

Generation and Reactions of Atomic Metal Anions in the Gas Phase. Determination of the Heterolytic and Homolytic Bond Energies for VH, CrH, FeH, CoH, and MoH

Larry Sallans, Kelley R. Lane, Robert R. Squires,* and Ben S. Freiser*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received January 2, 1985

Abstract: The atomic transition-metal anions V^- , Cr^- , Fe^- , Co^- , Mo^- , and W^- have been generated in the gas phase by collision-induced dissociation of the corresponding metal carbonyl negative ions in a Fourier transform mass spectrometer. Isolation of each ion by double resonance ejection techniques has enabled an examination of their ion-molecule reactions with added neutral substrates. Each atomic ion reacts with the parent metal carbonyl by dissociative electron transfer to produce mononuclear metal carbonyl anions while the cobalt ion gives both mononuclear and dinuclear product ions by metal-metal and metal-carbon bond cleavage, respectively. Vanadium, chromium, and molybdenum anions also produce dinuclear cluster ions in reactions with their parent neutral hexacarbonyls. The proton affinities of several of the atomic ions have been determined by bracketing methods and are found to be the following (kcal/mol): V^- , 339.4 ± 3 ; Fe^- , 339.4 ± 3 ; Cr^- , 339.4 ± 3 ; Co^- , 340.5 ± 3 ; Mo^- , 342.4 ± 3 . Combining these data with measured electron affinities of the metal yields homolytic bond energies for the hydrides $D[M-H]$ (kcal/mol): V-H, 37.9 ± 3 ; Fe-H, 29.6 ± 3 ; Cr-H, 41.2 ± 3 ; Co-H, 42.2 ± 3 ; Mo-H, 46.0 ± 3 . The new monohydride bond energies compare favorably with other experimental and theoretical data in the literature and have been used to derive additional thermodynamic properties for metal hydride ions and neutrals.

One of the most active frontiers for gas-phase ion research over the last decade has been the study of ion-molecule reactions involving transition-metal complexes and the chemistry of atomic and coordinated metal ions. The incentives for the considerable effort dedicated to this research are clearly illuminated in the current literature. Recent gas-phase studies involving inorganic and organometallic compounds have produced a wealth of important and useful thermodynamic data such as homolytic and heterolytic metal-hydrogen, metal-carbon, and metal-oxygen bond strengths,¹⁻⁹ relative ligand binding energies for atomic and molecular metal cations,¹⁰⁻¹⁵ and gas-phase basicities,¹⁶⁻¹⁸ hydride affinities,^{19,20} electron affinities,²¹⁻²⁵ and ionization potentials^{3,11,26}

for neutral transition-metal complexes. By far, the majority of this research has focused on the chemistry of coordinated and atomic metal *cations*. This is mainly due to the fact that these species can be generated readily by a variety of ionization methods such as laser desorption,^{27,28} surface ionization,⁸ and electron impact ionization²⁹ of volatile inorganic compounds such as metal carbonyls. Until fairly recently,³⁰⁻³⁴ only a relatively few studies of gas-phase ion-molecule reactions involving transition-metal negative ion complexes had been reported.^{1,12,16,35-40} Moreover,

(1) Sallans, L.; Lane, K.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6352-6354.

(2) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *103*, 6501-6502.

(3) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784-791.

(4) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403-4411.

(5) Murad, E. *J. Chem. Phys.* **1980**, *73*, 1381-1385.

(6) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Organometallics* **1982**, *1*, 963-968.

(7) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449-2457.

(8) Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.*, in press.

(9) Cassidy, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176-6179.

(10) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998-4000.

(11) Michels, G. D.; Flesch, G. D.; Svec, H. J. *Inorg. Chem.* **1980**, *19*, 479-485.

(12) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1982**, *16*, 3135-3139.

(13) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2296-2300.

(14) McLuckey, S. A.; Schoen, A. E.; Cooks, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 848-850.

(15) Holland, P. M.; Castleman, A. W., Jr. *J. Chem. Phys.* **1982**, *76*, 4195-4205.

(16) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808-4817.

(17) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1976**, *15*, 665.

(18) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 190-192.

(19) Lane, K. R.; Sallans, L.; Squires, R. R. *Organometallics* **1985**, *3*, 408-410.

(20) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543-2549.

(21) Feigerle, C. S.; Corderman, R. R.; Bobashev, S. V.; Lineberger, W. C. *J. Chem. Phys.* **1981**, *74*, 1580-1598.

(22) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569-5573.

(23) Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 5026-5031.

(24) Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Chem. Phys.* **1983**, *78*, 5420-5431.

(25) Mead, R. D.; Stevens, A. E.; Lineberger, W. C. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 22.

(26) Hildenbrand, D. L.; Kleinschmidt, P. D.; Lau, K. H. *Gov. Rep. Announcement (U.S.)* **1978**, *78*, 110.

(27) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom Ion Phys.* **1980**, *33*, 37-43.

(28) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360-4367.

(29) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332-1333.

(30) (a) Lane, K. R.; Lee, R. E.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5767-5772. (b) Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719-2721.

(31) McDonald, R. N.; Schell, P. L.; McGhee, W. D. *Organometallics* **1984**, *3*, 182-184.

(32) McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095-6096.

(33) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67-71.

(34) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39-84.

(35) Dunbar, R. C.; Ennever, J. E.; Fackler, J. P., Jr. *Inorg. Chem.* **1973**, *12*, 2734-2736.

(36) George, P. M.; Beauchamp, J. L. *Chem. Phys.* **1979**, *36*, 345-351.

(37) Richardson, J. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 3671-3673.

(38) Dunbar, R. C.; Hutchinson, B. B. *J. Am. Chem. Soc.* **1974**, *96*, 3816-3820.

(39) Winters, R. E.; Kistler, R. W. *J. Chem. Phys.* **1966**, *44*, 1964-1966.

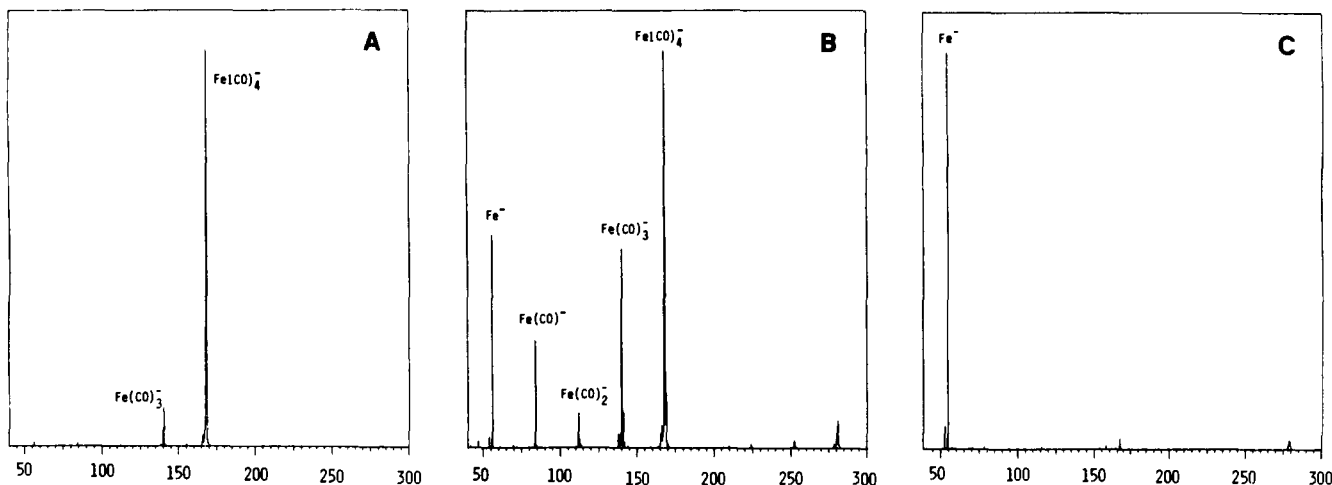


Figure 1. Fourier transformed mass spectra illustrating the generation of Fe^- from (A) electron impact ionization of $\text{Fe}(\text{CO})_5$, (B) irradiation of $\text{Fe}(\text{CO})_4^-$ at its cyclotron frequency with an 18.5-V, 0.100-ms CID pulse in the presence of 6×10^{-6} torr of Ar, and (C) double-resonance ejection of all ions from the cell except Fe^- . All plots are normalized to the largest peak in the spectrum.

the chemistry of *atomic* metal anions is virtually unexplored. One of the most widely used sources of atomic negative ions is the cesium beam sputter-ion source such as the type described by Middleton.⁴¹ While these sources have provided a variety of atomic transition-metal anions for study in tandem accelerators⁴² and photoelectron spectrometers,⁴³ they have not been employed in conjunction with instrumentation which would permit examination of the chemical reactions of atomic anions with neutral substrates.

We recently reported that atomic transition-metal anions can be generated in a Fourier transform mass spectrometer by collision-induced dissociation (CID) of metal carbonyl negative ions.¹ Using Cr^- produced from $\text{Cr}(\text{CO})_5^-$ as the exemplar, we demonstrated that atomic metal anions may be generated in good yields and their subsequent gas-phase reactions with neutral substrates may be examined. In addition, new estimates of the heterolytic and homolytic CrH bond energies were derived from the observed reactions of Cr^- with a series of Brønsted acids. We now wish to report the full details of these studies as well as the analogous results for V^- , Fe^- , Co^- , Mo^- , and W^- .

Experimental Section

The theory and instrumental techniques regarding Fourier transform mass spectrometry (FTMS) and its historical precursor, ion cyclotron resonance (ICR) spectroscopy, are well documented in the literature.⁴⁴⁻⁴⁶ All experiments were performed with a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail.⁴⁷ The instrument is equipped with a 5.2 cm cubic trapping cell situated between the poles of a 15-in. electromagnet maintained at 0.9 T. Trapping plate potentials were set to -2.5 V for trapping negative ions and $+1.8$ V for positive ions. Positive ion spectra were used as a means of confirming the presence and purity of the various neutral reactants introduced into the system.

All chemicals used 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. The liquid samples, as well as 1-phenyl-1,4-butanedione, were introduced into the FTMS cell by means of a leak valve to pressures of approximately 6×10^{-7} torr.

p-Aminobenzoic acid, 5,5-dimethyl-1,3-cyclohexanedione (Dimedone), and *m*-hydroxybenzoic acid were introduced by utilizing a solid probe heated to approximately 50°C . Argon was used as the collision gas for collision-induced dissociation (CID) 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 which corresponded to a pressure of ca. 5×10^{-8} torr. Pressure measurements were made with an uncalibrated Bayard-Alpert ionization gauge.

Atomic metal anions were generated from the corresponding neutral metal carbonyl with a pulse sequence that began with a 150 ms, -12.9 eV electron beam pulse. A typical spectral sequence is shown for Fe^- in Figure 1. Figure 1A shows the electron impact spectrum of $\text{Fe}(\text{CO})_5^-$ which consists predominantly of $\text{Fe}(\text{CO})_4^-$, with some $\text{Fe}(\text{CO})_3^-$ also observed. After 100 ms, $\text{Fe}(\text{CO})_4^-$ was irradiated at its cyclotron frequency for 0.100 ms with an 18.5 V CID pulse corresponding to a kinetic energy of about 95.2 eV.^{47b} A 100 ms time interval was then allowed for subsequent collisions and fragmentation of $\text{Fe}(\text{CO})_4^-$ which resulted in the daughter ion spectrum shown in Figure 1B. Next, Fe^- was isolated from the other CID products with a broad-band double-resonance ejection pulse⁴⁵ swept at 20 Hz/ μs with a pulse amplitude of 23.2 V, as shown in Figure 1C.

Metal anions generated by this sequence were permitted to interact with a reagent gas for a variable reaction time between 100 ms and 3 s followed by detection and cell quenching. Product ion precursors were identified by standard double-resonance techniques.⁴⁵ Additional double-resonance pulses were also employed to isolate ion-molecule reaction products for further study.

Results and Discussion

Metal Anion Formation. Electron-impact ionization of simple metal carbonyls generally results in formation of a major fragment anion from dissociative electron capture.⁴⁸ The mononuclear carbonyls $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ each yield predominantly 17-electron anions by a single CO loss ($\text{Cr}(\text{CO})_5^-$, $\text{Fe}(\text{CO})_4^-$, $\text{Mo}(\text{CO})_5^-$, and $\text{W}(\text{CO})_5^-$, respectively), while $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ produce the 18-electron ions $\text{Mn}(\text{CO})_5^-$ and $\text{Co}(\text{CO})_4^-$ by metal-metal bond cleavage. Electron impact on $\text{V}(\text{CO})_6$ gives mainly the 16-electron ion, $\text{V}(\text{CO})_5^-$. Irradiating each of these ions at its characteristic cyclotron frequency in the presence of 6×10^{-6} torr of Ar target gas results in collisional activation and subsequent fragmentation by CO loss. Under these conditions, multiple activating collisions occur between the translationally excited metal anion complex and argon, with energy deposition proceeding in a stepwise fashion.⁴⁹ Plots of relative daughter ion abundance as a function of average parent ion kinetic energy have been shown to approximate breakdown curves which exhibit branching behavior explicitly as a function of parent ion

(40) Flesch, G. D.; White, Z. W. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *3*, 339-363.

(41) Middleton, R. *Nucl. Instrum. Methods* **1977**, *144*, 373-399.

(42) Dawton, R. H. V. M. *IEEE Trans. Nucl. Sci.* **1972**, *NS-19*, 231-257.

(43) Corderman, R. R.; Engelking, P. C.; Lineberger, W. C. *Appl. Phys. Lett.* **1980**, *36*, 533-535.

(44) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527-561.

(45) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413-416. (b) Comisarow, M. B. *Adv. Mass Spectrom.*, **1980**, *8*, 1698-1706.

(46) Johlman, C. L.; White, R. L.; Wilkins, C. L. *Mass. Spec. Rev.* **1983**, *2*, 389-415.

(47) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199-204. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96-101.

(48) George, P. M.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2959-2964.

(49) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436-7441.

internal energy.⁵⁰ CID breakdown curves derived in this way for each of the seven metal carbonyl anions are presented in Figure 2. Generally, the extent of CO loss increases sequentially as the kinetic energy of the parent ion is increased, and the atomic ion appears as the dominant fragment in the higher energy range for all but $\text{Mn}(\text{CO})_5^-$ and $\text{W}(\text{CO})_5^-$. The complete absence of Mn^- is in accord with the proposed negative electron affinity for Mn ,²⁵ while for the massive tungsten carbonyl ion only trace amounts of W^- could be generated under conditions suitable for producing the other atomic ions, with insignificant improvement achieved by use of xenon target gas. The daughter ion profiles strongly suggest that a consecutive fragmentation mechanism is operative.⁵¹ This is most clearly displayed by $\text{V}(\text{CO})_5^-$ and $\text{Co}(\text{CO})_4^-$ where clear progressions in both the thresholds and maxima are evident. $\text{Fe}(\text{CO})_4^-$ and $\text{Mo}(\text{CO})_5^-$ exhibit significantly broader distributions over a similar energy range, while for $\text{Mn}(\text{CO})_5^-$ they are essentially monotonic. This latter type of behavior is often symptomatic of competitive fragmentations; in the present case multiple, synchronous CO dissociations may occur for a given value of the $\text{Mn}(\text{CO})_5^-$ internal energy. We have tested for sequential vs. competitive CO loss from the manganese ion using double-resonance ejection techniques. Following excitation of the $\text{Mn}(\text{CO})_5^-$ parent ion, daughter ion spectra were obtained with and without continuous ejection of $\text{Mn}(\text{CO})_4^-$ during the CID time interval prior to ion detection.⁵² If competitive fragmentations were operative, involving simultaneous multiple carbonyl losses from $\text{Mn}(\text{CO})_5^-$, then $\text{Mn}(\text{CO})_n^-$, $n = 1-3$, daughter ions would be observed despite the absence of $\text{Mn}(\text{CO})_4^-$. Alternatively, if sequential CO dissociation occurs, then no fragments would appear because the $\text{Mn}(\text{CO})_4^-$ precursor is rapidly ejected⁵² from the FTMS cell as soon as it is formed. Only the latter behavior was observed, indicating that $\text{Mn}(\text{CO})_5^-$ undergoes consecutive fragmentation, at least within the 400 μs time interval between parent ion excitation and $\text{Mn}(\text{CO})_4^-$ ejection. This is consistent with the view that energy deposition in an ion undergoing CID in the FTMS occurs in a stepwise fashion as a result of multiple activating collisions.^{51,53} In considering alternative explanations for the broad daughter ion profiles exhibited in the $\text{Mn}(\text{CO})_5^-$ breakdown graph, it is important to realize that the observed daughter ion abundances can be sensitive functions of not only the unimolecular CO dissociation rates for the parent ion and each fragment ion but also the disappearance rates for each daughter ion due to electron autodetachment. Thus, either significantly lower unimolecular decomposition rates for activated $\text{Mn}(\text{CO})_n^-$ ($n = 1-5$) ions relative to those for other metal carbonyls or increasing autodetachment (loss) rates for the lower fragments may give rise to the type of daughter ion distribution shown in Figure 2C. Additional qualitative information about relative metal/CO binding energies may be derived from the plots in Figure 2. For example, note that the relative intensities for the CrCO^- and MoCO^- fragments remain essentially zero over the entire range of CID energies applied to $\text{Cr}(\text{CO})_5^-$ (Figure 2B) and $\text{Mo}(\text{CO})_5^-$ (Figure 2F), respectively. This can be ascribed to a relatively weak metal-carbonyl bond for these species which may be viewed as a reflection of the inherent stability of the $n d^5(n+1)s^2$ electron configurations for the corresponding atomic anions.²⁵ That is, while the exact bonding configurations for CrCO^- and MoCO^- are not known, we may anticipate substantial repulsive interactions between the σ -bonding pair from CO and the metal ($n+1$)s orbital which becomes fully occupied in the atomic anion.²⁵

Collisional activation of a negative ion can result in not only fragmentation but also electron detachment, with branching

Table I. Thermodynamic Data Referenced in This Study (all values are in kcal/mol)

A	ΔH_f° [A,g]	ref	A-B	D [A-B]	ref
V	122.9	74	$(\text{CO})_4\text{Fe}-\text{CO}$	41.5	55
Cr	94.8	74	$(\text{CO})_5\text{Cr}-\text{CO}$	36.8	55
Fe	99.5	74	$(\text{CO})_5\text{Mo}-\text{CO}$	40.5	55
Co	101.5	74	$(\text{CO})_4\text{Co}-\text{Co}(\text{CO})_4$	15.1	78
Mo	157.3	74	$(\text{CO})_4\text{Co}-\text{H}$	54	77
$\text{Cr}(\text{CO})_6$	-240.7	76	$(\text{CO})_4\text{Co}-\text{H}^+$	<314	56
$\text{Fe}(\text{CO})_5$	-173.0	76	$\text{Fe}-\text{CO}$	46	22
$\text{Co}_2(\text{CO})_8$	-283.3	76	$(\text{CO})\text{Fe}-\text{CO}$	23	22
$\text{Mo}(\text{CO})_6$	-218.0	76	$(\text{CO})_2\text{Fe}-\text{CO}$	46	22
CO	-26.4	74	$(\text{CO})_3\text{Fe}-\text{CO}$	14	22
H	52.1	74	Cr^+-H	35	2
$\text{HCo}(\text{CO})_4$	-136.0	76	Fe^+-H	58	2
			Co^+-H	52	2

A	EA(A)	ref	A	EA(A)	ref
FeCO	29.1	22	Co	15.3	25
$\text{Fe}(\text{CO})_2$	28.1	22	Mo	17.2	25
$\text{Fe}(\text{CO})_3$	41.5	22	V	12.1	25
$\text{Fe}(\text{CO})_4$	55.3	22	FeH	21.5	25
Cr	15.4	25	CoD	15.5	25
Fe	3.8	25			

A	IP(A)	ref
H	313.6	69

mainly controlled by the relative free energy barriers for each channel. Qualitative experiments show CO dissociation to be the dominant parent ion loss process in the lower energy ranges of the CID breakdown curves (Figure 2). That is, the absolute daughter ion intensities generally account for the majority of the parent metal ion intensity decrease at a given value of the CID energy. At high CID energies, parent ion loss by complete ejection from the FTMS cell predominates. Isolation and collisional activation of $\text{Fe}(\text{CO})_3^-$ (from electron impact on $\text{Fe}(\text{CO})_5^-$) showed an increase in the intensity of $\text{Fe}(\text{CO})_4^-$, presumably by electron detachment from $\text{Fe}(\text{CO})_3^-$ followed by dissociative electron attachment to $\text{Fe}(\text{CO})_5^-$ which was present in the FTMS cell. However, simultaneous dissociative charge-transfer reactions between the CID daughter ions (e.g., Fe^-) and $\text{Fe}(\text{CO})_5^-$ cannot be ruled out (vide infra). Therefore, although it appears that some electron detachment does occur upon collision, unambiguous evidence is difficult to obtain. Similar difficulties in distinguishing photodissociation from photodetachment were encountered in earlier studies of metal carbonyl anions.^{37,38} For iron pentacarbonyl, where thermodynamic data are available,²² the $\text{Fe}(\text{CO})_n^-$ electron affinities and $(\text{CO})_{n-1}\text{Fe}^--\text{CO}$ bond energies are of a similar magnitude for $n = 2$ and 3, strongly favor electron detachment for $n = 1$ and strongly favor dissociation for $n = 4$ (Table I). The fact that dissociation appears to predominate may imply that a significant barrier exists for transition between the high vibrational levels populated by collisional activation and the electronic states responsible for electron detachment, viz., inefficient vibration-to-electronic (v-e) energy transfer.⁵⁴ Furthermore, photodissociation of metal carbonyl negative ions apparently predominates over electron photodetachment,^{37,38} implying that electronic excitation can be rapidly transferred into dissociative, vibronic excitation.

Metal Anion Reactions with the Parent Carbonyl. Isolation of the atomic anions as outlined in the Experimental Section permits an examination of their bimolecular ion-molecule reactions with added neutral substrates. Insufficient signal intensities for W^- were obtained from $\text{W}(\text{CO})_5^-$ to allow examination of its subsequent reactions; thus it will be omitted from the remainder of the discussion. Each of the other atomic metal ions was observed to react rapidly with its parent metal carbonyl (eq 1-5). Reactions 1-5 represent the major reaction pathways (>5%), and the branching ratios shown are reproducible to within 10% absolute. Dissociative electron transfer is a major reaction channel for each

(50) McLuckey, S. A.; Sallans, L.; Cody, R. B.; Burnier, R. C.; Verma, S.; Freiser, B. S.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 215-229.

(51) McLafferty, F. W., Ed. "Tandem Mass Spectroscopy"; John Wiley: New York, 1983.

(52) Double resonance ejection conditions were carefully chosen to remove $\text{Mn}(\text{CO})_4^-$ from the FTMS cell as rapidly as possible while excluding any possible broad-band ion ejection.

(53) Blom, K.; Munson, B. *J. Am. Chem. Soc.* **1983**, *105*, 3793-3799.

(54) Acharya, P. K.; Kendall, R. A.; Simons, J. *J. Am. Chem. Soc.* **1984**, *106*, 3402-3407.

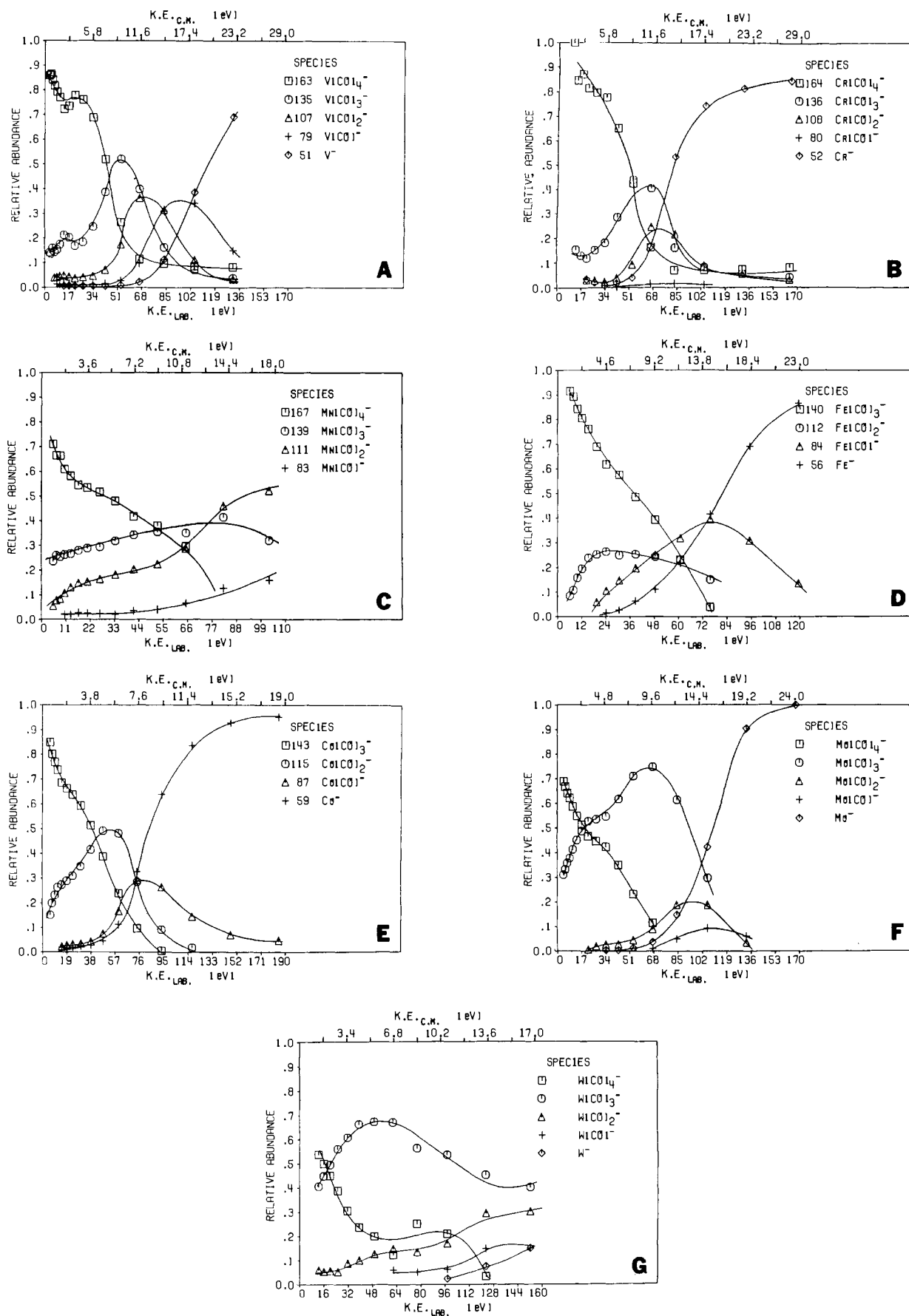
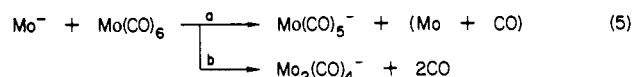
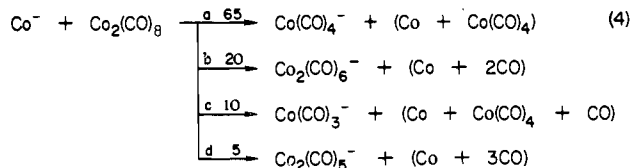
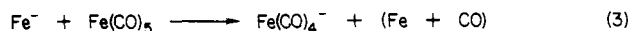
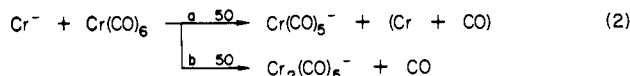
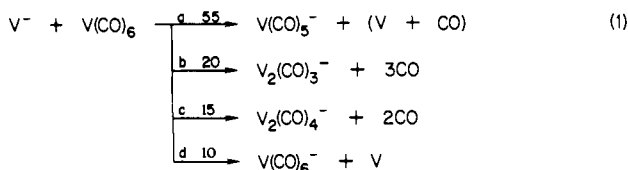
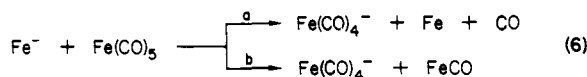


Figure 2. Daughter ion branching ratios plotted as a function of laboratory and center-of-mass kinetic energy for the collision-induced dissociation of (A) $V(CO)_5^-$, (B) $Cr(CO)_5^-$, (C) $Mn(CO)_5^-$, (D) $Fe(CO)_4^-$, (E) $Co(CO)_4^-$, (F) $Mo(CO)_5^-$, (G) $W(CO)_5^-$. The argon collision gas pressure was 6×10^{-6} torr. Ion translational energies were calculated by the methods described in ref 47b. For the Mo and W complexes, selective excitation of a single isotope was not possible and, thus, the intensities shown represent a summation of all of the isotopic products observed and the kinetic energy scale is an average for the various isotopes.

atomic anion, with V^- , Cr^- , and Mo^- also yielding dinuclear cluster



ions from which one or more CO ligands are expelled. The vanadium ion also yields a small amount of the electron-transfer product, $V(CO)_6^-$, and traces of trinuclear cluster ions can be observed from the cobalt system. Control experiments employing $^{54}Fe^-$ show that the product of eq 3 is exclusively $Fe(CO)_4^-$ and not the isobaric cluster $Fe_2(CO)_2^-$. Double resonance confirms that each atomic anion is a precursor for the products indicated, though a portion of the charge-transfer products (e.g., $Fe(CO)_4^-$, $Cr(CO)_5^-$, etc.) is also derived from ionization of the neutral metal carbonyls by trapped electrons.⁴⁸ Thermochemical data are available from the literature which permit estimates of the energies for a few of the reactions listed in eq 1–5. In general, dissociative electron transfer involving an atomic metal anion and a metal carbonyl may yield a free metal atom and uncomplexed CO molecules as products or, alternatively, neutral metal carbonyl fragments may be produced (eq 6). The enthalpy of reaction 6a is given by $EA(Fe) + D[(CO)_4Fe-CO] - EA(Fe(CO)_4)$, while reaction 6b is more exothermic by the metal-carbon bond strength in $FeCO$, $D[Fe-CO]$. Using the appropriate electron affinities

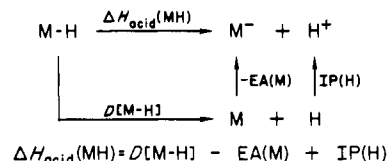


and iron-carbonyl bond energies given by Lineberger and co-workers,²² along with the recently established value for $D[(C-O)_4Fe-CO]$ ⁵⁵ (Table I), gives estimates for $\Delta H(6a) = -10$ kcal/mol and $\Delta H(6b) = -31$ kcal/mol. At present, we cannot identify unambiguously which pathway is operable. Similarly, the enthalpy of reaction for the major channel in eq 4 is given by $D[(CO)_4Co-Co(CO)_4] + EA(Co) - EA(Co(CO)_4)$, provided three separate metal fragments are produced as shown. The last term, $EA(Co(CO)_4)$, may be derived from recent gas-phase acidity measurements for $HCo(CO)_4$,⁵⁶ while the Co-Co bond strength for $Co_2(CO)_8$ may be estimated from $\Delta H_f^\circ[Co_2(CO)_8, g]$ and $D[H-Co(CO)_4]$ (Table I). From these data we arrive at the conclusion that reaction 4a is exothermic by at least 23 kcal/mol. Any higher degree of association of the neutral products would render the reaction even more exothermic. There are insufficient thermochemical data available to justify further quantitative statements about reaction 4. However, the appearance of both dinuclear and mononuclear product ions but no significant trinuclear cluster ions suggests that the metal-metal bonding interactions in tricobalt negative ions may be relatively weak. An analogous treatment of reactions 1, 2, and 5 is prevented by the

(55) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905–3912.

(56) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.*, in press.

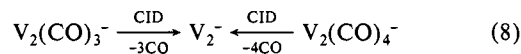
Scheme I



lack of sufficient thermodynamic data. For example, only $EA(Cr(CO)_5)$ is required to establish the exothermicity of eq 2a, as written, since $\Delta H(2a) = D[(CO)_5Cr-CO] + EA(Cr) - EA(Cr(CO)_5)$. From the occurrence of this reaction and the pertinent data listed in Table I, a lower limit for $EA(Cr(CO)_5) > 52.2$ kcal/mol may be derived. Independent support for this limit is given by the observation that allyl anion undergoes dissociative electron transfer with $Cr(CO)_6$ in a flowing afterglow apparatus (eq 7).⁵⁷ The occurrence of this reaction requires that $EA(Cr(CO)_5) > D[(CO)_5Cr-CO] + EA(C_3H_5) = 45.0$ kcal/mol.⁵⁸



The cluster ion products of reactions 1, 2, and 5 are presently under further investigation.⁵⁹ As noted earlier,¹ the metal-metal bond in $Cr_2(CO)_5^-$ is a relatively weak one. This is shown by the exclusive loss of Cr when this ion is collisionally activated at low collision energies. An analogous adduct forms between Mo^- and $Mo(CO)_6$ (eq 5b) with an additional CO expelled from the product. Stronger metal-metal bonding in the second-row cluster ion may account for this.⁶⁰ Unfortunately, CID of $Mo_2(CO)_4^-$ was not possible due to its low abundance which results from the low intensity of the Mo^- precursor as well as its partitioning among 14 isotopic peaks. The vanadium ion reacts to form two major adducts, $V_2(CO)_3^-$ and $V_2(CO)_4^-$. The extensive CO loss from these condensation reactions can be attributed to two factors. First, early transition metals such as vanadium generally exhibit weaker metal-carbonyl bonds than later metals along a given row since relatively fewer metal electrons are available for back-bonding.⁶¹ Accordingly, a greater number of CO ligands may be expelled as a result of exothermic metal-metal bond formation in the divanadium adduct. Secondly, vanadium-vanadium bonds can be quite strong as shown, for example, by the relative bond strengths in homonuclear transition-metal diatomics of the first row.⁶² Divanadium, V_2 , possesses an unusually high bond-dissociation energy (2.48 eV),⁶³ with a bond order of two assigned by Harris and Jones.⁶⁴ While we recognize that the bonding configurations in the divanadium carbonyl anions are likely to be somewhat different from that in V_2 , the strong metal-metal bond in the diatomic evidently does not require a high bond multiplicity and, therefore, a similar strong interaction is possible in the cluster ion. In support of this, we find that both $V_2(CO)_4^-$ and $V_2(CO)_3^-$ undergo CID exclusively by loss of carbonyls and not vanadium (eq 8).⁵⁹ Thus, unlike $Cr_2(CO)_5^-$, metal-metal bonding is maintained at the expense of metal carbon bonds.



Metal Anion Basicity: Heterolytic and Homolytic MH Bond Energies. Proton-transfer reactions between a series of reference

(57) Lane, K. R.; Squires, R. R., unpublished results.

(58) The electron affinity of the allyl radical has recently been redetermined by laser photodetachment to be 8.35 ± 0.46 kcal/mol: Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734–7741.

(59) Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S., manuscript in preparation.

(60) Cotton, F. A.; Walton, R. W. "Multiple Bonds Between Metal Atoms"; John Wiley and Sons: New York, 1982.

(61) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; John Wiley and Sons: New York, 1980.

(62) Moskovits, M.; Ozin, G. A. In "Cryochemistry"; John Wiley and Sons: New York, 1976; Chapter 9 and references cited therein.

(63) Kant, A.; Lin, S. S. *J. Chem. Phys.* **1969**, *51*, 1644–1647.

(64) Harris, J.; Jones, R. O. *J. Chem. Phys.* **1979**, *70*, 830–841.

Table II. Results for Proton Abstraction by Atomic Metal Anions

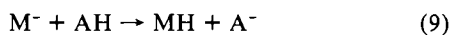
reference acid	$\Delta H_{\text{acid}}^{\circ a}$	V ⁻	Cr ⁻	Fe ⁻	Co ⁻	Mo ⁻
CH ₃ CH ₂ COOH	347.3 ± 2					no
HCOOH	345.2 ± 2		no	no	no	no
CH ₃ COCH ₂ COCH ₃	343.7 ± 2	no	no	no	no	no
<i>p</i> -H ₂ NC ₆ H ₄ COOH	341.1 ± 2	no	no	no	no	yes
C ₆ H ₅ COCH ₂ COCH ₃	339.9 ± 2	no	no	no	yes	yes
5,5-dimethylcyclohexane-1,3-dione	338.9 ± 2	yes	yes	yes	yes	yes
C ₆ H ₅ SH	338.9 ± 3.5	yes	yes	yes	yes	yes
<i>m</i> -HOC ₆ H ₄ COOH	337.5 ± 2	yes		yes	yes	yes
CH ₂ (CN) ₂	336.0 ± 2	yes				yes

^akcal/mol; ref 65.**Table III.** A Summary of the Metal-Hydride Gas-Phase Acidities and Homolytic Bond-Dissociation Energies (kcal/mol)

M	$\Delta H_{\text{acid}}^{\circ}(\text{MH})$	$D[\text{M}-\text{H}]$
Fe	339.4 ± 3	29.6 ± 3
V	339.4 ± 3	37.9 ± 3
Cr	339.4 ± 3	41.2 ± 3
Co	340.5 ± 3	42.2 ± 3
Mo	342.4 ± 3	46.0 ± 3

acids and V⁻, Fe⁻, Cr⁻, Co⁻, and Mo⁻ have been examined in order to obtain quantitative estimates of atomic metal anion basicities. These data are of interest since they provide a measure of heterolytic metal-hydrogen bond energies for diatomic metal hydrides, $D[\text{M}^--\text{H}^+]$ ($\Delta H_{\text{acid}}^{\circ}(\text{MH})$). Metal hydride acidities may be used in conjunction with the thermodynamic cycle shown in Scheme I to yield estimates of the corresponding homolytic bond energies, where $D[\text{M}-\text{H}]$ is the corresponding homolytic bond energy and EA(M) and IP(H) are the metal atom electron affinity and hydrogen ionization potential, respectively.

The atomic metal anion of interest is generated by CID, isolated from other ions by broad-band ejection pulses, and then allowed to react with neutral proton donors with established gas-phase acidities.⁶⁵ The occurrence of reaction 9, subject to verification by double resonance, implies that $\Delta H_{\text{acid}}^{\circ}(\text{MH}) \geq \Delta H_{\text{acid}}^{\circ}(\text{AH})$. The underlying assumptions here are that the occurrence or non-occurrence of reaction is controlled by thermodynamic, as opposed to kinetic, factors and that the diatomic hydride is the only neutral metal product. These assumptions are justified,



provided the following caveat. Since diatomic metal hydrides are not available for use as neutral reactants, the reverse of eq 9 cannot be employed to confirm a particular outcome for any metal ion-reference acid pair. That is, our proton affinity bracketing is necessarily "one-sided". Furthermore, under the conditions of the FTMS, a gas-phase proton transfer may occur, albeit slowly, which is up to 2 kcal/mol endothermic.⁶⁶

A summary of results obtained for the five atomic metal anions and ten reference acids which span a range of ca. 10 kcal/mol in gas-phase acidity⁶⁵ is given in Table II. All of the proton donors except C₆H₅SH and CH₂(CN)₂ are oxy acids (presuming the diketones to be predominately in their enol form)⁶⁷ and, therefore, exothermic proton abstraction should not be impeded by high kinetic barriers.⁶⁸ Furthermore, the observed thresholds for proton transfer are reproducible under a variety of conditions in the FTMS, as are the positive double resonance connections between the atomic anions and the conjugate base anions of the reference acids. From these thresholds, gas-phase acidities for the metal hydrides, $\Delta H_{\text{acid}}^{\circ}(\text{MH})$, were assigned and are summarized in Table III. A conservative uncertainty estimate of ±3 kcal/mol is assigned on the basis of the reported error limits for the reference

Table IV. Comparison of Metal-Hydride Bond-Dissociation Energies

M	$D[\text{M}-\text{H}]$, kcal/mol					
	this study	Birge-Sponer ^a	KM ^b	Das ^c	WB ^d	other
V	37.9 ± 3				38.5	50.8
Cr	41.2 ± 3	66.9 ± 11.9	<45	43.9	46.3	
Fe	29.6 ± 3	39.9 ± 6.9	<43	31.1	42.7	
Co	42.2 ± 3		45.1 ± 3	47.9		38.9 ± 4.5 ^e

^aReferences 73 and 75. ^bReference 70. ^cReference 71: values corrected to D_0 . ^dReference 72: values corrected to D_0 . ^eReference 2.

Table V. Heat of Formation, Ionization Potentials, and MH⁻ Bond Energies Derived from Metal-Hydride Bond-Dissociation Energies

M	$\Delta H_f^{\circ}[\text{MH}, \text{g}]$, kcal/mol	IP(MH), eV	$D[\text{M}-\text{H}]$, kcal/mol	$D[\text{M}-\text{H}]^{\circ}$, kcal/mol
V	137 ± 3	6.2 ± 0.3		
Cr	106 ± 3	7.0 ± 0.3		
Fe	122 ± 3	6.6 ± 0.3	47.3 ± 3	33.7 ± 3
Co	111 ± 3	7.4 ± 0.3	42.4 ± 3	40.3 ± 3
Mo	163 ± 3			

^a $D[\text{M}^--\text{H}] + \text{EA}(\text{M}) - \text{EA}(\text{H})$; ref 25.

acidities⁶⁵ as well as the limitations of one-sided bracketing procedures mentioned previously. Atomic electron affinities for each of the metals are available from laser photoelectron spectroscopic measurements.²⁵ Combining these data (Table I) with our acidity measurements and IP(H) = 313.6 kcal/mol⁶⁹ according to Scheme I gives the metal-hydride bond-dissociation energies also listed in Table III. These bond energies are in reasonable agreement with previously reported values derived from various methods, as shown in Table IV. Kant and Moon (KM) assayed high-temperature equilibria between metal atoms, hydrogen, and the diatomic hydrides in an effusion cell using mass spectrometry and derived bond energies by a third law analysis.⁷⁰ A modified Phillips-Kleinman pseudopotential MCSCF method was employed by Das⁷¹ and a CASSCF/CI(SD) procedure by Walch and Bauschlicher (WB)⁷² in calculating spectroscopic constants for first-row metal hydrides. An error limit of ±0.2 eV is assigned by Das for the CrH bond energy. Armentrout and Beauchamp combined measurements of $D[\text{Co}^+-\text{H}]$ and IP(CoH) using an ion beam apparatus to derive the Co-H bond energy,³ and the values for FeH⁷³ and CrH⁷⁵ were determined from Birge-Sponer extrapolations. While our bond energies appear to be systematically lower than most previous estimates, all the values lie within the given experimental error limits. Indeed, it is satisfying that these

(69) Rosenstock, H. M.; Draxl, K. K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref.* **1977**, *6*, Suppl. 1.

(70) Kant, A.; Moon, K. *High Temp. Sci.*, **1981**, *14*, 23-31.

(71) Das, G. *J. Chem. Phys.* **1981**, *74*, 5766-5774.

(72) Walch, S. P.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1983**, *78*, 4597-4605.

(73) Dendramis, R. J.; Van Zee, R. J.; Weltner, W., Jr. *Astrophys. J.* **1979**, *231*, 632-636.

(74) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(75) Gaydon, A. G. "Dissociation Energies and Spectra of Diatomic Molecules", 3rd ed.; Chapman and Hall: London, 1968.

(65) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 11.

(66) Mautner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5-10.

(67) Forsen, S.; Nilsson, M. "The Chemistry of the Carbonyl Group"; Zabicky, J., Ed.; Interscience: London, 1978; Vol. 2.

(68) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891-7898.

diverse experimental methods are in such good agreement, not only with each other but with theory as well.

Additional thermodynamic properties for diatomic metal hydrides may be derived by combining our $D[M-H]$ values with other data from the literature (Table I). For example, $\Delta H_f^\circ[MH, g]$ is obtained from metal sublimation enthalpies⁷⁴ and eq 10, and recent measurements of $D[M^+-H]^2$ together with $IP(M)$ ⁶⁹ yield $IP(MH)$ according to eq 11. Furthermore, homolytic bond energies for MH^- ions may be derived from eq 12 and measured values for $EA(MH)$ and $EA(M)$. Properties derived in this way for each of the five metals are listed in Table V.

$$\Delta H_f^\circ[MH, g] = \Delta H_{\text{sub}}^\circ(M) + \frac{1}{2}D[H-H] - D[M-H] \quad (10)$$

$$IP(MH) = D[M-H] + IP(M) - D[M^+-H] \quad (11)$$

$$D[M-H] = D[M-H] + EA(MH) - EA(M) \quad (12)$$

Conclusions

The gas-phase chemistry of atomic metal anions is a rich new area for research. In this paper, we report the first in-depth study of the reactivity of these species. Pulsed techniques using FTMS

(76) Pilcher, G.; Skinner, H. A. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Eds.; John Wiley: New York, 1982.

(77) Ungvary, F. J. *Organomet. Chem.* **1972**, *36*, 363-370.

(78) Calculated from $D^\circ[(CO)_4Co-H]$ and $\Delta H_f^\circ[(Co_2(CO)_8, g]$. A value of 30 kcal/mol is given by: A. K. Vaier *Russ. J. Phys. Chem.* **1980**, *54*, 1-5.

are shown to be well suited for both the generation of atomic transition-metal anions by CID and the subsequent investigation of their reactions with neutral substrates. Atomic metal anions are observed to react with their parent neutral metal carbonyls. In all cases, dissociative electron-transfer reactions occur, while V^- , Cr^- , Co^- , and Mo^- also produce dinuclear adduct ions from which one or more CO ligands are expelled. Bracketing methods have provided estimates of the proton affinities for several of the atomic metal anions from which new values for homolytic metal-hydrogen bond-dissociation energies have been derived. A striking feature of the metal hydride acidities measured in this study is that they are all very nearly the same. The generality and origins of this remarkable trend are explored in the following paper in this issue.

Acknowledgment. The authors wish to thank H. I. Kenttämaa and Professor R. G. Cooks for stimulating and helpful discussions. B.S.F. acknowledges The Department of Energy (DE-AC02-80-ER10689) and the National Science Foundation (CHE-8002685) for providing funds to purchase the FTMS.

Registry No. Cr(CO)₆, 13007-92-6; Fe(CO)₅, 13463-40-6; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; Mn₂(CO)₁₀, 10170-69-1; Co₂(CO)₈, 10210-68-1; V(CO)₆, 14024-00-1; FeH, 15600-68-7; VH, 13966-93-3; CrH, 13966-79-5; CoH, 14994-20-8; MoH, 15587-51-6; VH⁻, 64911-45-1; CrH⁻, 96348-78-6; FeH⁻, 64899-88-3; CoH⁻, 64899-90-7; MoH⁻, 96348-79-7; V⁻, 16727-17-6; Fe⁻, 22325-61-7; Cr⁻, 19498-56-7; Co⁻, 16727-18-7; Mo⁻, 54604-28-3.

Correlation of Electron and Hydrogen Atom Binding Energies for Transition-Metal Atoms

Robert R. Squires

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received January 2, 1985

Abstract: A collection and analysis of thermochemical data for neutral metal atoms, atomic negative ions, and diatomic metal hydrides is described which exposes a new periodic property correlation for transition-series elements. Diatomic metal hydrides are shown to exhibit a constant gas-phase acidity (ΔH_{acid}) equal to 341 ± 5 kcal/mol. This behavior is unique to neutral monohydrides since cationic metal hydrides (MH^+), main-group monohydrides, and polyatomic metal hydride complexes each exhibit a wide range in ΔH_{acid} as the metal atom is varied. The origin of this trend is shown to be a general linear correlation between transition-metal atom electron affinity and homolytic bond-dissociation energy for the corresponding diatomic hydride, i.e., $D[M-H] = EA(M) + 27.5$ kcal/mol. Detailed consideration of the electron configurations of atomic transition-metal negative ions and diatomic metal hydrides exposes a simple analogy between electron and hydrogen atom binding by most all metal atoms. Formation of most atomic negative ions and neutral monohydrides from transition-metal atoms generally results in an electron configuration characterized by an additional (nonbonding) d electron and a stabilized, doubly-occupied s or σ orbital. Atomic electron affinities and diatomic hydride bond energies for the first-row transition metals except Sc and Ti are found to inversely parallel the atomic promotion energies $\Delta E[3d^n4s^2 \rightarrow 3d^{n+1}4s^1]$ required to achieve the nominal H atom and electron binding configurations of the atoms. Deviation by Sc and Ti is ascribed to enhanced ionic character of the monohydrides which makes the electron configurations of the atomic anions and diatomic hydrides dissimilar. The weak metal-hydrogen bonds known for FeH and MnH are shown to be due to the relatively high promotion energies required for bonding and a minimal ionic character of the hydrides due to high atomic ionization potentials. On the basis of the correlation equation given above and measured electron affinities, bond-dissociation energies for several second- and third-row transition-metal diatomic hydrides are predicted. The columnar trends in MH bond energies so exposed are discussed.

Diatomic transition-metal hydrides represent one of the simplest classes of molecules with which to study periodic bonding patterns of the transition series elements and the role of d electrons in prototype metal σ bonds.¹⁻³ Small molecular metal hydrides are of long-standing astrophysical and cosmochemical interest since

many examples have been detected from electronic and infrared spectra of cool stellar atmospheres.^{4,5} Furthermore, diatomic metal hydrides and polyhydrides continue to play a key role in the development of models for catalytic activation of molecular hydrogen on metal surfaces.⁶⁻⁹ Accordingly, a large number of

(1) Schaefer, H. F., III *Acc. Chem. Res.* **1977**, *10*, 287-293.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; John Wiley and Sons: New York, 1980.

(3) Gibb, T. R. P., Jr. In "Progress in Inorganic Chemistry"; Cotton, F. A., Ed.; Interscience: New York, 1962; Vol. 3.

(4) Bar-Nun, A.; Pasternak, M.; Barrett, P. H. *Astron. Astrophys.* **1983**, *87*, 328-89.

(5) Weltner, W. *Science* **1967**, *155*, 155-164.

(6) Meutterties, E. L. "Transition Metal Hydrides"; Marcel Dekker: New York, 1971.