Thermochemistry of Transition Metal Benzene Complexes: Binding Energies of $M(C_6H_6)_x^+$ ($x = 1, 2$) for M = Ti to Cu

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Abstract: The sequential bond energies of the mono- and bis-benzene complexes of the first-row transition metal ions, $M^+ = Ti^+-Cu^+$, are determined by collision-induced dissociation with Xe in a guided ion beam tandem mass spectrometer. Values for the 0 K $M^+-C_6H_6$ bond energies are found to be in good agreement with theoretical predictions and with most previous experimental values in those cases where they are available. Such agreement can be obtained only with ions prepared at a controlled internal energy and with careful consideration of the effects of multiple collisions, the internal energy of the ions, and their dissociation lifetimes, which require a knowledge of the vibrational frequencies of the ions and transition states leading to dissociation. Thresholds for dissociation of the benzene ligand from the bis-benzene complexes are calculated to have large kinetic shifts that may limit the absolute accuracy of the bond energies determined for $(C_6H_6)M^+-C_6H_6$. For the case of M = Cr, the sum of the first and second bond energies compares reasonably well with literature values; but for M = V, the agreement is poor, a result attributed to an inaccurate heat of formation for $V(C_6H_6)_2$. Revised heats of formation for gas-phase $M(C_6H_6)_2$ species where M = V and Cr are derived from the present results. The trends in the metal–benzene bond energies across the periodic table are discussed.

Introduction

It was 1919 when Hein and co-workers prepared the first arene–metal complexes,[1] though a definitive structural characterization was not achieved until the mid-1950s. Starting with the first efficient synthesis of bis-benzene metal compounds by Fischer and Hafner,[2] extensive studies concerned with the reactivity, structure, and theoretical aspects of these sandwich complexes have been carried out.[3,4] Metal atoms,[5] metal complexes,[3] metal clusters,[6] and metal surfaces[7] have meanwhile been shown to interact with aromatic hydrocarbons. Fundamental to our understanding of the bonding in these systems as well as their physical and chemical properties is the knowledge of bond dissociation energies (BDEs) of the parent benzene bound to different metals M or metal fragments ML_n in the absence of solvent effects. As solvation effects do not exist in the gas phase, the latter is an ideal environment for detailed investigations in this regard. However, relatively few gas-phase studies on the thermochemistry of transition metal benzene species have been carried out to date.[8-12]

In recent work, we have demonstrated that collision-induced dissociation (CID) in a guided ion beam mass spectrometer is a useful tool to obtain accurate thermochemical information about ligated metal ions ML_x^+, where the ligands L studied have included CO,[13-18] H_2O,[19,20] CH_4,[19,21] N_2, and NO.[15] We have also measured the binding energy of benzene to Ag^+ by CID[10] and obtained good agreement with theory[22] and other experimental values.[11] Here, we apply this technique to determine the BDEs for $M(C_6H_6)^+$ and $M(C_6H_6)_2^+$ ions of the 3d transition metals, M = Ti–Cu.

The bis-benzene complex ions represent one of the most challenging metal–ligand systems that we have studied to date. The number of vibrational frequencies is high (69), which means that energy flow into the reaction coordinate leading to dissociation will be disfavored statistically. Also, the ligands can be formally thought of as tridentate, which may mean that the transition state for ligand dissociation is highly constrained because three metal–ligand bonds need to be broken simultaneously. One means of checking the accuracy of the thermochemistry determined here is to compare the sum of the first and second metal–benzene ion bond energies with the enthalpy for complete fragmentation of a known bis-benzene metal cation.

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Table 1. Literature Heats of Formation (kJ/mol)[a]

species	0 K	298 K
C_6H_6	100.4 ± 1.0[b]	82.9 ± 0.3[b]
Cr	395.3 ± 4.2	397.5 ± 4.2
Cr^+	1048.1 ± 1.5	1056.5 ± 4.2
$Cr(C_6H_6)_2$	265 ± 12[c]	227 ± 12[c]
	285 ± 56[c]	246 ± 56[c]
	319 ± 20[d]	281 ± 20[d]
$Cr(C_6H_6)_2^+$	793 ± 12[c]	761 ± 12[c]
	813 ± 56[c]	781 ± 56[c]
	848 ± 20[d]	815 ± 20[d]
V	512.2 ± 8	515 ± 8
V^+	1162.5 ± 8	1172 ± 8
$V(C_6H_6)_2$	107 ± 8[c]	68 ± 8[c]
	310 ± 23[d]	271 ± 23[d]
$V(C_6H_6)_2^+$	681 ± 13[c]	648 ± 13[c]
	884 ± 21[d]	851 ± 21[d]

[a] Reference 29 except as noted. Ion values use the thermal electron convention. [b] Reference 28. [c] See text. [d] This study.

The most prominent of these complexes is bis-benzene chromium such that the dissociation is reaction 1 with an enthalpy, $\Delta_r H^\circ(1)$. Thermochemistry is also available for bis-benzene

$$Cr(C_6H_6)_2^+ \rightarrow Cr^+ + 2C_6H_6 \qquad (1)$$

vanadium ion, which dissociates in reaction 2 with enthalpy $\Delta_r H^\circ(2)$.

$$V(C_6H_6)_2^+ \rightarrow V^+ + 2\,C_6H_6 \qquad (2)$$

Literature Thermochemistry

Calculating accurate values for the enthalpies of reactions 1 and 2 requires a knowledge of the heats of formation $\Delta_f H^\circ$ for each of the species in the reaction. The thermochemistry of M^+ and C_6H_6 is well established, Table 1. To obtain $\Delta_f H^\circ[M(C_6H_6)_2^+]$, we need the ionization energy of $M(C_6H_6)_2$ and $\Delta_f H^\circ[M(C_6H_6)_2(g)]$, which is the sum of the heats of formation and sublimation of solid $M(C_6H_6)_2$.

Several inconsistent values for $\Delta_f H^\circ_{298}[Cr(C_6H_6)_2(s)]$ measured via conventional bomb calorimetry have been reported in the literature. Two different studies by Fischer and coworkers yielded 213 ± 8 and 220 ± 8 kJ/mol for $\Delta_f H^\circ_{298}[Cr(C_6H_6)_2(s)]$,[23] while Fischer, Cotton, and Wilkinson obtained a value of 88 ± 33 kJ/mol[24] and Tel'noi et al. reported 146 ± 8 kJ/mol.[25] In subsequent work, Connor, Skinner, and Virmani[26] point out that these heats of formation must be accepted with caution because of problems such as incomplete combustion of the metal and the ill-defined nature of the products when conventional bomb calorimetry is used. They recommend $\Delta_f H^\circ_{298}[Cr(C_6H_6)_2(s)] = 142 \pm 8$ kJ/mol obtained from the heat of reaction with iodine vapor in a high-temperature microcalorimeter, in good agreement with the value of Tel'noi et al. Overall, this latter value seems likely to be the best, but a more conservative value comes from the average of all five determinations, 162 ± 55 kJ/mol. The enthalpy of sublimation of $Cr(C_6H_6)_2$ at 298 K has been measured as 78 kJ/mol by Fischer et al.[23] and 91 kJ/mol by Andrews et al.[27] Taking the mean of these two values in combination with a heat of formation of 142 ± 8 kJ/mol results in $\Delta_f H^\circ_{298}[Cr(C_6H_6)_2(g)] = 227 \pm 12$ kJ/mol, close to the value of 222 ± 8 kJ/mol cited in the critical compilation of Lias et al.[28] The more conservative value is 246 ± 56 kJ/mol.

The heats of formation of a polyatomic molecule at 298.15 and 0 K are related as follows:[29]

$$\Delta_f H^\circ_0 = \Delta_f H^\circ_{298} + [H^\circ_0 - H^\circ_{298}]_{\text{compound}} - \sum [H^\circ_0 - H^\circ_{298}]_{\text{elements}} \qquad (3)$$

where for a nonlinear polyatomic molecule

$$[H^\circ_0 - H^\circ_T]_{\text{compound}} \approx -4RT - RT\sum u/(e^u - 1) \qquad (4)$$

and $u = h\nu_i/k_B T$. The $4RT$ term in eq 4 has contributions of $3RT/2$ from translation, $3RT/2$ from rotation, and RT from $\Delta PV = \Delta nRT$ for 1 mol of ideal gas. The summation in eq 4 is carried out over the vibrational frequencies of the polyatomic molecule, ν_i. The vibrational frequencies for $Cr(C_6H_6)_2$[30] lead to an enthalpy contribution of $-7.67RT$. Thus, $[H^\circ_0 - H^\circ_{298}]$ for $Cr(C_6H_6)_2$ is $-11.67RT = -28.93$ kJ/mol. The enthalpy changes, $[H^\circ_0 - H^\circ_{298}]$, of the elements are −4.057, −12.612, and −50.802 kJ/mol for Cr(c), 12 C(graphite) and 6 H_2, respectively.[29] Substituting these values in eq 3, we obtain $\Delta_f H^\circ_0[Cr(C_6H_6)_2(g)] = 265 \pm 12$ kJ/mol and a more conservative value of 285 ± 56 kJ/mol.

Finally, we need an accurate value for $IE[Cr(C_6H_6)_2]$, which has been measured as 5.70 ± 0.1,[31] 5.91 ± 0.1,[32] 5.4,[33] 5.7,[34] 5.45 ± 0.02,[35] 5.4,[36] and 5.473 ± 0.005 eV.[37] We take the latter value, obtained from a recent high-resolution photoelectron spectrum, to be the best determination of the ionization energy. Thus, the heat of formation of $Cr(C_6H_6)_2^+$ is 793 ± 12 kJ/mol at 0 K and 761 ± 12 kJ/mol at 298 K in the thermal electron convention (with more conservative values of 813 ± 56 and 781 ± 56 kJ/mol, respectively). Given these data and those in Table 1, the enthalpy $\Delta_r H^\circ(1)$ is calculated to be 456 ± 13 kJ/mol (4.73 ± 0.13 eV) at 0 K (with a more conservative value being 436 ± 56 kJ/mol = 4.52 ± 0.58 eV).

The only other bis-benzene metal complex for which thermochemical information is available is the vanadium compound, $V(C_6H_6)_2$. Fischer and Reckziegel reported $\Delta_f H^\circ_{298}[V(C_6H_6)_2(s)] = 31 \pm 8$ kJ/mol[38] measured by conventional bomb calorimetry and a heat of sublimation of 37 kJ/mol. This leads to a value of 68 ± 8 kJ/mol for $\Delta_f H^\circ_{298}[V(C_6H_6)_2(g)]$. The vibrational frequencies for $V(C_6H_6)_2$ are assumed to equal those of $Cr(C_6H_6)_2$. Following the same method outlined above and $[H^\circ_0 - H^\circ_{298}]$ for V(c) of −4.640 kJ/mol, we obtain $\Delta_f H^\circ_0[V(C_6H_6)_2(g)] = 107 \pm 8$ kJ/mol. The ionization energy of $V(C_6H_6)_2$ is not well established. A value of 6.26 ± 0.1 eV was derived from an early mass spectrometric appearance energy,[32] while a more recent photoelectron study gave IE-

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$[V(C_6H_6)_2] = 5.95$ eV.[39] We take the latter value as the best estimate of the true IE and assign an uncertainty of ±0.1 eV. This yields a heat of formation for $V(C_6H_6)_2^+$ of 681 ± 13 kJ/mol at 0 K and 648 ± 13 kJ/mol at 298 K in the thermal electron convention. From these data and the well-known heats of formation of V^+ and C_6H_6, Table 1, we can calculate the heat of reaction for fragmentation of $V(C_6H_6)_2^+$, reaction 2, to be 682 ± 15 kJ/mol (7.07 ± 0.16 eV) at 0 K. This thermochemistry should be accepted with caution, as it is based on a single report of $\Delta_fH^\circ_{298}[V(C_6H_6)_2(s)]$ measured by conventional bomb calorimetry, a method that yielded inconsistent results in the case of $Cr(C_6H_6)_2$. The observation that the sum of the bond energies for $V(C_6H_6)_2^+$ is 50% greater than that for $Cr(C_6H_6)_2^+$ and that for neutral $V(C_6H_6)_2$ is 80% higher than for $Cr(C_6H_6)_2$ is probably an indication of the severity of this problem.

Experimental Methods

General. Complete descriptions of the apparatus and experimental procedures are given elsewhere.[40,41] Production of ligated metal ions is described below. The ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. Mass-selected ions are slowed to a desired kinetic energy and focused into an octopole ion guide that radially traps the ions. The octopole passes through a static gas cell containing the neutral reactant, Xe, at relatively low pressures (0.05−0.22 mTorr). After exiting the gas cell, product and unreacted beam ions drift to the end of the octopole, where they are directed into a quadrupole mass filter for mass analysis and then detected. Ion intensities are converted to absolute cross sections as described previously.[40] Absolute uncertainties in cross sections are about 20%; relative uncertainties are 5%.

Laboratory ion energies are related to center-of-mass (CM) frame energies by $E(\mathrm{CM}) = E(\mathrm{lab})m/(M + m)$ where M and m are the masses of the ion and neutral reactant, respectively. The absolute energy scale and the corresponding full width at half maximum (fwhm) of the ion beam kinetic energy distribution are determined by using the octopole as a retarding energy analyzer, as described previously.[40] The absolute uncertainty in the energy scale is 0.05 eV (lab). The energy distributions are nearly Gaussian with a fwhm of 0.20−0.45 eV (lab).

Ion Source. The $M(C_6H_6)^+$ and $M(C_6H_6)_2^+$ species are formed in a 1 m long flow tube operated with a mixture of 90% He and 10% Ar at a total pressure of 500−800 mTorr. Two methods are used to produce the ligated ions with typical intensities between 5×10^4 and 2×10^6 ions/s. In the first method, metal ions are generated in a continuous dc discharge by argon ion sputtering of a cathode consisting of a rod of the metal of interest or a tantalum "boat" containing a powder of the metal in the case of manganese. Typical operating conditions of the cathode are negative voltages of 1−3 kV. Benzene is introduced to the flow 50 cm downstream from the dc discharge, and the desired metal complexes are formed by three-body collisions. While traversing the remaining 50 cm length of the flow tube, the metal benzene ions undergo $\sim 10^5$ collisions with the carrier gases. Their internal energy distribution is therefore believed to be thermalized to 300 K, the temperature of the flow tube. Previous work on a number of systems is consistent with the production of thermalized ions under similar conditions.[13,14,20,42] In the case of $Cr(C_6H_6)^+$, unidentified impurities with masses similar to the reactant complex did not allow the collection of CID data from ions produced by this method. In the case of titanium, vanadium, cobalt, nickel, and copper complexes, some experiments were performed in which CH_4 (Ti, V, and Co) or O_2 (Ni and Cu) was admitted several centimeters downstream from the dc discharge at a pressure of ~1 mTorr before addition of benzene. Reactions with methane are known to remove excited states of Ti^+,[43] V^+,[44−46] and Co^+,[47] and O_2 has been used to successfully quench excited state complexes of Ni^+.[15]

Table 2. Frequencies for $M(C_6H_6)^+$ Species (cm^{-1})[a]

metal	metal−ligand modes
Ti	230, 66, 19
V	203, 58, 17
Cr	174, 50, 14
Mn	165, 47, 14
Fe	208, 59, 17
Co	216, 61, 18
Ni	212, 60, 17
Cu	191, 54, 15

[a] The 30 benzene modes are taken from ref 10 and calculated by Bauschlicher et al.: Bauschlicher, C. W., Jr.; Partridge, H.; Langhoff, S. R. Personal communication.

In the second method, used to produce $Cr(C_6H_6)^+$ and $Cr(C_6H_6)_2^+$ ions, He^+ and He* formed in a microwave discharge react with the vapor of crystalline bis-benzene chromium (obtained from Strem Chemicals) in a tantalum boat placed inside the flow tube a few centimeters downstream from the discharge source.

Data Analysis. In our previous studies of collision-induced dissociation (CID) of metal complex ions,[13−21] we examined several systematic effects on deriving accurate thermodynamic information from CID thresholds. These effects include (a) internal excitation of reactant ions above thermal; (b) multiple collisions with Xe; (c) thermal energy of the reactant ions that might contribute to the measured thresholds; and (d) the lifetime of the dissociating ions. Here, we account for each of the factors mentioned above as follows.

First, the ions that traverse the 1 m flow tube are very likely thermalized by the 10^5 collisions they undergo, such that excess internal excitation is unlikely. Second, effects due to multiple collisions with Xe are examined by performing the experiments at two different pressures of about 0.18 and 0.05 mTorr for all ions. Pressure effects are eliminated, following a procedure developed previously,[48] by linearly extrapolating the cross sections to zero-pressure, rigorously single collision conditions. It is these extrapolated cross sections that are further analyzed for their thresholds, except for $V(C_6H_6)^+$, the single case where no pressure dependence of the cross sections was observed.

Third, we have shown that a very important systematic effect on CID thresholds is the rotational and vibrational energy of the thermalized ions. Because the rotational energy distribution is relatively narrow, we simply add the average rotational energy ($3kT/2 = 0.039$ eV for nonlinear ions at 298 K) to the measured threshold. The vibrational energy of the ions is best handled by explicitly considering the entire distribution of populated vibrational states. The model used to reproduce the experimental cross section is then given by eq 5,

$$\sigma(E) = \sigma_0 \sum g_i (E + E_{\mathrm{rot}} + E_i - E_0)^n / E \tag{5}$$

where σ_0 is an energy-independent scaling parameter, E is the relative collision energy, E_{rot} is the rotational energy of the reactants, E_0 is the reaction threshold at 0 K, and n is an adjustable parameter. The summation is over the vibrational states i having energies E_i and populations g_i, where $\sum g_i = 1$. We assume that the relative reactivity, as reflected by σ_0 and n, is the same for all vibrational states. Details of our implementation of this equation are given elsewhere.[13] Briefly, the Beyer−Swinehart algorithm[49] is used to evaluate the density of the ion vibrational states, and then the relative populations g_i are calculated by the appropriate Maxwell−Boltzmann distribution at 300 K.

The vibrational frequencies of the $M(C_6H_6)^+$ and $M(C_6H_6)_2^+$ ions used in our modeling are given in Tables 2 and 3. For $M(C_6H_6)^+$ ions,

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Table 3. Frequencies for $M(C_6H_6)_2^+$ Species (cm^{-1})

metal	ligand modes
Ti−Cu	3095(2), 3074(4), 3040(4), 2855(2), 1620(4), 1430(4), 1375, 1350, 1308(2), 1148(4), 1142(2), 1010(2), 1000(4), 993(2), 972(2), 910(4), 857(4), 795(2), 709(2), 616(4), 409(4)

metal	metal−ligand modes
Ti	485, 432(2), 348(2), 290, 178(2), 158
V	471, 419(2), 338(2), 282, 173(2), 154
Cr	466, 415(2), 335(2), 279, 171(2), 152
Mn, Fe	419, 374(2), 302(2), 251, 154(2), 137
Co	391, 349(2), 281(2), 234, 144(2), 128
Ni, Cu	377, 336(2), 271(2), 226, 139(2), 123

we scale the 30 benzene modes calculated by Bauschlicher, Partridge, and Langhoff for $Ag(C_6H_6)^+$,[50] and listed in our CID study of this molecule,[10] by 90%. The metal−ligand stretching frequencies are obtained from that for $Ag(C_6H_6)^+$ (142 cm^{-1} after scaling) by a relationship based on a Morse potential, $[(\mu/D_e)_M/(\mu/D_e)_{Ag}]^{1/2}$, where μ and D_e are the reduced mass and the bond energies, respectively. The D_e values were taken from the theoretical study on $M(C_6H_6)^+$ ions by Bauschlicher, Partridge, and Langhoff (BPL).[22] To determine the two metal−benzene bending frequencies for $M(C_6H_6)^+$ ions, corresponding values for $Ag(C_6H_6)^+$ (40 and 12 cm^{-1}) were increased by the same factor used for the stretching mode. The use of the same factor for stretches, bends, and torsions proved to be reasonable in relating the vibrational frequencies of carbonyl complexes of Cu^+ and Ag^+ in other work.[16]

The 69 vibrational frequencies for $Cr(C_6H_6)_2^+$ (Table 3) are a combination of the known frequencies of $Cr(C_6H_6)_2$[30] and the experimentally observed ones of $[Cr(C_6H_6)_2]I$.[51] The 60 ligand modes are assumed to be equal for all $M(C_6H_6)_2^+$ complexes. Following the same method outlined above, we determine the frequencies for the remaining nine metal−benzene modes of other $M(C_6H_6)_2^+$ ions by relating them to those of $Cr(C_6H_6)_2^+$ by the relationship based on a Morse potential, as noted above. The D_e values in this case are obtained by fitting the data in an iterative procedure starting with the vibrational frequencies of $Cr(C_6H_6)_2^+$.

Finally, we explicitly examine lifetime effects on the thresholds by considering whether all ions with energies in excess of the dissociation energy dissociate within our experimental time window. The dissociation of $M(C_6H_6)^+$ and $M(C_6H_6)_2^+$ species must occur during the flight time from the gas cell to the quadrupole mass filter that is used for mass analysis. While this time does depend on the kinetic energies of the ions, it is roughly 10^{-4} s (as previously determined by time of flight measurements) in the threshold regions of the experiments described here. Dissociation of ions is expected to become slower as the number of vibrational modes where internal energy can randomize increases. This effect is included in our data analysis by using RRKM theory to determine a dissociation probability and incorporating it in eq 5 as described elsewhere.[14] One piece of additional information required to calculate this dissociation probability is the set of vibrational frequencies appropriate to the transition state (TS) for dissociation. In correspondence with the procedure employed for $Ag(C_6H_6)^+$,[10] we use two limiting sets of frequencies for both the mono- and bis-benzene complexes. For the former, a tight TS limit consists of the frequencies of the energized molecule minus the metal−benzene stretching mode. Our loose TS estimate is the 30 frequencies of pure benzene plus the two metal−ligand bending frequencies of each complex reduced by a factor of 3 (with error limits assessed by reducing these frequencies by factors of 2−6). For $M(C_6H_6)_2^+$ ions, a tight TS limit comes from the frequencies of the energized molecule with removal of only one metal−ligand stretching mode (taken as the average of the symmetric and asymmetric stretches of the complex). Our loose TS estimate consists of the 30 frequencies of pure benzene plus the 33 benzene modes of the appropriate $M(C_6H_6)^+$ ion plus five metal−ligand vibrational frequencies for the tight TS reduced by a factor of 3 (with error limits assessed by reducing these frequencies by factors of 2−6). The ratio of the rotational partition functions of the TS and the energized molecule, $Q^\dagger/Q$, is needed for the RRKM analysis and is evaluated using the basis of the method of Waage and Rabinovitch,[52] as described in detail previously.[14] To implement this, we require the polarizability of the neutral product, $\alpha = 6.45$ Å^3 for the perpendicular polarizability of benzene,[53] and the equilibrium distances of the undissociated complexes. For $M(C_6H_6)^+$ ions, we use the metal−benzene equilibrium distances r_e calculated by BPL.[22] In the case of $Cr(C_6H_6)_2^+$, X-ray crystallographic[54] and electron-diffraction studies[55] reveal a chromium−benzene distance of 1.61 Å for the neutral compound. Thus the equilibrium distance between the dissociating fragments of $M(C_6H_6)_2^+$ in our CID experiments is taken as the distance between a benzene ring and the center of mass of the remaining $M(C_6H_6)^+$ fragment, $r_e = 2.25$ Å. This value is assumed to be the same for all $M(C_6H_6)_2^+$ ions studied.

Before comparison with the experimental data, the model cross section of eq 5 (or its form that incorporates lifetime effects)[14] is convoluted over the ion and neutral translational energy distributions, as described previously.[40] The parameters in eq 5, σ_0, E_0, and n, are then optimized by using a nonlinear least squares analysis to best reproduce the data. The optimized value of E_0 is taken to be the measured threshold for a given data set. Uncertainties in the reported thresholds are derived from the spread of E_0 values from different data sets, from the absolute error in the energy scale (0.05 eV in the laboratory frame), from variation of the time scale for dissociation by a factor of 2, and from variations in the subtraction of the low-energy feature (described below). For the loose TS model, the uncertainties also include the variation in the metal−ligand frequencies of the TS, as described above.

In our analysis of the CID excitation functions for bis-benzene metal ions, we also use a modified form of eq 5 that accounts for a decline in the product ion cross section at higher kinetic energies due to further dissociation. This model has been described in detail previously[56] and depends on E_D, the energy at which the dissociation channel can begin, and p, a parameter similar to n in eq 5.

Results

Collision-induced dissociation (CID) spectra were recorded for complexes of monopositive titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper ions with one and two benzene ligands. The main processes observed in all systems over the energy range studied (typically 0−10 eV for the monoligated species and 0−15 eV for the bis-benzene complexes) are the sequential loss of benzene molecules and the ligand exchange reaction 6. Although ligand exchange is

$$M(C_6H_6)^+ + Xe \rightarrow MXe^+ + C_6H_6 \qquad (6)$$

likely to also take place with $M(C_6H_6)_2^+$, we did not measure the cross sections for the corresponding $M(C_6H_6)Xe^+$ products as their masses are beyond the range of our instrument. At elevated energies, we also observed minor dissociation processes in which the benzene ligand dissociates by C_2H_2 or C_3H_3 loss, but the cross sections for these reactions are much smaller than those for loss of intact benzene ligands.

CID of $Cr(C_6H_6)_x^+$. Because of the availability of thermochemical information in this case, we discuss our analysis of the chromium ion system in full detail as a model system. Results for the interaction of $Cr(C_6H_6)^+$ with Xe are shown in Figure 1. The Cr^+ product resulting from CID rises from an apparent threshold near 1.5 eV. Ligand exchange to form $CrXe^+$ exhibits a lower apparent threshold and a cross section that declines above 2 eV. The latter behavior is clearly due to

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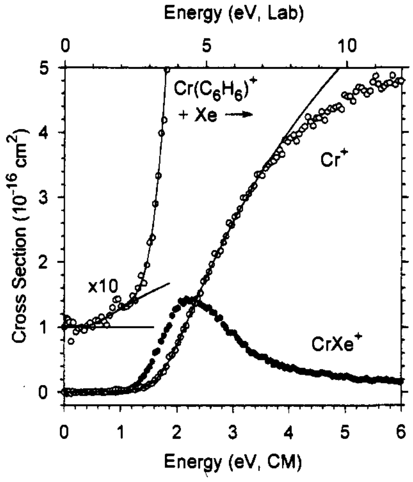

Figure 1. Cross section for collision-induced dissociation of $Cr(C_6H_6)^+$ with Xe as a function of kinetic energy in the center of mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). The full line shows the model of eq 5 with the parameters in Table 4 for the loose TS model convoluted over the experimental kinetic energy distributions plus a model for the low-energy feature. Data for the Cr^+ channel and its model are also shown expanded by a factor of 10 with the zero offset.

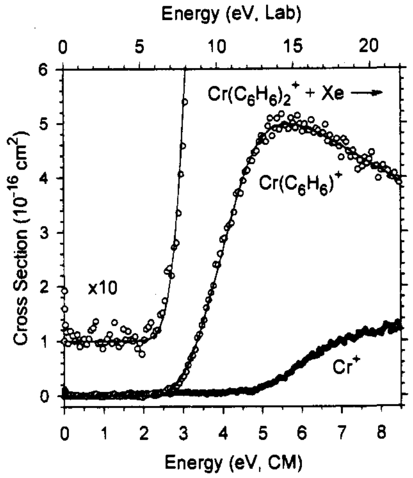

Figure 2. Cross section for collision-induced dissociation of $Cr(C_6H_6)_2^+$ with Xe as a function of kinetic energy in the center of mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). The full line shows the model of eq 5 with the parameters in Table 4 for the loose TS model convoluted over the experimental kinetic energy distributions. Data for the $Cr(C_6H_6)^+$ channel and its model are also shown expanded by a factor of 10 with the zero offset.

competition between ligand exchange and CID. The mass resolution of the quadrupole mass spectrometer was set sufficiently low that the cross sections shown in Figure 1 should represent the product intensities for all isotopes of Xe.

Results for the CID reaction of $Cr(C_6H_6)_2^+$ with Xe are shown in Figure 2. The cross section for the primary product $Cu(C_6H_6)^+$ has an apparent threshold of about 2.5 eV and goes through a maximum at the onset for the Cr^+ secondary product, behavior in correspondence with a sequential loss of the benzene ligands. The general appearance of the CID patterns for all other $M(C_6H_6)_x^+$ complexes studied is similar to those for the chromium system. For the mono-benzene metal complexes, the absolute magnitudes of the CID cross sections vary by less than a factor of 2 across the periodic table.[57] For the bis-benzene complexes, the magnitudes vary considerably. Cross sections for loss of one benzene ligand are 10−15 Å^2 for M = Ti, V, Fe, and Co; 23−25 Å^2 for the late transition metals, nickel and copper; and smallest, 5−10 Å^2, for metals in the middle, M = Cr and Mn. Interestingly, loss of both ligands from $M(C_6H_6)_2^+$ to form M^+ is most efficient for these latter two metals, reaching cross sections of about 2 Å^2 by 12 eV, and less efficient for all other metals, with cross sections of 0.4−1.0 Å^2.

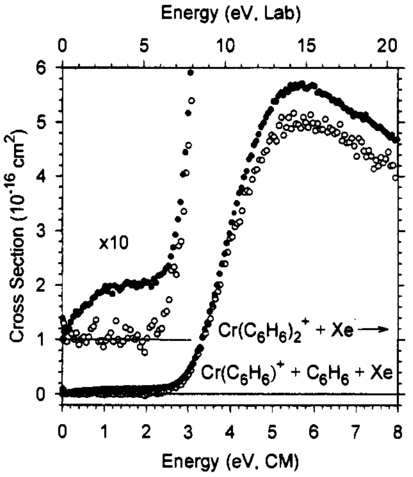

Figure 3. Cross section for collision-induced dissociation of $Cr(C_6H_6)_2^+$ with Xe as a function of kinetic energy in the center of mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). The open and closed circles show data for ions formed in the microwave discharge and dc discharge sources, respectively. Both data sets are also shown expanded by a factor of 10 with the zero offset.

Features at Low Kinetic Energy. All the CID data obtained from ions produced by the dc discharge source show a nonzero cross section at kinetic energies below the CID thresholds, as depicted for $Cr(C_6H_6)^+$ in Figure 1 and $Cr(C_6H_6)_2^+$ in Figure 3. As in these cases, the low-energy features for all ions are much smaller than the dominant cross section feature and the two features are quite distinct from one another. Such low-energy features can be attributed either to contamination of the ion beam or to excited states of the $M(C_6H_6)_x^+$ species. If the former were true, then we would expect to observe other product ions formed by CID at low energies, but no such products were observed except in the case of $V(C_6H_6)^+$. It is possible that a ligand other than benzene also having a mass of 78 amu might be present, but we can think of no species that should be so weakly bound to metal ions. Thus, we believe that these low-energy features can probably be attributed to electronically excited $M(C_6H_6)^+$ species. Vibrational and rotational excitation (which should exhibit broad distributions, given the large excitation energies of 1.4−3.3 eV) is excluded by the distinct difference between the low- and high-energy features (Figures 1 and 3).

Further evidence pointing to electronic excitation comes from the cases of $Ti(C_6H_6)^+$ and $Cr(C_6H_6)_2^+$. In the former system, the addition of CH_4 to the flow tube considerably decreases the magnitude of the low-energy feature, suggesting that a quenching process is occurring. We attempted to perform such quenching for other metals as well; however, addition of CH_4 in the case of the vanadium and cobalt complexes or of O_2 in the case of nickel and copper species (methods that have proven to efficiently remove excited state ions for other complexes of these metals)[15,43−47] had no effect on the low-energy features. The bis-benzene chromium ion is the only system where data from two different ion sources are available. As illustrated in Figure 3, the CID excitation function obtained with the

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(57) In the case of vanadium, the analyzer quadrupole had to be operated at a much higher resolution than for the other metals in order to discriminate against impurities in the beam having similar mass to the desired $V(C_6H_6)^+$ ions. Under such mass resolution conditions, mass discrimination is introduced such that the measured cross sections have smaller magnitudes than those taken under lower resolution conditions. We have verified that the shape of the cross sections (upon which the threshold analysis depends) does not depend upon the mass resolution.

microwave discharge source does not show a nonzero cross section below the threshold of the dominant part of the cross section. The main features of these excitation functions are identical within experimental error.

If these low-energy features are truly the result of electronically excited complexes, it is interesting to address why such species are observed in this study but are generally absent in our previous studies of metal–ligand complexes. Similar low-energy features have been observed for $NiCO^+$ and $Ni(CO)_2^+$, but could be quenched effectively by addition of O_2 to the flow tube.[15] We speculate that the observation of such metastable states in the present system is due largely to the strong binding energies of the multidentate benzene ligand to M^+ and $M(C_6H_6)^+$. Thus, benzene is able to form metastable complexes with the small numbers of excited metal ions that are not efficiently quenched in the flow tube by the flow gases or added quench gases, while the more weakly bound monodentate ligands that have been studied previously cannot. Because of the large energy separation (1.4–3.3 eV) between these excited states and the ground state ions of the $M(C_6H_6)_x^+$ complexes, quenching of the complexes is also apparently inefficient. Because the two electronic states are largely decoupled from one another, both populations can reach equilibrium with the flow gases at 300 K in all other degrees of freedom (vibrational and rotational).

The presence of these low-energy features clearly complicates the data analysis. In the case of $Cr(C_6H_6)_2^+$, data from the microwave discharge source is analyzed. In the case of $Ti(C_6H_6)^+$, the low-energy feature is eliminated by extrapolating the cross sections obtained without and with addition of CH_4 to a zero base line at low energies. It is these extrapolated cross sections that are further analyzed for their thresholds. In all other cases, the low-energy feature is analyzed with eq 5 (with internal energies but no lifetime effects included) over several energy ranges to provide various models that reproduce the low-energy data. Because the low-energy features are distinct from the high-energy features over a wide range of energies (at least 1 eV), the analysis of these features is straightforward. These models are subtracted from the experimental CID excitation functions before the cross sections are modeled with eq 5, as described below. An example of this procedure is shown in Figure 1. The variations in the low-energy models lead to slightly different cross sections for the dominant CID process, and this leads to a range of thresholds obtained in the further analysis. These variations are included in the uncertainties reported for these thresholds. A check on this procedure is to compare the thresholds obtained in this manner for $Cr(C_6H_6)_2^+$ with those obtained from the data obtained using the microwave discharge source. The values for the CID thresholds obtained using these two methods of analysis yield thresholds that are the same within the experimental errors associated with the procedure for subtracting the low-energy feature (which are smaller than the total uncertainty in the final numbers).

BDEs from Primary Thresholds. In our previous CID studies,[13–21] we concluded that our best measure of the bond dissociation energies (BDEs) for metal ligand ions comes from analyses of the primary dissociation channels. For $M(C_6H_6)_x^+$, this is reaction 7 where $x = 1$ and 2. Listed in Table 4 are the

$$M(C_6H_6)_x^+ + Xe \rightarrow M(C_6H_6)_{x-1}^+ + C_6H_6 + Xe \qquad (7)$$

optimized parameters of eq 5 obtained from analyses of reactions 7 for between two and seven independent data sets for all ions.

Three analyses (each with similar values for σ_0 and n) are listed in every case: one ignoring lifetime effects and one including the RRKM analysis for a tight and loose TS for the dissociating ions. The degree of "tightness" or "looseness" of the TS is usefully characterized by the entropy of activation at 1000 K, $\Delta S^{\ddagger}_{1000}$.[14,58] Choosing the sets of vibrational frequencies outlined above, we obtain values for $\Delta S^{\ddagger}_{1000}$ in the range 0.4–2.0 eu for a tight TS and 4.8–6.5 eu for a loose TS of the dissociating mono-benzene complexes. Values for the tight and loose TS for loss of one ligand from the bis-benzene metal ions lie in the ranges 2.9–3.5 and 18–22 eu, respectively. This can be compared to values of $\Delta S^{\ddagger}_{1000}$ in the range 7–11 eu collected by Lifshitz[58] for several simple bond cleavage dissociations of ions. Faulck and Dunbar[59] consider $\Delta S^{\ddagger}_{1000}$ values of 0.9 and 12.7 eu as lower and upper limits for the photodissociation of the ferrocene cation, and Lin and Dunbar[60] recently obtained $\Delta S^{\ddagger}_{1000} = 6.3 \pm 1.7$ eu for dissociation of the nickelocene cation.

Table 4. Summary of Parameters in Eq 5 for Loss of Benzene from $M(C_6H_6)_x^+$ [a]

M	x	σ_0	n	E_0		
					RRKM	
				no RRKM	(loose TS)	(tight TS)
Ti	1	5.5 (1.0)	1.5 (0.1)	3.10 (0.07)	2.68 (0.09)	2.55 (0.08)
	2	20 (4)	1.3 (0.2)	3.64 (0.15)	2.62 (0.19)	2.21 (0.10)
V	1	0.3 (0.1)	1.8 (0.1)	2.73 (0.10)	2.42 (0.10)	2.31 (0.09)
	2	11 (4)	1.5 (0.2)	3.51 (0.08)	2.55 (0.19)	2.15 (0.10)
Cr	1	5.5 (0.2)	1.3 (0.1)	1.85 (0.09)	1.76 (0.10)	1.70 (0.09)
	2	12 (6)	1.3 (0.2)	3.26 (0.10)	2.40 (0.19)	2.04 (0.10)
Mn	1	6.5 (0.2)	1.7 (0.1)	1.40 (0.09)	1.38 (0.09)	1.36 (0.08)
	2	9 (3)	1.5 (0.2)	2.64 (0.12)	2.10 (0.17)	1.76 (0.10)
Fe	1	2.6 (0.4)	1.7 (0.1)	2.35 (0.10)	2.15 (0.10)	2.06 (0.10)
	2	11 (2)	1.9 (0.2)	2.47 (0.08)	1.94 (0.17)	1.64 (0.09)
Co	1	1.4 (0.2)	1.6 (0.1)	3.07 (0.10)	2.65 (0.11)	2.54 (0.10)
	2	11 (2)	1.8 (0.1)	2.07 (0.12)	1.73 (0.14)	1.50 (0.11)
Ni	1	1.9 (0.2)	1.4 (0.1)	2.86 (0.10)	2.52 (0.11)	2.42 (0.10)
	2	21 (2)	1.7 (0.1)	1.79 (0.09)	1.52 (0.12)	1.33 (0.10)
Cu	1	2.7 (0.5)	1.4 (0.1)	2.49 (0.09)	2.26 (0.10)	2.17 (0.09)
	2	29 (5)	1.4 (0.2)	1.88 (0.10)	1.61 (0.12)	1.39 (0.09)

[a] Uncertainties in parentheses.

We think it likely that the metal benzene ion complexes adopt rather loose "product-like" transition states upon dissociation. As the C_5H_5 ligand can form a covalent bond with metal ions while C_6H_6 bonds datively, we expect that our systems should be looser than the nickelocene result of Lin and Dunbar. Thus we suggest our values coming from an analysis including lifetime effects with a loose TS to be the best measure of the BDEs for the systems studied. Further support for this choice is provided by comparison with literature thermochemistry, see below. We note that lifetime effects turn out to be much larger in the bis-benzene metal systems than in other metal–ligand systems we have studied. This is primarily because the previous work all involves monodentate ligands and generally smaller bond energies.[13–21] Comparable lifetime effects have been observed in our studies of the dissociation of bare transition metal cluster ions, where the density of states is also very large.[61] In the present study, the lifetime effects for the bis-benzene metal ions lead to thresholds that are an average of 33 ± 6% smaller for a tight TS (maximum value of 39% for M = Ti) and 21 ± 6% smaller for a loose TS (maximum value of 28% for M = Ti) than those obtained without RRKM analysis. (For the mono-benzene metal ions, the average differences are 13 ± 5% and 9 ± 4% for tight and loose TSs, respectively.) More precise information on the looseness of the TS will allow more

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definitive analysis of these thresholds and a more accurate determination of the BDEs for these species.

Because the vibrational, rotational, and translational energy distributions of the reactants are explicitly included in our modeling, the thresholds listed in Table 4 correspond to 0 K values. Assuming that there are no activation barriers to dissociation in excess of the endothermicity, the 0 K thresholds equal $D_0[(C_6H_6)_{x-1}M^+-C_6H_6]$. As discussed in detail previously,[16,62] this has proven to be a reasonable assumption for several cationic metal ligand species and led to accurate BDEs in previous CID studies on those complexes,[13-21] including the $Ag(C_6H_6)^+$ system.[10]

One possible complexity in the accurate determination of BDEs by CID methods is whether the ligand exchange reactions of $M(C_6H_6)_x^+$ with Xe (e.g., reaction 6) might cause a competitive shift in the observed thresholds, especially if cross sections for the ligand exchange processes are large. It should be realized that this is a general problem for all CID reactions (even when the ligand exchange product is not collected) because the ligand exchange process will always have a lower threshold than CID, no matter what neutral reagent is used. We do not believe that this competition is likely to affect our threshold measurements, for the following reasons. First, CID reactions can occur both by indirect (transient formation of a $M(C_6H_6)_xXe^+$ complex) and direct pathways, and only the former would suffer from a competitive shift (although it can be noted that the distinction between the two pathways is primarily one of time scale, which depends on the energetics involved in the reactions). Second, competition between reaction channels can suppress the one having a higher threshold, but the true threshold can still be measured if the experiment has sufficient sensitivity. Thus, competitive shifts can be avoided if the data in the threshold region are reproduced carefully. In our studies, we attempt to accomplish this by reproducing our cross sections over a 2−3 order of magnitude range. In the present study, the data are reproduced over this range for all systems. Third, the cross section for the ligand exchange reaction 6 declines sharply once the CID product is formed (Figure 1). This is evidence for efficient energy transfer to the metal−benzene cation upon collision with the neutral gas. Fourth, BDEs obtained from CID reactions in previous studies are generally in excellent agreement with theory and other experiments for a number of metal−ligand systems.[13-21] As this previous work shows similar cross sections for the ligand exchange reactions, this agreement suggests that competitive shifts are small or nonexistent. Conservatively, the bond energies measured here and in any CID study constitute upper limits to the adiabatic BDEs under investigation (assuming that energy broadening effects are adequately compensated for and the data are analyzed over an extensive energy and magnitude range); however, previous experience suggests that such CID values are likely to be accurate measures of the true bond energies.

Comparison with Literature Thermochemistry. Previous results for many first-row transition metal ion benzene binding energies have been determined by photodissociation[8,11] (PD) and by ion−molecule reactions.[9,12] These values are listed in Table 5 together with the results of the present work (loose TS values) and the theoretical BDEs computed by BPL.[22] Strictly speaking, PD techniques employed by Hettich et al. (HJSF)[8] and by Willey et al. (WYRD)[11] for the mono-benzene complexes of V^+, Fe^+, Co^+, and Cu^+ yield upper bounds for the binding energies because there may be no optical transitions at the dissociation thresholds. These PD values are slightly higher than our CID results, except for the $Cu(C_6H_6)^+$ result, but agree reasonably well within experimental error. Collision-induced dissociation (CID) reactions of $MFe(C_6H_6)^+$ in conjunction with PD spectra of MFe^+ were used by Hettich and Freiser[9] to estimate BDEs for other $M(C_6H_6)^+$ species (M = Cr and Cu), although this method relies on the assumption that the competing dissociations have similar kinetics. The value for M = Cu is in reasonable agreement with our findings, but their $Cr(C_6H_6)^+$ BDE is significantly higher than our value. Hettich and Freiser find that Ti^+ triply dehydrogenates cyclohexane, providing a lower limit of 2.12 eV for the $Ti(C_6H_6)^+$ BDE.[9] The value cited for $Ni(C_6H_6)^+$ is obtained by Jacobson in an unspecified manner and is significantly higher than the BDE obtained in the present study. Schroder et al.[12] have estimated the BDE of $Fe(C_6H_6)^+$ to be 2.11 ± 0.11 eV, based on a series of bracketing experiments, in excellent agreement with our value. Overall, the six metal−benzene ion binding energies determined previously are larger than our values obtained with no lifetime analysis by an average of 0.03 ± 0.27 eV, larger than our loose TS values by an average of 0.28 ± 0.24 eV, and larger than our tight TS values by an average of 0.37 ± 0.24 eV. The average experimental uncertainties (square root of the sum of the squares of the experimental uncertainties) is ±0.28 eV. Thus, our values obtained with no lifetime effect and with the loose TS model agree with the literature values within experimental error, while the tight TS limit provides smaller values. This suggests that the tight TS limit overestimates the lifetime effect.

Table 5. Summary of 0 K values for $D_0[(C_6H_6)_{x-1}M^+-C_6H_6]^a$

M	x	this work[b]	theory[c]	lit. exptl
Ti	1	2.68 (0.09)	2.72 (0.22)[d]	>2.12[e]
	2	2.62 (0.19)		
V	1	2.42 (0.10)	2.22 (0.22)	2.69 (0.22)[f]
	2	2.55 (0.19)		2.47 (0.22)[f]
Cr	1	1.76 (0.10)	1.62 (0.22)	2.30 (0.39)[e]
	2	2.40 (0.19)		
Mn	1	1.38 (0.09)	1.52 (0.22)	
	2	2.10 (0.17)		
Fe	1	2.15 (0.10)	2.22 (0.22)[d]	2.39 (0.22),[f] 2.70,[g] 2.11 (0.11)[h]
	2	1.94 (0.17)		
Co	1	2.65 (0.11)	2.71 (0.22)	2.95 (0.22)[f]
	2	1.73 (0.14)		
Ni	1	2.52 (0.11)	2.57 (0.22)	2.95 (0.22)[i]
	2	1.52 (0.12)		
Cu	1	2.26 (0.10)	2.22 (0.22)	2.17 (0.39),[e] <1.98[g]
	2	1.61 (0.12)		

[a] Uncertainties are in parentheses. [b] E_0 RRKM (loose TS) values from Table 4. [c] Reference 22. [d] Dissociation energy was referenced to the diabatic asymptote and is empirically corrected to the adiabatic BDE. [e] Reference 9. [f] Reference 8. [g] Reference 11. [h] Reference 12. [i] Jacobson, D. B., as cited in ref 9.

In general, agreement between the theoretical BDEs[22] and our values for $M(C_6H_6)^+$ species is good, with the largest deviations occurring for V and Mn. Overall, the binding energies determined by Bauschlicher et al. are smaller than our values obtained with no lifetime analysis by an average of 0.26 ± 0.19 eV, differ from our loose TS values by an average of 0.00 ± 0.12 eV, and are larger than our tight TS values by an average of 0.09 ± 0.11 eV. Thus, on the basis of a comparison with theory, we conclude that the lifetime effect should be taken into account, but that either the loose or tight TS limits are acceptable. When combined with the conclusion drawn from comparison with the experimental results in the literature, it appears that the loose TS probably provides the most accurate thermochemistry. As noted above, this seems sensible given the likely characteristics of the dissociation processes considered here.

As pointed out in the Introduction, a test for the accuracy of our results is provided by comparing the sum of the BDEs for $Cr(C_6H_6)_2^+$ and $V(C_6H_6)_2^+$ with $\Delta_rH°_0(1)$ and $\Delta_rH°_0(2)$, re-

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(62) Armentrout, P. B.; Simons, J. J. Am. Chem. Soc. 1992, 114, 8627.

spectively. In our CID experiments for $Cr(C_6H_6)_x^+$, the sum of the two 0 K BDEs is 5.11 ± 0.09 eV if lifetime effects are not included, 4.16 ± 0.20 eV if lifetime effects (loose TS) are included in the analysis, and 3.74 ± 0.11 eV for the tight TS model. This range of values is close to that spanned by the conservative value derived above for $\Delta_rH°_0(1)$, 4.52 ± 0.58 eV. The more precise value of 4.73 ± 0.13 eV falls in between our experimental limits for no lifetime effects and the loose TS model, and it differs from the tight TS model appreciably. Unfortunately, because of the imperfect accuracy of the literature thermochemistry for $\Delta_rH°_0(1)$, a comparison to this work does not allow us to make a definitive judgment about which lifetime effect model is most correct.

Instead we can turn the situation around and take our bond energy sum of 4.16 ± 0.20 eV to determine $\Delta_fH°_0[Cr(C_6H_6)_2^+]$ = 848 ± 20 kJ/mol, $\Delta_fH°_0[Cr(C_6H_6)_2(g)]$ = 319 ± 20 kJ/mol, $\Delta_fH°_{298}[Cr(C_6H_6)_2(g)]$ = 281 ± 20 kJ/mol, and $\Delta_fH°_{298}[Cr(C_6H_6)_2(s)]$ = 196 ± 22 kJ/mol. The latter value is close to those reported by Fischer and co-workers, 213 ± 8 and 220 ± 8 kJ/mol.[23] A value for $\Delta_fH°_{298}[Cr(C_6H_6)_2(s)]$ obtained from our sum of BDEs with a tight TS lifetime analysis is 237 ± 14 kJ/mol, higher than any literature results, while that obtained with no lifetime analysis is 105 ± 14 kJ/mol, consistent with the 88 ± 33 kJ/mol value obtained by Fischer, Cotton, and Wilkinson.[24]

The sum of the two experimental BDEs for $V(C_6H_6)_2^+$ is 6.24 ± 0.10 eV if lifetime effects are not included in the analysis, 4.97 ± 0.20 eV for analysis including a loose TS, and 4.46 ± 0.11 eV for analysis including a tight TS. These values are all significantly smaller than $\Delta_rH°_0(2)$, 7.07 ± 0.16 eV as derived above from the literature thermochemistry. A photodissociation study on $V(C_6H_6)_2^+$ by HJSF yielded $D[(C_6H_6)V^+-C_6H_6]$ = 2.47 ± 0.22 eV,[8] in excellent agreement with our result obtained with a loose TS analysis, 2.55 ± 0.18 eV (Table 5). Thus, Freiser's PD results yield $\Delta_rH°_0(2)$ = 5.16 ± 0.31 eV, also much lower than the 7.07 eV value and comparable to our results for a loose TS. This agreement lends further support for our choice of a loose TS as the best model for the inclusion of lifetime effects in our analysis and casts considerable doubt on the literature thermochemistry for $V(C_6H_6)_2$. We can use our BDEs (loose TS model) and the information in Table 1 to determine $\Delta_fH°_0[V(C_6H_6)_2^+]$ = 884 ± 21 kJ/mol and $\Delta_fH°_{298}[V(C_6H_6)_2^+]$ = 851 ± 21 kJ/mol. If $IE[V(C_6H_6)_2]$ = 5.95 ± 0.1 eV is used,[39] then we derive $\Delta_fH°_0[V(C_6H_6)_2]$ = 310 ± 23 kJ/mol and $\Delta_fH°_{298}[V(C_6H_6)_2]$ = 271 ± 23 kJ/mol.

The comparison with literature thermochemistry suggests that our values for $D_0[M^+-C_6H_6]$ are accurate, but does not definitively ascertain the absolute accuracy of our values for the $(C_6H_6)M^+-C_6H_6$ BDEs. As noted above, the loose TS model probably provides our best results and the errors listed in Table 5 are believed to adequately represent the systematic uncertainties in the lifetime analysis. In any case, possible errors stemming from our inclusion of lifetime effects are systematic and fairly consistent across the transition row, such that the periodic trends in these values can still be discussed reliably. It should probably be emphasized that the reliability of these results depends critically on having prepared the ions with well-controlled internal energies. Further, it requires careful treatment of the data regarding multiple collisions, internal excitation of the ions, and the dissociation lifetime of the ions. In turn, the latter two effects depend on the availability of vibrational frequencies either calculated by theory or estimated from related experimental or theoretical work.

Periodic Trends across the Transition Row. Trends in BDEs for $M(C_6H_6)_x^+$ complexes across the transition row are illustrated graphically for $x = 1$ and 2 in Figure 4 along with the sum of the two bond energies for each metal. The bonding in $M(C_6H_6)^+$ has been described by BPL based on their ab initio calculations.[22] They predict the bonding to be predominantly electrostatic with a significant enhancement arising from metal 3d back-donation into the π^* orbitals of benzene. In the case of $Mn(C_6H_6)^+$, the ground state is computed to be $^7A_1$ corresponding to the $^7S(4s^13d^5)$ ground state configuration of Mn^+, while for all other $M(C_6H_6)^+$ species studied here, the metal ions are calculated to have high-spin ground states derived from a $3d^n$ configuration; i.e., $^4A_2$ for M = Ti; $^5E_1$ for V; $^6A_1$ for Cr; $^4A_2$ for Fe; $^3A_2$ for Co; $^2E_1$ for Ni; and $^1A_1$ for Cu. The $3d^n$ configuration corresponds to the ground state of the atomic metal ion in all of these cases but Ti^+ and Fe^+. For these ions, the promotion energy to the $3d^n$ configuration is fairly small, 0.11 and 0.25 eV.[63] If the $Ti(C_6H_6)^+$ and $Fe(C_6H_6)^+$ complexes were to experimentally dissociate diabatically to form M^+ product ions in these excited states, then the bond energies measured here should be reduced by the promotion energies in order to represent the adiabatic BDEs. This seems unlikely in the Ti case as dissociation to either $Ti^+(^4F,4s^13d^2)$ or $Ti^+(^4F,3d^3)$ is spin allowed, but the promotion energy is too small to judge whether such a correction can be justified empirically. In the Fe case, reduction of our measured BDE by the 0.25 eV promotion energy places it below both the theoretical results and the experimental results of Freiser, Table 5. Hence, no correction is made in either case and it seems likely that the BDEs measured are adiabatic values.

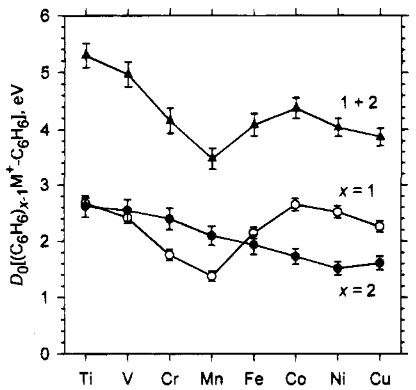

Figure 4. Bond energies for mono-benzene (open circles) and bis-benzene (closed circles) complexes of the first-row transition metal ions. The closed triangles show the sum of the first and second bond energies. All values are taken from Table 5. Vertical lines indicate the uncertainties.

In C_{6v} symmetry, the metal 3d orbitals in the $M(C_6H_6)_x^+$ complexes are energetically ordered as $3de_2(\delta) < 3da_1(\sigma) < 3de_1(\pi)$. While occupying the $3de_2(\delta)$ orbitals maximizes back-donation into the π^* orbitals on benzene and strengthens the metal–ligand interaction, the $3de_1(\pi)$ orbitals overlap with the benzene π orbitals and are antibonding. The overlap of the compact $3da_1(\sigma)$ with benzene should be small, because it points into the center of the aromatic ring.[22] Thus the decrease in BDEs in going from $Ti(C_6H_6)^+$ to $V(C_6H_6)^+$ to $Cr(C_6H_6)^+$ (with three, four, and five 3d electrons) as well as from $Co(C_6H_6)^+$ to $Ni(C_6H_6)^+$ and $Cu(C_6H_6)^+$ (with eight, nine, and 10 3d electrons) reflects the filling of the energetically unfavorable $3de_1(\pi)$ orbitals, which increases the repulsion with the benzene ligand. The BDE for $Mn(C_6H_6)^+$ is the smallest among the complexes studied, indicating that having an electron in the diffuse 4s orbital further increases the repulsion. The increase in BDEs in going from $Cr(C_6H_6)^+$ to $Fe(C_6H_6)^+$ reflects addition of electrons to the bonding $3de_2(\delta)$ orbitals. Another underlying effect should be the decreasing size of the metal ions as one

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(63) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 2.

moves to heavier elements, which should increase the electrostatic binding by allowing a shorter metal–ligand bond distance. This effect can be observed in the calculated bond distances.[22]

In contrast to the large nonmonotonic variations in bond energies for the $M(C_6H_6)^+$ species, the BDEs for loss of one ligand from the $M(C_6H_6)_2^+$ complexes show a relatively moderate monotonic decrease across the transition row. Consequently, trends in dissociation energies for the complete fragmentation, i.e., loss of both benzenes from $M(C_6H_6)_2^+$, parallel those found for the mono-benzene species (Figure 4). Assuming a 6-fold symmetry for both the mono- and bis-benzene metal ions, the relative ordering of the metal d orbitals is the same in both systems, but the splitting should approximately double such that spin pairing to form low-spin ground states is likely to occur in the case of the sandwich complexes. A $^2A_1(3de_2{}^4 3da_1{}^1)$ ground state of $Cr(C_6H_6)_2^+$ has been established by theory[64] and experiment.[36,65] Electron spin resonance and photoelectron studies[66] show that the ion ground states for the titanium and vanadium compounds are $^2E_2(3de_2{}^3)$ and $^3E_2(3de_2{}^3 3da_1{}^1)$, respectively. We expect the 18-electron complex, $Mn(C_6H_6)_2^+$, to be a singlet species, $^1A_1(3de_2{}^4 3da_1{}^2)$. Subsequent filling of the highest lying $3de_1(\pi)$ metal orbitals should then result in a $^2E_1$ ground state for $Fe(C_6H_6)_2^+$ and $^3A_2$, $^2E_1$, and $^1A_1$ ground states for the cobalt, nickel, and copper sandwich ions, respectively. Except for the three latter systems, where the spin states of $M(C_6H_6)^+$ and $M(C_6H_6)_2^+$ are the same, these assignments mean that spin changes have to occur for adiabatic dissociation of ground state $M(C_6H_6)_2^+$ to form ground state $M(C_6H_6)^+$ complexes, reaction 7 for $x = 2$. The question for M = Ti–Fe is whether the BDEs measured here for $(C_6H_6)M^+-C_6H_6$ correspond to such adiabatic dissociations (they must for M = Co, Ni, and Cu) or to diabatic dissociation to low-spin excited states of $M(C_6H_6)^+$. We assume that the former is true on the basis that BDEs that we have measured by CID for almost all metal–ligand complexes ($FeCO^+$ is an exception) do correspond to the adiabatic values. We can test this assumption by seeing whether the periodic trends in the BDEs are sensible.

Listed in Table 6 are the promotion energies, E_p's, for the spin pairing predicted from the difference in energy between the corresponding states of appropriate spin multiplicity for the bare metal ions.[63] In addition, we list the sum of this promotion energy and the two sequential BDEs for each transition metal taken from Table 5, i.e., the calculated dissociation energy for complete fragmentation of ground state $M(C_6H_6)_2^+$ species in a spin-conserving process. As expected from the order of successive filling of bonding and antibonding orbitals in low-spin $M(C_6H_6)_2^+$ sandwiches, these latter values reach a maximum for the 18-electron complex of manganese. Values for Ti and V and for Cr and Mn species are equal within combined experimental error. This is in accordance with the same number of bonding $3de_2(\delta)$ electrons and differing numbers of nonbonding $3da_1(\sigma)$ electrons for these pairs of metals. Indeed, given that the Ti and V complexes have three $3de_2(\delta)$ electrons and the Cr and Mn complexes have four, one can calculate that each of these electrons contributes about 2.1 ± 0.1 eV of energy to the bonding. As one moves further to the right in the periodic table, electrons are added to the antibonding $3de_1(\pi)$ orbitals. This results in increasingly smaller BDEs for the later transition metals, Fe–Cu. Thus, the periodic trends in the BDEs seem reasonable, suggesting that CID thresholds can be assigned to adiabatic dissociations. The observation that the BDEs for the second benzene ligand are relatively constant might then suggest that the low-spin states of the $M(C_6H_6)^+$ complexes are fairly low in energy, i.e., most of the promotion energy necessary for the change to low spin is paid by the first benzene ligand.

Table 6. Promotion Energies, E_p, for Metal Cations M^+ and Sum of E_p and the Sequential BDEs of $M(C_6H_6)_x^+$ (x = 1, 2)

metal	excitation	E_p (eV)	E_p + BDEs[a] (eV)
Ti	$^4F(3d^3) \rightarrow {}^2G(3d^3)$	1.00	6.30 (0.21)
V	$^5D(3d^4) \rightarrow {}^3P(3d^4)$	1.40	6.37 (0.22)
Cr	$^6S(3d^5) \rightarrow {}^2I(3d^5)$	3.74	7.90 (0.22)
Mn	$^7S(4s^1 3d^5) \rightarrow {}^1I(3d^6)$	4.80	8.28 (0.19)
Fe	$^6D(4s^1 3d^6) \rightarrow {}^2G(3d^7)$	1.96	6.05 (0.20)
Co	$^3F(3d^8)$	0.0	4.38 (0.18)
Ni	$^2D(3d^9)$	0.0	4.04 (0.16)
Cu	$^1S(3d^{10})$	0.0	3.87 (0.16)

[a] Bond energies are taken from Table 5.

Sequential Bond Energies. The benzene complexes of the early transition metal ions, Ti^+ and V^+, have similar BDEs for the first and second benzene ligand. For $Cr(C_6H_6)_x^+$ and $Mn(C_6H_6)_x^+$, the second ligand is more strongly bound than the first. In contrast, the later transition metals, Fe, Co, Ni, and Cu, exhibit a decrease in the BDEs in going from x = 1 to 2 which is substantial for all but Fe. Given that the $Mn(C_6H_6)_2^+$ complex is an 18-electron complex, this observation may indicate a reduction of hapticity in the sandwich complexes with more than 18 valence electrons. By using a fluxional η^4-like bonding of the benzene ligand rather than a η^6-bonding mode, the occupation of strongly antibonding orbitals can be avoided in these late metal systems, but the ligands are no longer tridentate and therefore more loosely bound. This may also occur for the mono-benzene complexes of the late transition metals. This can rationalize why BPL find that $AgC_6H_6^+$ does not have C_{6v} symmetry, but the silver ion is located over one of the C–C bonds.[22]

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