the range −1.6 to −10.6 kcal mol^{-1}.[22,23] With X = Br, the estimated enthalpies are somewhat less favorable (−0.2 to +9.9 kcal mol^{-1}), but this may be due to a low estimate[23] for the heat of formation of the acetylacetonate free radical arising from an underestimate of the degree of resonance stabilization in the radical. As with the parent complex, $\text{Metal}^{II}\cdot L\cdot X$ may be ionized by either resonance electron capture or halide addition to produce $[\text{Metal}^{I}\cdot L\cdot X]^-$ and $[\text{Metal}^{II}\cdot L\cdot X_2]^-$, respectively (reactions 17 and 18). Alternatively, the $\text{Metal}^{II}\cdot L\cdot X$ molecule may react with a second halogen radical to produce a molecule of the metal halide, $\text{Metal}^{II}\cdot X_2$ (reaction 19). Ionization of $\text{Metal}^{II}\cdot X_2$ by resonance electron capture and halide addition accounts for the formation of $[\text{Metal}^{I}\cdot X_2]^-$ and $[\text{Metal}^{II}\cdot X_3]^-$, respectively

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(reactions 20 and 21). It is noteworthy that with each complex, both $\mathrm{Metal^{II}\cdot L\cdot X}$ and $\mathrm{Metal^{II}\cdot X_2}$ follow the same ionization patterns as $\mathrm{Metal^{II}\cdot L_2}$. Thus, $\mathrm{Cu^{II}\cdot L_2}$, $\mathrm{Cu^{II}\cdot L\cdot X}$, and $\mathrm{Cu^{II}\cdot X_2}$ all tend to favor ionization by resonance electron capture whereas ionization of $\mathrm{Zn^{II}\cdot L_2}$, $\mathrm{Zn^{II}\cdot L\cdot X}$, and $\mathrm{Zn^{II}\cdot X_2}$ occurs exclusively by ion/molecule processes.

The absence of $[\mathrm{Metal^{II}\cdot F_3}]^-$, $[\mathrm{Metal^{I}\cdot L\cdot F}]^-$, and $[\mathrm{Metal^{I}\cdot F_2}]^-$ ions in the NF_3 NCI mass spectra suggests that atomic fluorine may have reaction channels open to it, such as hydrogen atom abstraction, that are more exothermic than the ligand displacement channel. Again, by use of the reaction with acetone as a guide to the likely enthalpy of the reactions involving the metal complexes, it is calculated that abstraction of a methyl hydrogen atom from acetone by $F^\bullet$ is exothermic by 38.0 kcal mol^{-1}.[22] This is substantially more exothermic than the enthalpy values calculated for the displacement of an acetylacetonate radical from the complexes by $F^\bullet$, which fall in the range −20.6 to −31.7 kcal mol^{-1}.[22] Consequently, some of the $[\mathrm{Metal^{II}\cdot L_2} - \mathrm{H}]^-$ ions formed in the NF_3 plasma may arise due to hydrogen atom abstraction followed by resonance electron capture.

Formation of ions of the type $[\mathrm{Metal^{I}\cdot L_2X} - \mathrm{H}]^-$ and $[\mathrm{Metal^{II}\cdot L_2\cdot X_2} - \mathrm{H}]^-$ indicates that halogen radicals also react with the metal complexes by an alternative reaction pathway involving homolytic substitution at a ligand methine carbon,[13] reaction 22. This produces a molecule of the form $(\mathrm{Metal^{II}\cdot L_2\cdot X} - \mathrm{H})$, which may be ionized by resonance electron capture or nucleophilic halide addition to form $[\mathrm{Metal^{I}\cdot L_2\cdot X} - \mathrm{H}]^-$ and $[\mathrm{Metal^{II}\cdot L_2\cdot X_2} - \mathrm{H}]^-$, respectively (reactions 23 and 24).

As CF_2Cl_2 and CF_3Br plasmas contain populations of the halogenated methyl radicals $^\bullet CF_2Cl$ and $^\bullet CF_3$, respectively, formation of the ions $[\mathrm{Metal^{II}\cdot L_2\cdot R}]^-$ and $[\mathrm{Metal^{III}\cdot L_2\cdot R\cdot X}]^-$, where R corresponds to CF_2Cl in the CF_2Cl_2 NCI mass spectra and CF_3 in the CF_3Br spectra, is attributed to radical/molecule reactions involving these halogenated methyl radicals. The adduct ions are observed only in the mass spectra of the cobalt complex. In a previous study[7,8] we demonstrated that certain cobalt(II) complexes including bis(acetylacetonato)cobalt(II) trap alkyl radicals in methane NCI plasmas to produce alkyl adduct molecules, which may be ionized to yield alkyl adduct negative ions. One-electron oxidative addition of an alkyl radical to the metal followed by resonance electron capture ionization of the product was indicated as the source of the alkyl adduct ions. Oxidative addition of halogenated methyl radicals to the cobalt complex in the CF_2Cl_2 and CF_3Br plasmas, reaction 25, is clearly analogous to the addition of methyl and other alkyl radicals in methane NCI plasmas. Ionization of the five-coordinate $\mathrm{Metal^{III}\cdot L_2\cdot R}$ molecule by resonance electron capture produces $[\mathrm{Metal^{II}\cdot L_2\cdot R}]^-$, while nucleophilic halide addition yields six-coordinate $[\mathrm{Metal^{III}\cdot L_2\cdot R\cdot X}]^-$ (reactions 26 and 27). This reaction sequence is prevalent with the cobalt complex because of the accessibility of the cobalt +3 oxidation state.

Cluster ions of the form $[\mathrm{Metal^{II}}_x\cdot \mathrm{L}_y\cdot \mathrm{X}_z]^-$ ($x = 2$ or 3; $y + z = 2x + 1$) are a further feature of the mass spectra. These ions are most prominent in the CF_2Cl_2 and CF_3Br mass spectra of the zinc complex, and their occurrence may be explained in terms of ion/molecule reactions between metal-containing ions and neutrals in the plasmas. For example, clustering of $[\mathrm{Metal^{II}\cdot L_2\cdot X}]^-$ with $\mathrm{Metal^{II}\cdot L_2}$, $\mathrm{Metal^{II}\cdot L\cdot X}$, and $\mathrm{Metal^{II}\cdot X_2}$ accounts for the formation of $[\mathrm{Metal^{II}_2\cdot L_4\cdot X}]^-$, $[\mathrm{Metal^{II}_2\cdot L_3\cdot X_2}]^-$, and $[\mathrm{Metal^{II}_2\cdot L_2\cdot X_3}]^-$, respectively. Further clustering of these ions is the probable source of ions containing three metal atoms. Formation of these clusters indicates the presence of neutral species such as $\mathrm{Metal^{II}\cdot X_2}$ in the plasmas.

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Registry No. $\mathrm{Co^{II}\cdot L_2}$, 14024-48-7; $\mathrm{Ni^{II}\cdot L_2}$, 3264-82-2; $\mathrm{Cu^{II}\cdot L_2}$, 13395-16-9; $\mathrm{Zn^{II}\cdot L_2}$, 14024-63-6; NF_3, 7783-54-2; CF_2Cl_2, 75-71-8; CF_3Br, 75-63-8; $[F]^-$, 16984-48-8; $[Cl]^-$, 16887-00-6; $[Br]^-$, 24959-67-9; CF_2Cl, 1691-89-0; CF_3, 2264-21-3; proton, 12408-02-5; hydrogen, 1333-74-0.

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Thermochemistry of Rare-Earth-Metal–Alkaline-Earth-Metal–Copper Oxide Superconductors[†]

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Enthalpies of formation of the perovskite-related oxides La_2CuO_4, $La_{1.85}Sr_{0.15}CuO_4$, and $YBa_2Cu_3O_y$ (y = 6.25, 6.47, 6.69, and 6.93) have been determined at 298.15 K by solution calorimetry. Room-temperature stabilities of these compounds have been assessed in terms of the parent binary oxides and of the oxygen content. High-temperature (to 900 °C) thermal behavior of $YBa_2Cu_3O_y$ has been used to determine thermodynamic properties (partial molal enthalpy, free energy, and entropy of oxygen) of this material in order to characterize the quenched state in relation to the high-temperature equilibrium state. The thermochemistry of oxygen has been used to interpret the relationship between the oxygen partial pressure and the defect chemistry in the nonstoichiometric phase of $YBa_2Cu_3O_y$. The relevance of the defect chemistry to conductivity is discussed.

Introduction

It has sometimes been asserted that the stability of a complex oxide or fluoride (as opposed to a double oxide or fluoride, the difference being the ability to identify a discrete polyatomic cluster in a complex compound) is greater than the sum of the parent binary oxides by virtue of a larger Madelung constant[1] or because of an acid–base difference in the parent oxides.[2] It is also often observed that cations of high oxidation state can be stabilized in complex salts.[3] The ease of preparation of the two classes of high-temperature superconducting oxides now known,[4] at least to the degree of purity defined by single-phase X-ray powder

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