precursors, have also been observed in high-energy (keV CAD) experiments, again suggesting that the common ion a is sampled. The major difference between the low-energy (eV CAD and SID) and high-energy (keV CAD) daughter spectra of $C_2H_3S^+$, the methyl cation (CH_3^+) abundance, is not due to different extents of activation but, it is proposed, to fragmentation via an excited electronic state in those CAD experiments that proceed via electronic excitation. Supporting evidence is presented from angle-resolved experiments, that CH_3^+ is generated competitively by vibrational excitation, a process which is expected to become increasingly favorable, compared with electronic excitation, at nonzero scattering angles.

It can be expected that excitation to still higher internal energies than those used here should make it possible to sample those $C_2H_3S^+$ ions that retain the original $C_2H_3S^+$ structures prior to activation and so lead to characteristically different daughter ion spectra. Not only does this study account for the remarkable difference between the high- and low-energy CAD and SID data but it accommodates the fact that the ion/molecule reactions also suggest a thioacylium structure. A further, although tentative, conclusion that emerges from this work is that the polyatomic ion/surface collisions studied lead chiefly to vibrational excitation of the $C_2H_3S^+$ ion.

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Gas-Phase Reactions of Fe^- and Co^- with Simple Thiols, Sulfides, and Disulfides by Fourier Transform Mass Spectrometry

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Abstract: Fe^- and Co^- are found to react with simple thiols, sulfides, and disulfides. The primary reaction products formed from these metal anions, M^-, and thiols include MS^-, MSH^-, and MSH_2^- and suggest a mechanism involving initial insertion of the metal into the weak C–S bond. Similarly, C–S insertion is the main mode of attack in the reactions with the sulfides and disulfides, in analogy to what is observed for the reaction of metal cations. Collision-induced dissociation is used to support the proposed structures for the primary products, $H-Fe^--SH$ and Fe^--SH. Some of the thermochemical data derived from this study include $D°(M^--S) > 103$ kcal/mol and $D°(M^--SH) = 83 \pm 9$ kcal/mol. Finally, a brief survey of the reactivity of V^-, Cr^-, and Mo^- with selected organosulfur compounds is also reported.

The ion–molecule chemistry of atomic and coordinated metal ions has proven to be a very rich and active area over the past decade. The incentives for these studies include the fact that organometallic compounds and ions are becoming increasingly recognized as essential components in a variety of environmental, chemical, and biological systems.[1] Another major factor fueling the considerable effort dedicated to gas-phase metal ion chemistry is that it provides fundamental kinetic, mechanistic, and thermodynamic information[2] that is crucial to the understanding of catalytic reaction mechanisms.

A considerable data base has already been obtained from gas-phase studies of atomic and molecular metal cations, including homolytic and heterolytic metal–hydrogen, metal–carbon, and metal–oxygen bond strengths[2,3-11] and relative ligand binding energies.[12-17] In addition, gas-phase Lewis basicities,[18-20] hydride affinities,[21,22] electron affinities,[23-27] and ionization potentials[5,13,28] for neutral transition-metal complexes have been obtained.

The majority of studies on gas-phase metal ion chemistry have involved metal cations,[29] primarily due to the ease of their formation. In particular we have shown that laser desorption on pure metal targets is a convenient method of generating virtually any atomic metal cation for study by Fourier transform mass spectrometry.[30-32] The scope of this work has continued to expand to include not only the ion–molecule reactions of the atomic metal cations with various organic molecules but also the chemistry of a variety of ligated metal cations[33-36] and small metal cluster ions.[37-40]

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Until fairly recently,[41-46] reports of gas-phase ion–molecule reactions involving anionic transition-metal complexes have been limited[1,3,14,19,20,45-54] primarily to metal carbonyls or carbonyl derivatives that are volatile enough to easily be introduced into the mass spectrometer and which are efficiently ionized by dissociative electron capture.[55] Studies with these compounds have included cluster reactions,[45-48] ligand displacement,[14] gas-phase acidity measurements,[19,56] oxidative addition,[44] hydride transfer,[43] and oxidation[42] to name a few. Transient intermediates that aid in verifying various catalytic mechanisms have also been determined through the use of gas-phase, anionic metal carbonyls.[41]

Although research on metal complexes has grown rapidly within the last few years, ion–molecule reactions involving atomic metal anions have only recently been introduced through a novel technique utilizing Fourier transform mass spectrometry collision-induced dissociation (FTMS–CID) of metal carbonyl anions.[3,57] Using this methodology, we published the first gas-phase reactions involving bare atomic metal anions with organics.[57] These reactions were primarily proton abstraction reactions used to bracket homolytic and heterolytic M–H bond energies. During the course of this study, it was discovered that metal anions react with organosulfur compounds by pathways other than simple proton abstraction, charge transfer, or dissociative charge transfer. This paper details these reactions and, whenever possible, provides thermochemical information.

Table I. Product Distribution for the Reactions of Fe^- and Co^- with Thiols

reactant	product[a]	neutral loss	relative[b] abundance		secondary products[a]
			Fe^-	Co^-	
H_2S	MS^-	H_2	100	100	MSS^-, $MSSH^-$
MeSH	MS^-	CH_4	25	63	$MSSH^-$
	MSH^-	$CH_3^\bullet$	75	37	$MSSCH_3^-$
EtSH	MS^-	C_2H_6	29	36	$MSSH^-$
	MSH^-	$C_2H_5^\bullet$	46	26	$MSSC_2H_5^-$
	MSH_2^-	C_2H_4	25	38	$HSCoSC_2H_5^-$
n-PrSH	MS^-	C_3H_8	30	31	$MSSH^-$
	MSH^-	$C_3H_7^\bullet$	20	13	$MSSC_3H_7^-$
	MSH_2^-	C_3H_6	50	56	$HSCoSC_3H_7^-$
i-PrSH	MS^-	C_3H_8	21	18	$MSSH^-$
	MSH^-	$C_3H_7^\bullet$	50	44	$MSSC_3H_7^-$
	MSH_2^-	C_3H_6	29	38	$HSCoSC_3H_7^-$
n-BuSH	MS^-	C_4H_{10}	33	32	$MSSH^-$
	MSH^-	$C_4H_9^\bullet$	14	10	$FeSSC_4H_9^-$
	MSH_2^-	C_4H_8	53	58	$HSCoSC_4H_9^-$, $CoSC_2H_4^-$
s-BuSH	MS^-	C_4H_{10}	14	12	$MSSH^-$
	MSH^-	$C_4H_9^\bullet$	47	34	$MSSC_4H_9^-$
	MSH_2^-	C_4H_8	39	54	$HSCoSC_4H_9^-$, $CoSC_2H_4^-$
t-BuSH	MS^-	C_4H_{10}	4	—	—
	MSH^-	$C_4H_9^\bullet$	88	94	$MSSC_4H_9^-$
	MSH_2^-	C_4H_8	8	6	—
PhSH	PhS^-	MH[a]	34	10	—
	MS^-	C_6H_6	66	90	MS_2^-
$PhCH_2SH$	MS^-	C_7H_8	56	72	MS_2H^-
	MSH^-	$C_7H_7^\bullet$	44	22	$MSSC_7H_7^-$
	MSH_2^-	C_7H_6	—	6	—

[a] M represents either iron or cobalt. [b] All values are given as percentages and are within 5%.

Experimental Section

The theory and instrumental techniques regarding Fourier transform mass spectrometry are well documented in the literature.[58-63] All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer.[32] The instrument is equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15 in. electromagnet maintained at 0.9 T. The cell is contained within a bakeable vacuum chamber that is directly pumped by using a 5 in. Alcatel diffusion pump with a background pressure of $\sim 1 \times 10^{-8}$ Torr. Trapping plate potentials were maintained at −2.5 V for trapping negative ions and generally at +1.8 V for positive ions.

All chemicals in this study were obtained commercially and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases from the liquid samples. Positive ion spectra revealed no detectable impurities. The samples were introduced into the FTMS cell by means of a leak valve to pressures of approximately 6×10^{-7} Torr. Sulfides that are classified as unreactive with Fe^- and Co^- have rate constants $<1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Argon was used as the target gas for collision-induced dissociation at approximately 6×10^{-6} Torr. The metal carbonyls were introduced via leak valves until a moderate signal was observed while monitoring the real time transient in the negative ion mode (duty cycle ca. 200 ms). This corresponded to a pressure in the mid-10^{-8} Torr range. Pressure monitoring was performed with an uncalibrated Bayard-Alpert ionization gauge.

Generation of bare metal anions by FTMS–CID has been previously described[3,57] and is summarized here. The experimental pulse sequence

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Table II. A Comparison between the Primary Ion Product Distribution for Co^- and Co^+

reactant	product[a]	neutral(s)	relative abundance[b] Co^-	relative abundance[b] Co^+
MeSH	MS	CH_4	63	70
	MSH	CH_3	37	—
	MCH_2S	H_2	—	30
EtSH	MS	C_2H_6	36	—
	MSH	$C_2H_5^•$	26	7
	MSH_2	C_2H_4	38	23
	MC_2H_4	H_2S	—	70
n-PrSH	MS	C_3H_8	31	—
	MSH	$C_3H_7^•$	13	—
	MSH_2	C_3H_6	56	15
	MC_3H_6	H_2S	—	70
	MCH_3SH	C_2H_4	—	5
	C_3H_7	MSH	—	10
i-PrSH	MS	C_3H_8	18	—
	MSH	$C_3H_7^•$	44	—
	MSH_2	C_3H_6	38	44
	MC_3H_6	H_2S	—	30
	C_4H_9	MSH	—	26
n-BuSH	MS	C_4H_{10}	32	—
	MSH	$C_4H_9^•$	10	—
	MSH_2	C_4H_8	58	7
	MC_2H_4	EtSH	—	7
	MC_4H_6	H_2S, H_2	—	39
	MC_4H_8	H_2S	—	8
	MC_2H_5SH	C_2H_4	—	5
	MC_4H_8S	H_2	—	14
	C_4H_9	MSH	—	20
s-BuSH	MS	C_4H_{10}	12	—
	MSH	C_4H_9	34	—
	MSH_2	C_4H_8	54	21
	MC_3H_6	MeSH	—	5
	MC_4H_6	H_2S, H_2	—	34
	MC_4H_8	H_2S	—	12
	MC_4H_8S	H_2	—	8
	C_4H_9	MSH	—	20
t-BuSH	MS	C_4H_{10}	—	—
	MSH	$C_4H_9^•$	94	—
	MSH_2	C_4H_8	6	13
	MC_4H_8	H_2S	—	73
	C_4H_9	MSH	—	14

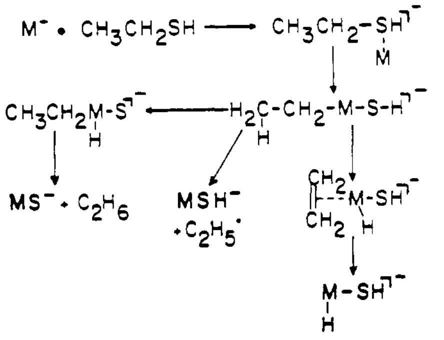
[a] The species in this column represents either an anion or a cation depending on whether the reactant is Co^- or Co^+, respectively. [b] Values are given as percentages. Positive ion values are from ref 64. "—" represents "no product observed".

was initiated by a 150 ms, 12.9 V electron beam pulse on either $Fe(CO)_5$ or $Co_2(CO)_8$. This resulted in dissociative electron attachment of secondary electrons to yield predominately $Fe(CO)_4^-$ or $Co(CO)_4^-$. Excellent signals have also been observed following electron production from a pulsed laser beam on a metal target.[64] After 100 ms, the dissociative electron detachment product was irradiated at its cyclotron frequency for 100 μs with an 18.5 V CID pulse. A 100-ms CID interaction time allowed for the subsequent collision and fragmentation of this species. The bare metal anion was then isolated from the parent and other daughter ions by use of a broad-band double resonance ejection pulse swept at 20 Hz/μs with a pulse amplitude of 23.2 V. Next, the metal anion was permitted to interact with a reagent gas for a variable reaction time between 3 ms and 3 s, followed by detection and cell quenching. Product precursors were identified by ejection prior to the reaction period or by continuous ejection throughout the entire reaction time. Additional double resonance pulses allowed isolation of reaction products to study their subsequent reactions and permitted CID of the reaction products. Metal anions produced by this method undoubtedly have a range of kinetic energies. Although the relatively high pressure of Ar present provided for some collisional cooling, the presence of "hot ion" reactions cannot be completely ruled out.

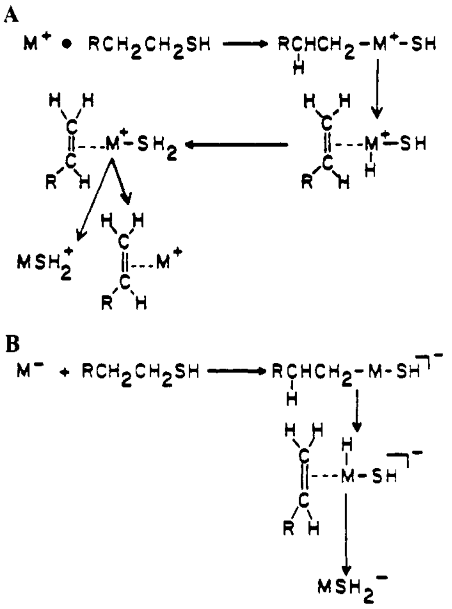
Results and Discussion

Thiols. The reaction products formed from metal anions and thiols, together with their relative abundances, are listed in Table I. The primary products, MS^-, MSH^-, and MSH_2^- (where M is the metal), can be entirely ascribed in terms of oxidative addition to the weak C–S bond, which ranges from 69 kcal/mol for *t*-BuSH to 75 kcal/mol for MeSH.[65] These values can be compared to an RS–H bond energy of ~92 kcal/mol.[65]

Scheme I



Scheme II



Hydrogen sulfide, the simplest sulfur-containing compound, displays a similar reactivity to the thiols. Fe^- and Co^- both react with H_2S to give MS^- as the exclusive product (reaction 1). One possible mechanism for this reaction is oxidative insertion into

$$M^- + H_2S \rightarrow MS^- + H_2 \qquad (1)$$

the H–SH bond followed by an α-H shift from the sulfur to the metal and reductive elimination of hydrogen. A similar mechanism has been proposed for metal cations with thiols,[64] although there is no reason intuitively to expect that anions and cations should react identically. Another interesting possibility is that, due to its greater electronegativity, sulfur acquires the majority of the negative charge upon anion coordination and, thus, it may be the neutral metal atom that actually undergoes the insertion and is responsible for the S–H bond cleavage.

Secondary reactions of MS^- with H_2S were observed and include not only reductive elimination of H_2, reaction 2, but also

$$MS^- + H_2S \rightarrow MS_2^- + H_2 \qquad (2)$$

$$MS^- + H_2S \rightarrow MS_2H^- + H^• \qquad (3)$$

M = Fe and CO

HS abstraction, reaction 3. As discussed below, this suggests that the sulfur ligand enhances the bonding of HS to M^-.

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The reactions of Fe⁻ and Co⁻ with ethanethiol are characteristic of reactions involving these metal anions with alkyl thiols. Alkane elimination (reaction 4), HS abstraction (reaction 5), and alkene loss (reaction 6; except for methanethiol where an unfavorable methylene loss would be required) are observed. A proposed mechanism is given in Scheme I. A comparison between the ion–molecule products of Co⁻ and Co⁺[64] with thiols is given in Table II. Although the products are clearly different, they can be explained as arising from similar mechanisms, as shown in Scheme II. Both mechanisms involve an initial oxidative insertion into the C–S bond, which can result in direct cleavage and formation of MSH cation or anion. Although this is a less favorable pathway for the metal cations, direct cleavage is observed with the charge frequently being retained by the alkyl fragment. For example, in the reaction between Co⁺ and C_3H_7SH, $C_3H_7^+$ retains the charge since the ionization potential is less for $C_3H_7^\bullet$ than CoSH.[64] The major difference between the cation and the anion mechanisms involves hydrogen transfer from the metal to the sulfur forming an alkene–M⁺–H_2S complex for the cationic system [refer to Scheme II] which can lose either the alkene or the H_2S ligand. In the metal anion system, the absence of the products alkene–M⁻ and H_2S^-, that would foreseeably arise from the corresponding anionic complex, alkene–M⁻–H_2S, implies that the alkene does not coordinate well with the anion and is assumed to be lost immediately upon hydrogen transfer (refer to Scheme IIB).

$$
\begin{aligned}
M^- + CH_3CH_2SH &\longrightarrow MS^- + C_2H_6 && (4)\\
&\longrightarrow MSH^- + CH_3CH_2^\bullet && (5)\\
&\longrightarrow MSH_2^- + C_2H_4 && (6)
\end{aligned}
$$

M = Fe and Co

Although most of the excess energy is believed to accompany the expulsion of ethylene, if MSH_2^- still has sufficient internal energy, it will undergo dehydrogenation to yield MS⁻. This is supported by CID of $FeSH_2^-$ which yields predominantly rearrangement to form FeS⁻ (reaction 7) at low collision energies. As the collision energy increases, HS⁻ becomes the dominant daughter ion which can further fragment to give S⁻ at still higher energies (reaction 8). These data also suggest the structure [H–Fe–SH]⁻, since a rearrangement of either $Fe(H_2S)^-$ or H_2FeS^- to give HS⁻ at high CID energies is doubtful. Although neutrals cannot be detected in FTMS, the lack of ions corresponding to either H loss (FeSH⁻) or Fe loss (H_2S^-) at any attainable collision energy supports FeH loss from HFeSH⁻ by direct cleavage in reaction 8 as opposed to simultaneous Fe and H loss.

$$FeSH_2^- \xrightarrow[\text{low } E]{\text{CID}} FeS^- + H_2 \qquad (7)$$

$$FeSH_2^- \xrightarrow[\text{high } E]{\text{CID}} FeH + SH^-, \quad SH^- \longrightarrow S^- + H \qquad (8)$$

Burinsky, Fukuda, and Compana demonstrated that CID of negative ion complexes can be utilized to determine gas-phase electron affinities[66] in a method analogous to that used by Cooks and Kruger to determine relative gas-phase acidities from CID of proton-bound dimers.[67] McLuckey and Cooks[68] have established that certain criteria must be met regarding the use of this kinetic method. One of the major requirements is that the ion must be loosely and not covalently bound for proton affinity measurements. In the case of electron affinities, it may be possible to quickly establish a statistical charge distribution within the ion–molecule complex. This would result in product ion abundances that are representative of the relative electron affinity of the fragments even though direct cleavage of a covalent bond may be involved. An analogous treatment of cations was performed by Armentrout and Beauchamp to bracket the ionization potentials of CoH and $CoCH_3$ with ion–molecule reactions.[5] Observation of HS⁻ and not FeH⁻ from CID of HFeSH⁻ does reflect the relative electron affinities of the fragments with EA(SH) = 53.4 kcal/mol[69] and EA(FeH) = 21.5 kcal/mol.[27] Once again, it is doubtful that the structure is $[Fe(H_2S)]^-$ since H_2S^- (EA(H_2S) = 25.6 kcal/mol[65]) was not observed at higher CID energies which favor cleavage.

Collision-induced dissociation of FeSH⁻ yields Fe loss exclusively at moderate CID energies, reaction 9. Again, the products observed could have been predicted considering EA(HS) > EA(Fe). This supports an [Fe–SH]⁻ structure, but it does not rule out the possibility that the HS⁻ daughter ion might arise as a rearrangement product of [H–Fe–S]⁻.

$$FeSH^- \xrightarrow{\text{CID}} Fe + SH^-, \quad SH^- \longrightarrow S^- + H \qquad (9)$$

Secondary reactions of MS⁻ and MSH⁻ (M = Fe or Co) with ethanethiol are also observed. Reaction 10 is assumed to proceed by initial C–S insertion followed by ethyl radical loss. The structure of MS(SEt)⁻ and the mechanism for reaction 11 are unknown. The reaction may involve C–S bond insertion followed by two α-hydrogen shifts from the sulfurs to the metal and reductive elimination of H_2. Insertion into the S–H bond may also occur. CID of MS(SEt)⁻ formed in reaction 11 is similar to CID of MSSEt⁻ formed by the reaction of M⁻ with EtSSEt discussed below. $FeSH_2^-$ is unreactive, but $CoSH_2^-$ undergoes reaction 12 with ethanethiol.

$$MS^- + EtSH \rightarrow MS_2H^- + Et^\bullet \qquad (10)$$

$$MSH^- + EtSH \rightarrow MS(SEt)^- + H_2 \qquad (11)$$

$$CoSH_2^- + EtSH \rightarrow EtSCoSH^- + H_2 \qquad (12)$$

The primary and secondary reactions of Fe⁻ and Co⁻ with the larger thiols presented in Table I are similar to the corresponding ethanethiol reactions. A noticeable trend involves a preference for HS abstraction as the stability of the radical increases (*i*-Pr• > *n*-Pr•; *t*-Bu• > *s*-Bu• > *n*-Bu•) and, consequently, as *D*(R–SH) decreases. Thus, for very stable radicals, such as the *tert*-butyl radical, FeSH⁻ and CoSH⁻ are almost the exclusive reaction products. In addition MSH_2^- is generally observed in greater abundance than MS⁻.

The secondary products of these ions are identical with those discovered in the ethanethiol reactions with the addition of $CoSC_2H_4^-$, which is a secondary product of $CoSH_2^-$ and 1- or 2-butanethiol. It is interesting to note that this ion is not observed in the *n*-PrSH reaction but is observed for the methyl homologue, 2-butanethiol. It is suggested that this ion may be a fragmentation product of CoSH(SBu)⁻ where the neutral loss is either EtSH or a combination of C_2H_4 and H_2S. Unfortunately, the low ion intensity of this secondary product prevented the support of this supposition by collision-induced dissociation.

Reactions of atomic metal anions with organosulfur compounds were first discovered with benzenethiol (thiophenol) during the proton affinity study.[57] Although it was surprising that desulfurization reaction 13 was more favorable than proton abstraction reaction 14, proton abstraction is only exothermic by approximately 1–2 kcal/mol.[57] MS⁻ reacts with benzenethiol to yield MS_2^- exclusively without any evidence of MS_2H^- or $C_6H_5S^-$.

$$
\begin{aligned}
M^- + C_6H_5SH &\longrightarrow MS^- + C_6H_6 && (13)\\
&\longrightarrow C_6H_5S^- + MH && (14)
\end{aligned}
$$

α-Toluenethiol (benzyl mercaptan) undergoes reductive elimination, reaction 15, and HS abstraction, reaction 16, in a manner similar to that of the alkyl thiols. The lack of β-hydrogens readily

$$
\begin{aligned}
M^- + C_6H_5CH_2SH &\longrightarrow MS^- + C_6H_5CH_3 && (15)\\
&\longrightarrow MSH^- + C_7H_7^\bullet && (16)
\end{aligned}
$$

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Table III. Thermochemical Information from the Reactions of Fe^- with H_2S, Thiols, and CS_2[a]

	$D°$-$[M^-–S]$[b]	$D°$-$[M^-–SH]$[c]	$\Delta H°_f$-(MS^-)[d]	$\Delta H°_f$-(MSH^-)[e]	$\Delta H°_f$-(MSH_2^-)[f]
H_2S	>71	<92[g]	<91	>39[g]	—
MeSH	>54	>75	<108	<56	—
EtSH	>57	>72	<105	<56	<72
n-PrSH	>58	>72	<104	<62	<75
i-PrSH	>61	>71	—	—	—
n-BuSH	—	>72	<102	<56	<72[h]
s-BuSH	>60	—	—	—	—
t-BuSH	>62	>69	—	<62	<76
PhSH	>59	—	<103	—	—
CS_2	>103.4[i]	—	<67.7[j]	—	—

[a] All values in kcal/mol. [b] $D°[M^-–S] \geq D°[HS–R] + D°[^{\bullet}S–H] - D°[R–H]$. [c] $D°[M^-–SH] \geq D°[R–SH]$. [d] $\Delta H°_f(MS^-) \leq \Delta H°_f(M^-) + \Delta H°_f(RSH) - \Delta H°_f(RH)$. [e] $\Delta H°_f(MSH^-) \leq \Delta H°_f(M^-) + \Delta H°_f(RSH) - \Delta H°_f(R^{\bullet})$. [f] $\Delta H°_f(MSH_2^-) < \Delta H°_f(M^-) + \Delta H°_f(RSH) - \Delta H°_f$(alkene product). [g] Predicted from arguments given in the text. [h] Assuming 1-butene as the neutral: *cis*-2-butene (74 kcal/mol); *trans*-2-butene (75 kcal/mol). [i] $D°[M^-–S] \geq D°[SC{=}S]$. [j] $\Delta H°_f(MS^-) \leq \Delta H°_f(CS_2) + \Delta H°_f(M^-) - \Delta H°_f(CS)$.

Table IV. Thermochemical Information from the Reaction of Co^- with H_2S, Thiols, and CS_2[a]

	$D°$-$[M^-–S]$[b]	$D°$-$[M^-–SH]$[c]	$\Delta H°_f$-(MS^-)[d]	$\Delta H°_f$-(MSH^-)[e]	$\Delta H°_f$-(MSH_2^-)[f]
H_2S	>71	<92[g]	<81	>29[g]	—
MeSH	>54	>75	<99	<46	—
EtSH	>57	>72	<95	<47	<63
n-PrSH	>58	>72	<95	<52	<65
i-PrSH	>61	>71	—	—	—
n-BuSH	—	>72	<92	<47	<62[h]
s-BuSH	>60	—	—	—	—
t-BuSH	>62	>69	—	<52	<66
PhSH	>59	—	<93	—	—
CS_2	>103.4[i]	—	<58.3[j]	—	—

[a] All values in kcal/mol. [b] $D°[M^-–S] \geq D°[HS–R] + D°[^{\bullet}S–H] - D°[R–H]$. [c] $D°[M^-–SH] \geq D°[R–SH]$. [d] $\Delta H°_f(MS^-) \leq \Delta H°_f(M^-) + \Delta H°_f(RSH) - \Delta H°_f(RH)$. [e] $\Delta H°_f(MSH^-) \leq \Delta H°_f(M^-) + \Delta H°_f(RSH) - \Delta H°_f(R^{\bullet})$. [f] $\Delta H°_f(MSH_2^-) < \Delta H°_f(M^-) + \Delta H°_f(RSH) - \Delta H°_f$(alkene product). [g] Predicted from arguments given in the text. [h] Assuming 1-butene as the neutral; *cis*-2-butene (64 kcal/mol); *trans*-2-butene (65 kcal/mol). [i] $D°[M^-–S] \geq D°[SC{=}S]$. [j] $\Delta H°_f(MS^-) \leq \Delta H°_f(CS_2) + \Delta H°_f(M^-) - \Delta H°_f(CS)$.

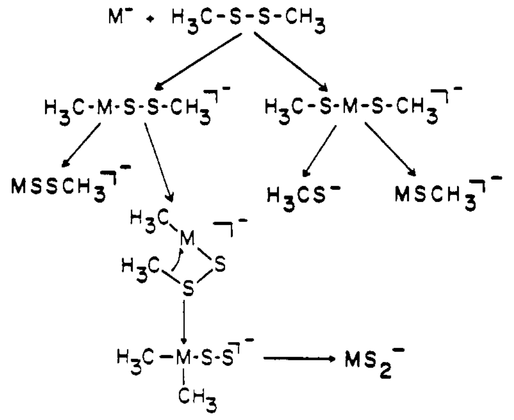
explains the absence of the product MSH_2^-. The secondary reactions 17 and 18 are also analogous to those observed for the alkyl homologues.

$$MS^- + C_6H_5CH_2SH \rightarrow MS_2H^- + C_7H_7^{\bullet} \qquad (17)$$

$$MSH^- + C_6H_5CH_2SH \rightarrow MS(C_6H_5CH_2S)^- + H_2 \qquad (18)$$

Limits for bond dissociation energies and formation enthalpies obtained from the thiol reactions are given in Tables III and IV. The best lower limit for the M^-–SH bond strength is obtained from the reaction of the metal anions with methanethiol ($D°[H_3C–SH]$ = 75 kcal/mol). This, of course, assumes the $(Fe–SH)^-$ structure as opposed to $(H–Fe–S)^-$, which is supported by CID as previously discussed. The lack of MSH^- for Fe^- and Co^- with H_2S tentatively suggests an upper limit for $D°(M^-–SH)$. The presence of MS^- indicates that both S–H bonds in H_2S are broken; any kinetic effects should favor MSH^-, unless it is thermodynamically unfavorable or an unusual concerted mechanism is present. Assuming thermodynamic factors are involved, an upper limit of 92 kcal/mol is obtained for $D°[M^-–SH]$, thereby yielding a range of 75 to 92 kcal/mol for both the iron and cobalt systems or $D°(M^-–SH)$ = 83 ± 9 kcal/mol. Thermodynamic effects are evident by the increase in relative abundance of MSH^- with increasing radical stability. The absence of a direct cleavage product with C_6H_5–SH would have decreased this upper limit to 86.5 kcal/mol. Unfortunately, an alternative mechanism involving initial insertion into the weaker S–H bond (82 kcal/mol) or H^+ abstraction cannot be disregarded. The M^-–SH bond energies yield an estimated range for the formation enthalpies of $FeSH^-$ of 47 ± 9 kcal/mol and of $CoSH^-$ of 38 ± 9 kcal/mol.

Scheme III



The observation of MS^- from the reaction of Fe^- or Co^- with CS_2, reaction 19, provides the best estimate of a lower limit for

$$M^- + CS_2 \rightarrow MS^- + CS \qquad (19)$$

$$MS^- + CS_2 \rightarrow MS_2^- + CS \qquad (20)$$

the bond energy of $D°[M^-–S]$ of >103.4 kcal/mol, yielding $\Delta H_f(FeS^-)$ < 67.7 kcal/mol and $\Delta H_f(CoS^-)$ < 58.3 kcal/mol. Thus, as indicated in Tables III and IV, formation of MS^- from the alkyl thiols is a highly exothermic process. In addition the bond energy order $D°[Fe^-–S]$ > 103 kcal/mol > $D°[Fe–S]$ = 77 kcal/mol[70] > $D°[Fe^+–S]$ ~ 65 kcal/mol[71] mimics a similar trend for iron oxide of $D°[Fe^-–O]$ = 139 ± 13 kcal/mol[72] > $D°[Fe–O]$ = 98 kcal/mol[7] > $D°[Fe^+–O]$ ~ 68 kcal/mol.[8] Finally, from the values of $D°[Fe^-–S]$, $D°[Fe–S]$, and EA(Fe) (3.8 kcal/mol[26]), the electron affinity EA(FeS) > 29.8 kcal/mol is obtained and from the values of $\Delta H_f(MSH^-)$ and $\Delta H_f(MS^-)$, $D°[FeS^-–H]$ < 73 ± 9 kcal/mol and $D°[CoS^-–H]$ < 72 ± 9 kcal/mol are estimated. Thus, the presence of the metal anion substantially reduces the S–H bond strength (normally ~90 kcal/mol) as expected due to electron donation.

The detection of MSH_2^- from the reaction of M^- (M = Fe and Co) with alkyl thiol allows a calculation of $\Delta H_f(MSH_2^-)$ with eq 21. As seen in Tables III and IV, upper limits of 72 and 62 kcal/mol are obtained for $FeSH_2^-$ and $CoSH_2^-$, respectively.

$$\Delta H_f(MSH_2^-) \leq \Delta H_f(M^-) + \Delta H_f(RSH) - \Delta H_f(\text{alkene}) \qquad (21)$$

Using these limits and the estimates for $\Delta H_f(MSH^-)$ yields $D°[FeSH^-–H]$ > 27 ± 9 kcal/mol and $D°[CoSH^-–H]$ ≥ 28 kcal/mol. Although these values are considerably lower than $D°(HS–H)$ = 92 kcal/mol, they are only lower limits and cannot be used to corroborate the proposed structure $HMSH^-$.

Disulfides. Similar to what was observed for the thiols, reactions with disulfides are believed to involve initial metal insertion into the C–S bond, although some S–S bond insertion also occurs. The C–S bond in the disulfides is surprisingly weak at 57 kcal/mol for MeSS–Me and 54 kcal/mol for EtSS–Et, as compared to the notoriously weak S–S bond (74 kcal/mol for RS–SR).[65] Following C–S insertion, direct cleavage and, where possible, dehydrogenation or alkene loss are observed to occur.

The most likely mechanism for the reaction of Fe^- and Co^- with disulfides involves both C–S and S–S bond insertion (refer to Scheme III). Assuming that only RS^- and MSR^- arise from S–S bond insertion, the majority of the products (70–80%) involve insertion into the weak C–S bond (see Table V).

The presence of the thiomethoxy ion was unexpected since it and its ethyl homologue were the only product ions in this study that did not incorporate the metal. Dissociative charge transfer

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Table V. Product Distributions for the Reactions of Fe^- and Co^- with Disulfides

reactant	product[a]	neutral loss	relative[b] abundance	
			Fe^-	Co^-
CH_3SSCH_3	CH_3S^-	$MSCH_3$	14	16
	$MSCH_3^-$	$CH_3S^\bullet$	11	4
	MSS^-	C_2H_6	42	5
	$MSSCH_3^-$	$CH_3^\bullet$	33	75
$C_2H_5SSC_2H_5$	$C_2H_5S^-$	MSC_2H_5	27	30
	$HMSS^-$	$C_2H_5^\bullet$, C_2H_4	30	26
	$MSSC_2H_3^-$	$C_2H_5^\bullet$, H_2	32	15
	$MSSC_2H_5^-$	$C_2H_5^\bullet$	11	29

[a] M represents either iron or cobalt. [b] All values are given as percentages and are within 5%.

(reaction 22) by even the loosely bound Fe^- is endothermic ($\Delta H_{rxn}(R = Me) = +34.9$ kcal/mol; $\Delta H_{rxn}(R = Et) = +27.2$ kcal/mol). Even the favorable entropy factor should not offset

$$Fe^- + RSSR \rightarrow Fe + RS^- + RS \qquad (22)$$

an unfavorable enthalpy of this magnitude. It is interesting to note that $\Delta H_f(FeH) = 122 \pm 3$ kcal/mol[57] can be used to rule out iron hydride and thioformaldehyde as neutral products, with reaction 23 being endothermic by 47.5 kcal/mol.

$$Fe^- + MeSSMe \rightarrow MeS^- + FeH + H_2C{=}S \qquad (23)$$

The S–S bond insertion products provide a means to estimate electron affinities. In accord with the proposed mechanism, it is assumed that after S–S bond insertion a simple cleavage will take place with loss of either $CH_3S^\bullet$ or $FeSCH_3^\bullet$. The fragment with the greater electron affinity would be expected to acquire the charge. Since both ions are observed (reactions 24 through 27), the electron affinity of MeS (42.9 kcal/mol[73]) is greater but probably close in magnitude to the electron affinities of FeSMe and CoSMe. This assumes that an ion–molecule complex exists,

$$Fe^- + MeSSMe \xrightarrow{14\%} MeS^- + FeSMe \qquad (24)$$

$$\xrightarrow{11\%} FeSMe^- + MeS^\bullet \qquad (25)$$

$$Co^- + MeSSMe \xrightarrow{16\%} MeS^- + CoSMe \qquad (26)$$

$$\xrightarrow{4\%} CoSMe^- + MeS^\bullet \qquad (27)$$

long lived enough to establish a charge distribution that is representative of the relative electron affinities of the fragments.

Insertion into the C–S bond of MeSSMe by Fe^- or Co^- can be accompanied by $CH_3^\bullet$ loss similar to the thiol case. Reductive elimination of ethane is also noted and proposed to involve a four-center intermediate as shown in Scheme III. Other mechanisms such as diradical (i.e., two $CH_3^\bullet$ radicals) loss, while unlikely, should not be ruled out.

The atomic metal anions react with diethyl disulfide to give EtS^-, involving S–S bond insertion (reaction 28), and three other products that involve insertion into the C–S bond accompanied by ethyl radical loss (reactions 29–31; refer to Table V). A

$$M^- + EtSSEt \longrightarrow EtS^- + MSEt \qquad (28)$$

$$\longrightarrow HMSS^- + Et^\bullet + C_2H_4 \qquad (29)$$

$$\longrightarrow MSSC_2H_3^- + Et^\bullet + H_2 \qquad (30)$$

$$\longrightarrow MSSEt^- + Et^\bullet \qquad (31)$$

proposed mechanism is illustrated in Scheme IV and discussed for Fe^- with the understanding that Co^- can undergo an identical pathway. Unlike the MeSSMe situation, $FeSEt^-$ is not observed. It is suggested with similar caution that this implies EA(FeSEt) < EA(EtS) (EA(EtS) = 45.04 kcal/mol[74]). In all cases involving C–S bond insertion, the ethyl radical is lost. Further hydrogen transfer to the metal via a five- or six-member ring can result in dehydrogenation or alkene loss (refer to Scheme IV). Although the ratio of C–S versus S–S interaction is comparable (70:30), the iron system undergoes greater dehydrogenation relative to the cobalt system.

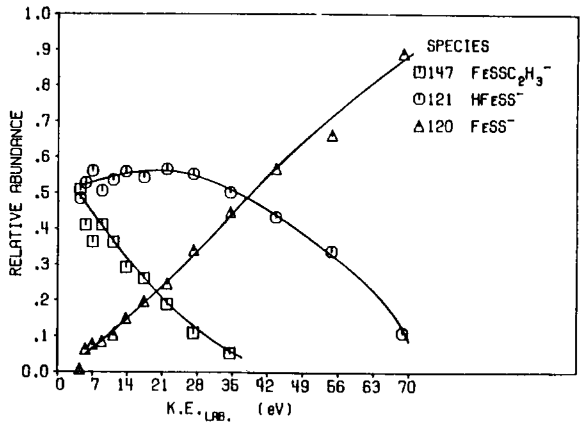


Figure 1. CID breakdown curve for $FeSSC_2H_5^-$ generated in reaction 31.

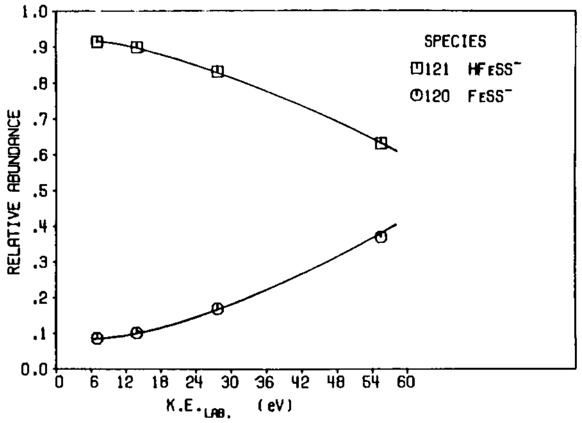
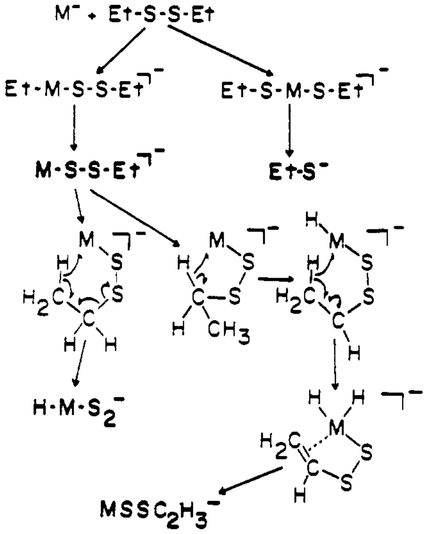


Figure 2. CID breakdown curve for $FeSSC_2H_3^-$ generated in reaction 30.

Scheme IV



Collision-induced dissociation of $FeSSEt^-$ (Figure 1) is summarized in reaction 32. Both daughter ions, $FeSSC_2H_3^-$ and

$$\begin{tikzcd}
FeSSEt^- \arrow[r, "\mathrm{CID}", "-H_2"'] \arrow[dr, "-C_2H_4"'] & FeSSC_2H_3^- \arrow[d, "-C_2H_2"] & \\
& HFeSS^- \arrow[r, "-H"'] & FeSS^-
\end{tikzcd} \qquad (32)$$

$HFeSS^-$, are observed even at the lowest energies. It appears that

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Table VI. Product Distributions for the Reactions of Fe^- and Co^- with Sulfides

			relative abundance[b]		
reactant	product[a]	neutral loss	Fe^-	Co^-	secondary products[a]
MeSMe	none observed				
MeSEt	none observed				
EtSEt	none observed				
i-PrS(*i*)Pr	none observed				
n-BuS(*n*)Bu	MS^-	(C_8H_{18})	22	13	$MSSH^-$
	MSH^-	*n*-Bu•, C_4H_8	31	29	MS(*n*-BuS)$^-$
	MSH_2^-	$2C_4H_8$	47	58	
s-BuS(*s*)Bu	MSH^-	$C_4H_9^\bullet$, C_4H_8	100[c]	—	
t-BuS(*t*)Bu	none observed				
$(n\text{-}C_5H_{11})_2S$	MS^-	$(C_{10}H_{22})$	10	28	MS_2H^-
	MSH^-	$C_5H_{11}^\bullet$, C_5H_{10}	11	9	
	MSH_2^-	$2C_5H_{10}$	3	9	
	$M(SCH_2)^-$	C_5H_{11}, C_4H_9	45	22	
	$CpMCH_3^-$[d]	(C_4H_8S)	18	16	
	$CpMH_2CH_3^-$[d]	(C_4H_6S)	13	16	
c-C_2H_4S	MS^-	C_2H_4	100	95	MS_2^-, $CoS(C_2H_4)$
	MSH_2^-	C_2H_2	—	5	
c-$CH(CH_3)CH_2S$	MS^-	C_3H_6	90	90	MS_2^-, CoS_2H^-
	MSH^-	C_3H_5	6	4	
	MSH_2^-	C_3H_4	4	6	
c-C_3H_6S	MS^-	C_3H_6	19	41	$CoSSH^-$
	MSH^-	C_3H_5	14	16	$SCo(SCH_2)^-$
	MSH_2^-	C_3H_4	4	10	
	$MSCH_2^-$	C_2H_4	63	29	
	$MSC_2H_3^-$	$CH_3^\bullet$	—	4	
c-C_4H_8S	none observed				
c-$C_5H_{10}S$	none observed				

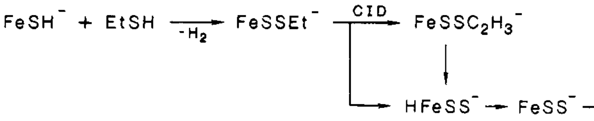
[a] M represents either iron or cobalt. [b] All values are given as percentages and are within 5%. [c] Only a slight amount is observed. [d] Proposed product; see text.

both daughter ions can be formed directly from $FeSSEt^-$ due to the concomitant increases in their absolute intensities as a function of time. However, the abundance of $HFeSS^-$ increases much faster and it can be shown that $HFeSS^-$ is also a CID daughter ion of $FeSSC_2H_3^-$ (the ion-molecule product ion of reaction 30) by loss of C_2H_2 (Figure 2; reaction 33). The fact that both $FeSSC_2H_3^-$ and $HFeSS^-$ can be formed from excited $FeSSEt^-$ corresponds

$$FeSSC_2H_3^- \xrightarrow{\text{CID}} HFeSS^- \rightarrow FeSS^- \qquad (33)$$

well with the mechanism given in Scheme IV. The only other CID product observed is $FeSS^-$ which appears to arise by H loss from $HFeSS^-$, although Et• loss by direct cleavage of $FeSS^-$–Et cannot be ruled out.

$FeSSEt^-$ can also be formed as a secondary product in the reaction between $FeSH^-$ and EtSH, reaction 11, as discussed earlier. Due to its low absolute ion abundance, an accurate breakdown curve was not possible. However, semiquantitative daughter ion intensities could be obtained by signal averaging. The CID daughter ions (reaction 34) were similar to those observed in the CID of $FeSSEt^-$ formed from the reaction between Fe^- and EtSSEt and suggests that the two ions may have the same structure. However, the presence of other structures such as EtS–Fe–S^- is also feasible.



(34)

Sulfides. Unlike the thiols and disulfides, the sulfides exhibit a reluctance to undergo reaction with either Fe^- or Co^-, showing limited reactivity for only the larger acyclic and smaller cyclic sulfides (refer to Table VI).

The lack of an observable reaction with the smaller acyclic sulfides is unexpected and difficult to rationalize. Kinetic arguments that elicit barriers for C–S bond cleavage or rely upon steric hindrance as their basis are unsupported and even disproven by the experimental evidence presented herein. The C–S bond dissociation energy for either EtS–Et or MeS–Et (both approximately 74 kcal/mol[65]) is comparable to the C–S bond in methanethiol (75 kcal/mol[65]). Any mechanism requiring the presence of a sulfur-residing hydrogen is discredited by the extensive reactivity observed for the disulfide compounds. The presence of reaction products for the larger acyclic sulfides in comparison to the smaller homologues, is contradictory to any arguments involving steric hindrance. Although polarization effects may seem attractive for hypothesizing an explanation on the reactivity of metal anions with larger alkyl sulfides, the zealous reactions of metal anions with small thiols (e.g., CH_3SH) still presents a dilemma. In summary, there is no obvious explanation for the lack of reactivity involving smaller acyclic sulfides.

Product ions observed for the reactions involving the larger sulfides mimic those obtained from the corresponding thiol reactions, with the exception of *n*-pentyl sulfide. Although the neutral products are not known and no mechanism is proposed, a substantial amount of dehydrogenation probably occurs and is supported by the relatively high abundance of MSH_2^- in the butyl sulfide case. Also from the butyl sulfide system, it is observed that as the major alkyl chain becomes shorter and more branched, the reactivity is dramatically reduced. Although the corrected pressure of *sec*-butyl sulfide[75] was more than twice that of the *n*-butyl sulfide, under similar $Fe(CO)_5$ pressure and reaction time (500 ms), only a 3% conversion of Fe^- to products (Table VI) was observed for the *sec*-butyl sulfide, whereas the *n*-butyl system gave a 23% conversion. Similar results were obtained for cobalt. No products were observed for reactions involving *tert*-butyl sulfide with either metal anion.

The primary products MS^-, MSH^-, and MSH_2^- along with the secondary product, MS_2H^-, are observed for the reaction of Fe^- or Co^- with *n*-pentyl sulfide. Three additional products are also observed: $MSCH_2^-$ and two ions corresponding to mass-to-charge ratios of 136 and 138 for the iron system (*m*/*z* 139 and 141 for the cobalt system). These latter two ions have definitely been established as primary products through double resonance ejection and correspond to $MC_6H_8^-$ and $MC_6H_{10}^-$.

Reactions of the metal anions with cyclic sulfides are simpler to interpret. Rapid and efficient reactions with the smaller cyclic compounds involve mainly desulfurization accompanied by alkene loss. No reactions are observed for either the five- or six-member ring compounds. Both ethylene and trimethylene sulfide com-

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Table VII. Reactions of Atomic Metal Anions with EtSH, EtSSEt, and CS_2

reactant	product	V^-	Cr^-	Fe^-	Co^-	Mo^-
EtSH	MS^-[a]	10[b]	—[c]	29	36	100
	MSH^-	86	—	46	26	—
	MSH_2^-	4	—	25	38	—
EtSSEt	EtS^-	60	18	27	30	Y[d]
	MSS^-	—	23	—	—	—
	$MSSH^-$	15	23	30	26	Y
	$MSSC_2H_3^-$	—	27	32	15	Y
	$MSSEt^-$	25	9	11	29	Y
CS_2	CS_2^-	NP[e]	—	45	—	—
	MS^-	NP[e]	—	55	100	100

[a] M represents the appropriate atomic metal anion. [b] Values are within 10%. [c] Dash indicates that no products were observed. [d] "Y" indicates that the molybdenum product was observed; however, the intensity was too low for accurate quantification (see text). [e] NP indicates that the experiment was not performed.

pounds possess ring strain similar to their carbon analogues, although to a lesser extent by about 8 kcal/mol.[65] Therefore, the primary driving force for reactions involving the 3- and 4-member ring compounds is the relief of ring strain. The lack of reactivity for the larger cyclic sulfides mimics the corresponding acyclic sulfides. Thus, tetramethylene sulfide may be viewed as resembling a constrained diethyl sulfide which shows a similar lack of reactivity.

Other Anions: V^-, Cr^-, and Mo^-. The relative reactivity of the atomic metal anions V^-, Cr^-, Fe^-, Co^-, and Mo^- with various organosulfur compounds varied immensely. As described above, Fe^- and Co^- generally react rapidly with each of the classes of sulfur compounds studied here with the exception of acyclic sulfides. Reactions involving Mo^- and Cr^- are relatively slow, and in some cases it appears that the Cr^- is unreactive. This may be related to the relatively stable d^5s^2 electronic structures of these anions. V^- falls between the two extremes in reactivity but is somewhat unusual in the type of products and their relative distribution. To some extent, this may be related to the larger electron deficiency of vanadium.

Polysulfide products arising from the sequential reactions of the metal anions and benzenethiol were observed in the proton abstraction study,[57] reaction 35. The relative inertness of either FeS_2^- or CoS_2^- to undergo further desulfurization may be at-

$$M^- + nC_6H_5SH \rightarrow MS_n^- + nC_6H_6 \quad (35)$$

$$M = \text{Fe and Co};\ n = 1 \text{ and } 2$$

$$M = \text{V and Cr};\ n = 1\text{–}3$$

tributed to the reluctance of the metal to form a species in the +5 oxidation state. Examples are known (e.g., K_3CoO_4) but are extremely rare with a strong tendency to form lower oxidation states such as the +3 oxidation state proposed for MS_2^-. This also suggests that the sulfur atoms are present as independent entities and not as the disulfide units observed in the ion-molecule chemistry of metal cations.[76] For the earlier transition members, the higher oxidation states are more common. The +5 oxidation state is stable and very well known for vanadium. This oxidation state is also recognized for chromium although generally restricted to peroxo complexes because of favorable disproportionation to Cr(III) and Cr(VI) in solution.[77] Only proton abstraction was observed for Mo^-. However, due to the low absolute ion abundances and the isotopic partitioning of the product (the major product ion, ^{98}Mo, is only 24% of the overall product), low intensity product ions may have been overlooked even with extensive signal averaging.

Reactions of various atomic metal anions with ethanethiol are compared in Table VII. Although under similar reaction conditions no product ions were observed for Cr^-, Mo^- reacted slowly to produce MoS^- which further reacted to give a secondary product corresponding to MoS_2^- and not MoS_2H^-, as would be expected from the corresponding Fe^- and Co^- reactions. V^- was also observed to give predictable primary products, VS^-, VSH^-, and VSH_2^-, but gave some unexpected secondary products. The major product, VSH^-, underwent further reactions with ethanethiol to produce secondary and tertiary products corresponding to desulfurization, VS_2H^- and VS_3H^-, and not the dehydrogenation product, $VS(SEt)^-$.

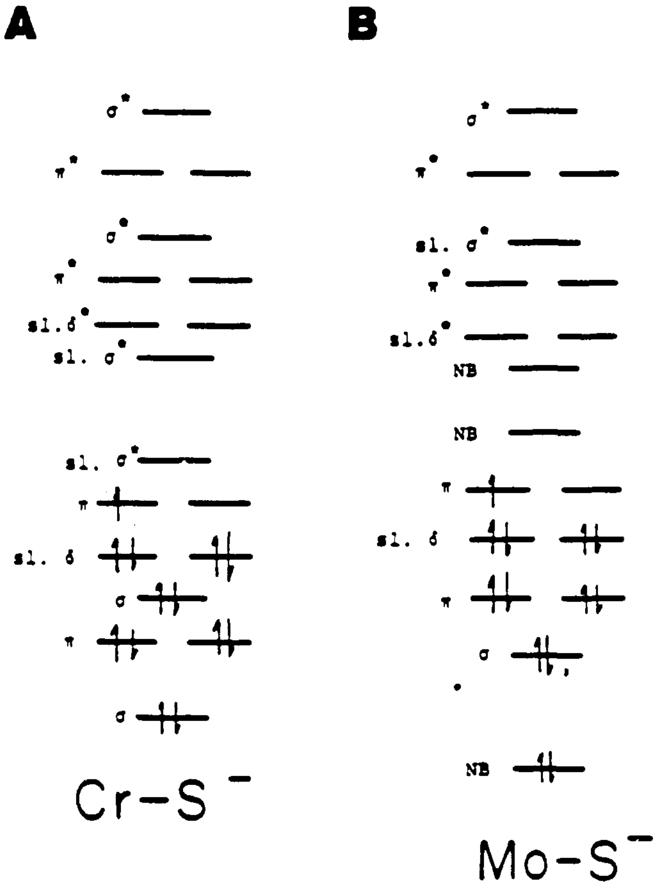

Figure 3. Molecular orbital diagrams for $Cr{-}S^-$ and $Mo{-}S^-$.

The inertness of Cr^- is further evident by the lack of reaction with carbon disulfide. Similar to the thiol case, Mo^- does react with CS_2 to produce MoS^- and the corresponding secondary product, MoS_2^-. The driving force for molybdenum relative to chromium may reside in a stronger Mo–S bond in comparison to Cr–S. Available data show that molybdenum bonds more strongly to oxygen (Mo–O 133.9 kcal/mol) than does chromium (Cr–O 103 kcal/mol).[78] It is reasonable to predict that the molybdenum–sulfur bond strength is also greater than the corresponding chromium–sulfur bond. The additional electron is added to a π-bonding orbital increasing the bond order, as shown by the molecular orbital diagrams calculated with Extended-Hückel theory (Figure 3). As stated earlier this mimics a similar trend reported for iron oxide[7,8,72] and, thus, $M^-{-}S$ (M = Cr or Mo) should be stronger than M–S as is the case for M = Fe and Co.

Cobalt and iron both form MS^- from CS_2 as a primary product which further reacts to produce MS_2^-. It is interesting to note that FeS^- (ca. 55%) is observed even though charge transfer to yield CS_2^- (ca. 45%) is exothermic by almost 20 kcal/mol (EA(CS_2) = 23 kcal/mol[79]).

Reactions involving atomic metal anions with diethyl disulfide yielded similar primary ions with the presence of $CrSS^-$ and the absence of $VSSC_2H_3^-$ as the only exceptions. The unusually high

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abundance of EtS^- for the vanadium system may indicate a preference for S–S bond insertion. Interestingly, the metal cation experiments show that V^+ and Ti^+ form stronger sulfur bonds than either Fe^+ or Co^+,[64] although it is unclear if a valid correlation with anions can be made through arguments involving the relative electron deficiency of earlier transition metals. The relatively low product intensities coupled with the isotope overlap of $MoSSC_2H_3^-$ and $MoSSEt^-$ prevented an accurate product branching ratio from being obtained for the molybdenum system.

Conclusion

It has been shown in this study that atomic metal anions react with organosulfur compounds in the gas phase. These reactions generally involve cleavage of the carbon–sulfur bond, and retention of the charge by the metal-bearing species. With the limited number of compounds studied, it appears that V^-, Cr^-, Mo^-, Fe^-, and Co^- all react similarly with regards to the product ions formed, but differ in the reactivity and extent of secondary reaction processes.

Reactions of metal anions with H_2S, thiols, and CS_2 yield useful limits on a variety of thermochemical parameters (refer to Tables III and IV). It was also noted in the thiol study that the direct cleavage pathway became more favorable over other reaction pathways as the stability of the alkyl radical increased. Reactions of Fe^- and Co^- with thiols are remarkable in their similarity to reactions involving the corresponding cations, Fe^+ and Co^+.[64] The major difference arises apparently from the immediate alkene loss upon hydrogen transfer to the metal anion center without subsequent transfer to the thiol portion of the species to form an H_2S-ligated system.

Both Fe^- and Co^- react rapidly with dimethyl disulfide and diethyl disulfide showing a distinct preference of cleaving the C–S bond over the S–S bond. Reactions involving diethyl disulfide also show a greater extent of dehydrogenation for the iron system relative to the cobalt. An estimate for the electron affinity of $MSCH_3^-$ and a limit for $MSC_2H_5^-$ ($M = Fe^-$ and Co^-) were also presented and are based on the assumption that a representative charge distribution occurs before cleavage.

In contrast to thiol and disulfides, the sulfides reacted sluggishly or displayed a complete lack of reactivity. Only the small, ring-strained cyclic sulfides reacted readily. At present, we have no valid explanation for this lack of reactivity.

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Registry No. Co^-, 16727-18-7; Fe^+, 22325-61-7; H_2S, 7783-06-4; MeSH, 74-93-1; EtSH, 75-08-1; *n*-PrSH, 107-03-9; *i*-PrSH, 75-33-2; *n*-BuSH, 109-79-5; *s*-BuSH, 513-53-1; *t*-BuSH, 75-66-1; PhSH, 108-98-5; $PhCH_2SH$, 100-53-8; FeS^-, 116784-36-2; $FeSH^-$, 116784-38-4; $FeSH_2^-$, 116784-37-3; CS_2, 75-15-0; CoS^-, 116784-39-5; $CoSH^-$, 116784-40-8; $CoSH_2^-$, 116784-41-9; FeS, 1317-37-9; CH_3SSCH_3, 624-92-0; $C_2H_5SSC_2H_5$, 110-81-6; MeSMe, 75-18-3; MeSEt, 624-89-5; EtSEt, 352-93-2; *i*-PrS(*i*)Pr, 625-80-9; *n*-BuS-*n*-Bu, 544-40-1; *s*-BuS-*s*-Bu, 626-26-6; *t*-BuS-*t*-Bu, 107-47-1; $(n\text{-}C_5H_{11})_2S$, 872-10-6; c-C_2H_4S, 420-12-2; c-$CH(CH_3)CH_2S$, 1072-43-1; c-C_3H_6S, 287-27-4; V^-, 16727-17-6; Cr^-, 19498-56-7; Mo^-, 54604-28-3; CrS^-, 116784-42-0; MoS^-, 116784-43-1.

Direct Evidence for the Existence and the Relative Stability of Gaseous Ethylenebenzenium Ions from a ^{13}C-Labeling Study

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Abstract: Direct evidence is reported for the existence of unsubstituted ethylenebenzenium ions in the gas phase, based on ^{13}C-labeling of a methylene position in the precursor β-phenylethyl alcohol or chloride. The ^{13}C location in the products of the substitution reaction induced by gaseous cations in the presence of methanol is consistent with the occurrence of ethylenebenzenium ions **3** which do not display a facile isomerization to benzylic ions **6**. The fate of the ^{13}C label in the reaction has been established by the mass spectrometric analysis of the products. It has been verified further by NMR spectrometry, applied for the first time to the analysis of an ion–molecule product from a gas-phase radiolytic study.

It is known, since Cram's pioneering work, that the presence of a β-aryl substituent markedly influences the reactivity of arylalkyl derivatives both in solvolytic and Friedel–Crafts alkylation reactions.[1] The extent of the intramolecular nucleophilic assistance by the β-aryl group depends on structural features of the substrate, such as the presence of substituents either in the side chain or on the aromatic nucleus, and on the medium, increasing in more ionizing, less nucleophilic solvents. With regard to the substrate structure, protonation of unsubstituted β-phenylethyl chloride in superacidic media leads irreversibly to symmetrical ethylenebenzenium ions, at variance with β-phenylethyl chlorides bearing methyl substituents in their side chain.[2] As to the medium effect, it is the purpose of this work to extend the investigation to the gas phase, where phenyl participation should be enhanced, due to the low concentration of external nucleophiles, provided of course that formation of ethylenebenzenium ion is energetically allowed. Indeed, formation of gaseous alkylenebenzenium ions was recently unambiguously inferred from the isomeric composition and the stereochemical features of the products obtained from the protonation or alkylation of 2-phenyl-3-X-butane, 2-phenyl-1-X-propane, and 1-phenyl-2-X-propane (X = Cl, OH), followed by trapping of the intermediate

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