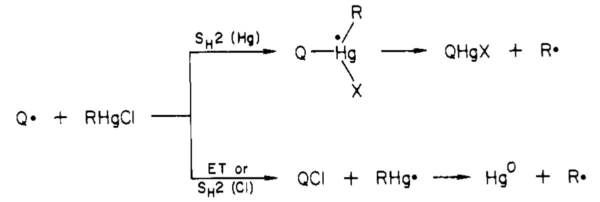
Scheme I



coupling products **3** or **4** are formed (R = 1°, 2°, or 3° alkyl) without contamination by the dimers R–R, $(PhCH{=}CH)_2$, or $(Ph_2C{=}CH)_2$.[5]

Evidence for the free radical chain follows from the observed photostimulation and initiation by AIBN or Bz_2O_2, the inhibitory effect of di-*tert*-butyl nitroxide, and the rearrangement of R = Δ^5-hexenyl to cyclopentylcarbinyl. The photostimulated reactions proceed more readily with R = *tert*-butyl than for R = isopropyl and more rapidly with 2° alkylmercurials than with 1° alkylmercurials. This reactivity sequence appears to reflect the efficiencies of the steps in which R· is formed in Scheme I although the rate of the photoinitiation process may also be involved. Mercurials can also provide heterocentered radicals by the reactions of Scheme I. Thus, $((EtO)_2PO)_2Hg$ or $(EtO)_2POHgCl$ forms the vinyl phosphonate in photostimulated chain reactions with **1** or **2** (Q = Bu_3Sn, HgX, I) (Table I) while $(PhSO_2)_2Hg$ or $(PhS)_2Hg$ give chain reactions forming the vinyl sulfones or sulfides.[6]

Tributyl-1-alkenyltins, including **1a**, have been reported to undergo a thermal substitution reaction with Br– or I–CH_2CO_2Et to give the β,γ-unsaturated ester in low yield.[7] This reaction can be photostimulated and substitution also occurs with *n*-BuI (Table I). However, reactions of **1a** or **2a** with isopropyl iodide or *tert*-butyl bromide with photostimulation or AIBN initiation are ineffective and only low yields of **3** or **4** can be detected.[8] On the other hand, **3** or **4** with R = CCl_3 are readily formed by the reaction of **1a** or **2a** with CCl_4, $BrCCl_3$, or CCl_3SO_2Cl.

The chain reaction of 1-alkenylmercurials with heterocentered radicals has been previously reported.[9] The 1-alkenyltin derivatives, with or without 2-phenyl substituents, also react by the free radical chain reaction of eq 1 with Q–Y reagents such as

$$(R_1)(R_2)C{=}CHMXn + Q{-}Y \xrightarrow[\text{AIBN}]{h\nu\text{ or}} (R_1)(R_2)C{=}CHQ + YMXn \quad (1)$$

RS–SR, $PhSO_2$–Cl, or *p*-$MeC_6H_4SO_2$–SePh. However, whereas PhSeSePh is reactive when MXn = HgCl, the reaction fails to occur with the corresponding 1-alkenyltins (MXn = $SnBu_3$). Competition studies support the conclusion that the 1-alkenylmercurials are more reactive than the 1-alkenyltins and that PhSe· will add to **1b**,**c** but not to **1a** at 35 °C.

Alkylmercury halides can also be substituted for alkyl halides in the free radical chain S_H2' substitution reaction with alkylstannanes[10] and with stannyl enol ethers. Some aromatic systems such as 2-substituted benzothiazoles (**5** = 2-iodo, **6** = 2-(phenylsulfonyl)) will also react with RHgX by the addition–elimination sequence to form the 2-alkylbenzothiazole (**7**) (Table I). The alkenes **1** or **2** with Q = HgX, $PhSO_2$, or PhSO also react with R_3B to yield **3** or **4** by a chain sequence inhibited by $(t\text{-}Bu)_2NO\cdot$, which most likely involves regioselective addition of R· to the styrenyl system rather than the formation of the β-styrenyl radical as suggested previously.[11]

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[5] Except when R = $PhCH_2\cdot$ where bibenzyl is the major product from the S_H2 substitution reaction, $PhCH_2\cdot + PhCH_2HgCl \rightarrow PhCH_2CH_2Ph + HgCl$.[3]

[6] Reactions of 1-alkenylmercury halides with R_2Hg (R = $(EtO)_2PO$, $PhSO_2$, PhS, $PhCOCH_2$) may form the (1-alkenyl)HgR as an intermediate which decomposes in a photostimulated free radical addition–elimination reaction in which the elimination fragment (RHg) decomposes to form R· and Hg°. Formation of PhCH=CHHgR or $Ph_2C{=}CHHgR$ may also be involved in the reaction of **1b** or **2c** with RHgX, RMgX, or R_3B (Table I).

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Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase. The Bond Energy of $FeCo^+$

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Transition-metal clusters[1] have been the focus of intense experimental[2,3] and theoretical[4] investigations due to their important role in catalysis. Gas-phase ion techniques are ideally suited for studying size-selected metal cluster ions. To date these cluster ions have been generated by either electron impact or multiphoton ionization,[5] typically on multinuclear carbonyl complexes. The former method has been employed, for example, to generate and study the gas-phase chemistry of Co_2^+ and Mn_2^+ by ion cyclotron resonance spectrometry[6] and ion beam techniques.[7]

In this report we describe a general technique for in situ synthesis and subsequent study of metal cluster ions using Fourier transform mass spectrometry–collision induced dissociation (FTMS–CID). This technique promises to greatly extend the variety and size of metal clusters now accessible by electron impact and multiphoton ionization. The methodology is demonstrated for $FeCo^+$ with use of a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer[8,9] equipped with laser ionization.[10]

Transition-metal ions and metal–carbonyl fragment ions react rapidly with the parent metal carbonyl in the gas phase generating cluster ions.[11-13] Laser-desorbed cobalt and iron cations react

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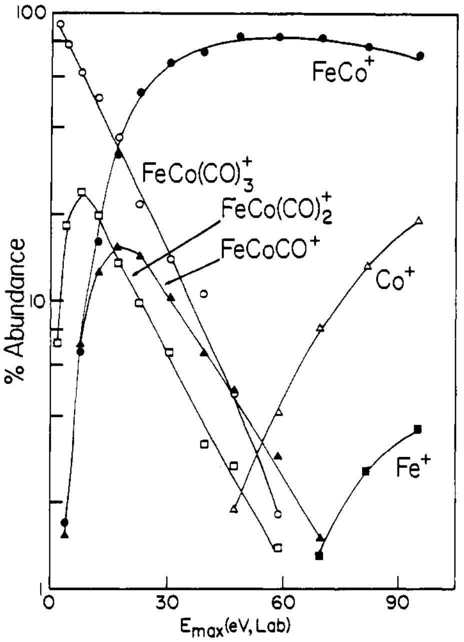

Figure 1. Variation of ion abundances as a function of kinetic energy for CID of $CoFe(CO)_3^+$ produced in reaction 1. Argon was used as the collision gas at approximately 5×10^{-6} torr, and a 40-ms delay between CID excitation and detection was used to permit fragmentations.

with $Fe(CO)_5$ yielding the products in reactions 1-3. Collisional activation[8,14,15] of the products of reactions 1 and 3 results in sequential elimination of carbonyls, reaction 4. An alternative method for carbonyl elimination is by multiphoton infrared photodissociation of the cluster.[16] The main advantage of the CID technique is that only ~40 ms is required to convert virtually all of the ions to $FeCo^+$ and Fe_2^+, whereas several seconds would generally be required to achieve this using photodissociation. The variation of ion abundances as a function of kinetic energy for CID of $CoFe(CO)_3^+$ is shown in Figure 1. Both $FeCo^+$ and Fe_2^+, which were optimized by using a CID energy of 31 eV, were isolated by swept double-resonance ejection pulses[9] and allowed to react with a specific reagent gas. Process 4 undoubtedly results in formation of $FeCo^+$ and Fe_2^+ with a distribution of internal energies. The CID collision-gas pressure was kept high (~5×10^{-6} torr) relative to the reagent gas pressure (~1×10^{-7} torr), therefore, in order to allow the excess energy to be dissipated by thermalizing collisions with argon prior to reaction.

$$Co^+ + Fe(CO)_5 \xrightarrow{95\%} CoFe(CO)_3^+ + 2CO \quad (1)$$

$$Co^+ + Fe(CO)_5 \xrightarrow{5\%} CoFe(CO)_4^+ + CO \quad (2)$$

$$Fe^+ + Fe(CO)_5 \rightarrow Fe_2(CO)_4^+ + CO \quad (3)$$

$$M'M(CO)_x^+ \xrightarrow{-CO} M'M(CO)_{x-1}^+ \xrightarrow{-CO} M'M(CO)_{x-2}^+ \xrightarrow{-(x-2)CO} M'M^+ \quad (4)$$

Displacement reactions have been used to bracket metal ion-ligand bond energies and were used here to probe the $FeCo^+$ bond energy. The following order of Co^+-ligand bond strengths has been determined by displacement reactions: $D°(Co^+-OH) = 71 \pm 3$ kcal/mol > $D°(Co^+-benzene)$ > $D°(Co^+-CH_3CN)$ > $D°(Co^+-CH_3) = 61 \pm 4$ kcal/mol.[17-19] With Fe^+, the order of bond strengths is $D°(Fe^+-OH) = 73 \pm 3$ kcal/mol > $D°(Fe^+-CH_3) = 69 \pm 5$ kcal/mol > $D°(Fe^+-benzene)$ ~ $D°(Fe^+-H) = 58 \pm 5$ kcal/mol > $D°(Fe^+-CH_3CN)$.[17-20]

$FeCo^+$ is unreactive with acetonitrile but reacts readily with benzene to displace Fe exclusively, reaction 5. In addition, the complex $FeCo(benzene)^+$ loses Fe exclusively upon collisional activation. These results yield a limit of 71 ± 3 kcal/mol > $D°(Co^+-Fe) > 61 \pm 4$ kcal/mol from which we assign $D°(Co^+-Fe) = 66 \pm 7$ kcal/mol and $\Delta H_f°(FeCo^+) = 315.5 \pm 7$ kcal/mol.[21] $D°(Fe^+-Co)$ is very nearly identical with $D°(Co^+-Fe)$ due to the slight difference in the ionization potential of Fe and Co.[21] Complete absence of Co displacement by benzene with $FeCo^+$ implies $D°(Co^+-benzene) > D°(Fe^+-benzene)$ in agreement with displacement studies. Benzene reacts slowly with Fe_2^+ yielding $FeC_6H_6^+$. CID of $Fe_2C_6H_6^+$, generated by reaction of Fe_2^+ with cyclohexene, yields predominantly Fe_2^+ with only a trace of $FeC_6H_6^+$. These results indicate that $D°(Fe^+-Fe) > D°(Fe^+-benzene)$. CID of $Fe_2(CH_3)^+$, generated in reaction 6, produces Fe_2^+ and $FeCH_3^+$ in roughly equal amounts. Collisional activation of $Fe_2(OH)^+$, formed in reaction 7a, generates $FeOH^+$ exclusively. This yields the following order of bond strengths: $D°(Fe^+-OH) = 73 \pm 3$ kcal/mol > $D°(Fe^+-CH_3) = 69 \pm 5$ kcal/mol ~ $D°(Fe^+-Fe) > D°(Fe^+-benzene) = 58 \pm 5$ kcal/mol.[17-20] This result compares well with a calculated value for $D°(Fe^+-Fe)$ of 63.5 ± 7 kcal/mol with use of equation 8, $D°(Fe-Fe) = 18 \pm 4$ kcal/mol[4b] and $IP(Fe_2) = 5.90 \pm 0.2$ eV.[22]

$$FeCo^+ + benzene \rightarrow Co(benzene)^+ + Fe \quad (5)$$

$$FeCH_3^+ + Fe(CO)_5 \xrightarrow{-CO} Fe_2(CH_3)(CO)_4^+ \xrightarrow{CID} Fe_2(CH_3)^+ + 4CO \quad (6)$$

$$FeOH^+ + Fe(CO)_5 \xrightarrow{-2CO} Fe_2(OH)(CO)_3^+ \xrightarrow{CID} Fe_2(OH)^+ + 3CO \quad (7)$$

$$D°(Fe^+-Fe) = D°(Fe-Fe) + IP(Fe) - IP(Fe_2) \quad (8)$$

Therefore, bracketing appears to be a valid method for determining bond dissociation energies of gas-phase diatomic transition-metal cations. Armentrout and co-workers have determined $D°(Mn^+-Mn) = 20 \pm 4$ kcal/mol directly by using ion beam techniques.[7b]

The above method for in situ synthesis of diatomic transition-metal cluster ions appears to be general with $NiFe^+$, $CuFe^+$, VFe^+, and $RhFe^+$ obtained from reactions of Ni^+, Cu^+, V^+, and Rh^+ with $Fe(CO)_5$, respectively. The bond-dissociation energy of these diatomic clusters is currently under investigation as well as the study of the chemistry of these cluster ions. Synthesis of larger clusters utilizing this method is also underway in our laboratory.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (CHE-8310039) for providing funds for the advancement of FTMS methodology.

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(20) The bond energy of Fe^+ to benzene is assigned as 58 ± 5 kcal/mol since CID of $FeC_6H_7^+$ produces roughly equal amounts of FeH^+ and $FeC_6H_6^+$ at low kinetic energy indicating benzene and hydrogen atom have similar binding energies to Fe^+. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

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