Radiative Association Kinetics and Binding Energies of Chromium Ions with Benzene and Benzene Derivatives

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The radiative association reactions of gas-phase Cr^+ with benzene and three of its methyl derivatives (toluene, *p*-xylene, and mesitylene) were studied in the Fourier-transform ion cyclotron resonance ion trap. Sequential formation of the monomer complexes and the sandwich dimer complexes was observed, and the kinetics were analyzed by a recently developed canonical transition-state theory approach to give estimates of the binding energies. The bond strength of $Cr^+-(C_6H_6)$ was assigned as 1.70 ± 0.15 eV, and the bond strengths increased slightly with increasing methyl substitution, reaching 2.0 eV for mesitylene. The bond strength for $Cr^+(C_6H_6)-(C_6H_6)$ was assigned as 2.2 ± 0.4 eV, with similar values (within large uncertainties) for the other sandwich complexes. The $Cr^+-(C_6H_6)$ value was in good agreement with the value from collision-induced dissociation, and a best value of 1.73 ± 0.10 eV for this bond strength is recommended.

Introduction

The study of interactions between metal ions and a variety of ligands has been an active area in gas-phase ion chemistry.[1−4] Diverse experimental techniques, including collision-induced dissociation,[5−8] photodissociation,[9−14] and ligand exchange reactions,[15] have been applied to measuring ligand/metal-ion bond energies.

Many of the traditional approaches to finding gas-phase ionic binding energies are based on locating thresholds for ion dissociation and these can run into difficulty with metal−ligand systems. Such systems often have many low-frequency vibrations, as well as relatively low thresholds, characteristics which make near-threshold dissociation slow and introduce substantial kinetic shifts into threshold determinations. Various approaches to overcoming these problems are being explored. As examples, we cite the method of dissociative photoionization in an ion trap, which alleviates kinetic shift problems by allowing the energized near-threshold ions a long time to complete their dissociation;[16−18] and the method of rate−energy curve extrapolation, which proceeds by plotting out the dissociative rate−energy curve and extrapolating to the (unob-

servable) threshold at which the dissociation rate goes to zero. This can be done via photodissociation[10,14,17,19] or via photoelectron−photoion coincidence (PEPICO) ionization.[20,21] In a similar spirit, the present paper offers an illustration of another route to circumventing these kinetic shift problems and obtaining binding energies for large ion−neutral complexes; in this case, the strategy focuses on the association kinetics to form the complex, an approach we have termed the radiative association (RA) kinetics method. This RA kinetics approach has been employed recently by our group to estimate binding energies for various complexes,[19,22] including both metal-ion complexes[23−25] and nonmetal-containing systems.[26−29]
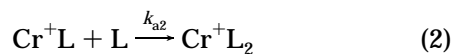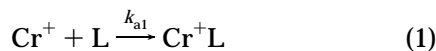
Radiative association reactions involve collisions between ions and neutral molecules to form metastable collisional complexes, which are then stabilized by photon emission. For typical polyatomic ions under low-pressure conditions (≤10^{-7} Torr), where third-body

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collisional stabilization is slow, collisional complexes are stabilized predominately by emission of infrared photons. Although the IR radiation from such association complexes has not been observed directly, there is an abundant body of evidence supporting the importance of such radiative stabilization, including indirect observations of radiative ion cooling,[30] quantitative kinetic modeling of radiative association,[22,31] and quantum calculations,[30] giving us confidence in the correctness of this picture and our ability to predict and understand it. The probability of the formation of a stabilized complex under these conditions then depends on the competition between IR photon emission and redissociation of the metastable complex back to reactants. The strong dependence of re-dissociation rates on bond energy is the key to exploiting this process in the RA kinetics method for determining ligand/metal-ion bond energies.[22,31-34]

Examining the trends in ligand/metal-ion bond energies across a series of ligands with differing methyl substitution is valuable for isolating the electronic bonding (which should be reasonably constant) from substituent-dependent effects, including variations in polarizability, steric interactions, heat capacity, and IR spectroscopic characteristics. In the present work, the radiative association reactions of the chromium cation with the neutral ligands benzene, toluene, *p*-xylene, and 1,3,5-mesitylene were studied in a FT-ICR mass spectrometer, which form both monomer complexes and dimer complexes (presumed to be sandwiches) according to the scheme

$$Cr^+ + L \xrightarrow{k_{a1}} Cr^+L \quad\quad\quad (1)$$

$$Cr^+L + L \xrightarrow{k_{a2}} Cr^+L_2 \quad\quad\quad (2)$$

where k_{a1} and k_{a2} are apparent bimolecular rate constants for the first and second radiative association reactions and L represents C_6H_6, C_7H_8, C_8H_{10}, or C_9H_{12}. In deriving the ligand/metal-ion bond energies from these experimental results, we will draw on the RA kinetics analysis based on the variable reaction coordinate transition state theory (VRC-TST) recently elaborated in collaboration with Klippenstein.[28] The vibrational frequencies and infrared intensities of $Cr^+(C_6H_6)$ and $Cr^+(C_7H_8)$ required for this modeling were calculated by *ab initio* methods.

The RA rate constants for Cr^+ with toluene (1.6×10^{-10} cm^3 molecule^{-1} s^{-1}) and mesitylene (7.36×10^{-10}) were recently measured by Crestoni and Fornarini.[35] Although their work had a different perspective from the present study and bond strengths were not derived, their rate data give a useful point of comparison, as well as an independent check on the pressure calibration of the present measurements.

Experimental Section

The radiative association experiments were performed on a home-built ion cyclotron resonance (ICR) mass spectrom-

eter[10] controlled by an IonSpec Fourier-transform data system. A 1 in. cubical cell is located in a magnetic field of 0.9 T. A high-vacuum chamber was pumped by an ion-pump (ULTEK), which gives a background pressure below 1×10^{-9} Torr.

The precursor ion, Cr^+, was initially generated from the vapor of $Cr(CO)_6$ by electron impact at a nominal electron energy of 12 eV. The filament was operated in a pulsed mode,[10,36] so that after the ionization pulse ($\sim$1 s) it was turned off and allowed to cool for the rest of the trapping time. Neutral reagent molecules were introduced into the ICR cell through a leak valve, and a static pressure was maintained. A time delay of about 5 s was provided to cool ions translationally, followed by a series of ejection pulses to isolate the precursor ion. The reactions were studied by monitoring the time-dependent chromium ion depletion and product ion formation. The reaction time was varied from 1 to 30 s.

Temperature measurements were done with a copper-constantan thermocouple mounted on one trapping plate of the ICR cell.[36] By operating the filament in a pulsed mode and reducing the filament-on duty cycle ($\sim$10%), the cell temperature was well-maintained at room temperature ($\sim$300 K). As described previously for experiments using this instrument to observe ZTRID (zero-pressure thermal radiation induced dissociation),[36] the operation of the electron-beam filament in a pulsed mode was employed to avoid the radiation from a white-hot filament.

Pressures were measured with an ionization gauge, and gauge calibrations were derived from the literature ionization gauge factors,[37,38] which have been found to be reasonably accurate for this instrument in comparisons against known reaction rates. An independent confirmation of the absolute calibration comes from the agreement within 20% of the present rate constants for toluene and mesitylene with the values obtained by Crestoni and Fornarini.[35]

Results

Figure 1a shows an illustrative plot of the sequential addition of benzene molecules, forming $Cr^+(C_6H_6)$ and $Cr^+(C_6H_6)_2$. Similarly, Figure 1b shows the time evolution of the association reactions in the Cr^+/C_7H_8 system. In Figure 1, the solid lines are the best fits according to the sequential scheme of eqs 1 and 2. The excellent fit of the calculated curves to the data confirms the sequential reaction scheme and gives values for the rate constants k_{a1} and k_{a2}. Table 1 summarizes the observed bimolecular rate constants for C_6H_6, C_7H_8, C_8H_{10}, and C_9H_{12}. The largest uncertainty in these values derives from the uncertainty in pressures, which we estimate as 30%.

The rate constants were measured at several different neutral pressures. Figure 2 illustrates the pressure dependence of the association reaction of Cr^+ with C_7H_8, showing that there is no dependence of k_{a1} on pressure up to at least 4×10^{-8} Torr. Similarly, the reaction with C_6H_6 showed no pressure dependence up to at least 7×10^{-8} Torr, and the reactions with C_8H_{10} and C_9H_{12} similarly showed no pressure dependence. This indicates that these experiments were done at pressures well below the point at which three-body collisional stabilization becomes significant.

***Ab Initio* Calculations.** A key set of input parameters in the present kinetic modeling is the vibrational frequencies and infrared intensities for the normal modes of the complex ion. The full optimized structures and vibrational frequencies and intensities of Cr^+–

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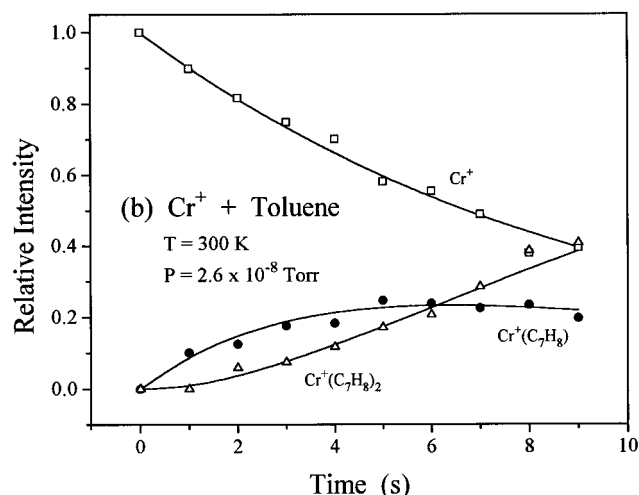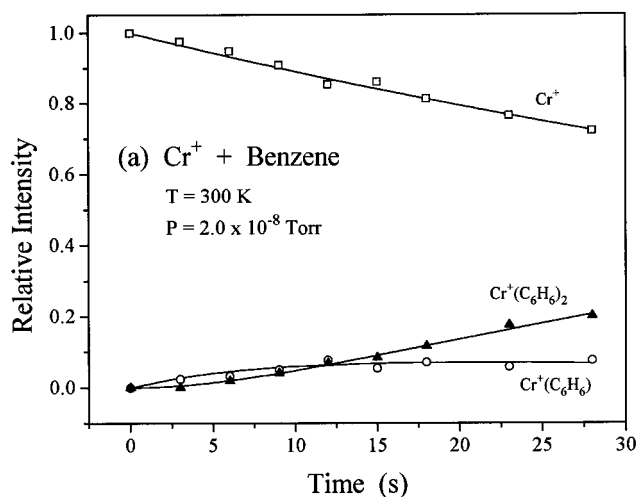
Figure 1. Time plots for association reactions of Cr^+ with (a) C_6H_6 at 2.0×10^{-8} Torr and (b) C_7H_8 at 2.6×10^{-8} Torr.

Table 1. Apparent Bimolecular Rate Constants

reactants	association rate constant (cm^3 molecule^{-1} s^{-1})	
	$k_{a1}{}^a$	$k_{a2}{}^a$
Cr^+, C_6H_6	1.77×10^{-11}	2.25×10^{-10}
Cr^+, C_7H_8	1.29×10^{-10}	3.22×10^{-10}
Cr^+, C_8H_{10}	4.13×10^{-10}	6.51×10^{-10}
Cr^+, C_9H_{12}	8.07×10^{-10}	1.22×10^{-9}

^{a} k_{a1} and k_{a2} are the apparent bimolecular rate constants for the first and second radiative association reactions (see eqs 1 and 2).

(C_6H_6) and $Cr^+-(C_7H_8)$ were computed using the GAUSSIAN 92 program suite[39] at the HF/LANL2DZ[40] level. The optimized structure of $Cr^+-(C_6H_6)$ has C_{6v} symmetry with the six carbons on the same plane and the six hydrogens bent slightly out of plane by 2.6°. Cr is above the center of the carbon ring (opposite the hydrogens) at a distance of 2.526 Å. Given our lower level of *ab initio* calculation, the agreement with Bauschlicher's calculation[41] on this ion is satisfactory. For

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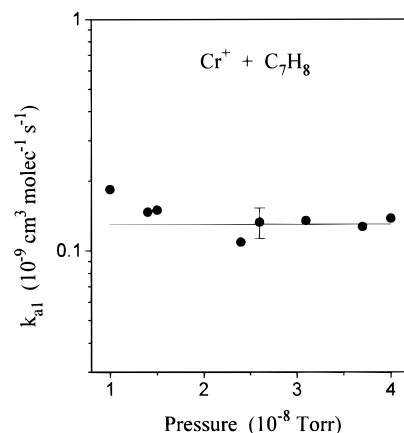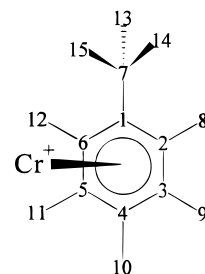

Figure 2. Pressure dependence study of the association reaction of Cr^+ with C_7H_8.

Chart 1. Schematic Structure of $Cr^+(C_7H_8)^a$

^{a} Some bond lengths and bond angles are shown in Table 2.

Table 2. Bond Lengths (Å) and Bond Angles (deg) from *ab Initio* Calculations^a

$Cr^+-(C_6H_6)$ (C_{6v})		$Cr^+-(C_7H_8)^b$ (C_s)	
$r(Cr^+-ring)$	2.526	$r(Cr^+-ring)$	2.500
$r(C-C)$	1.403	$r(C_1-C_2)$	1.409
		$r(C_2-C_3)$	1.402
		$r(C_3-C_4)$	1.403
		$r(C_1-C_7)$	1.514
$r(C-H)$	1.071	$r(C_2-H_8)$	1.072
		$r(C_7-H_{13})$	1.083
$\angle HCC$	177.4	$\angle H_8C_2C_5$	177.4
		$\angle C_1C_4C_7$	177.5

^{a} HF/LANL2DZ//HF/LANL2DZ. ^{b} See Chart 1.

$Cr^+-(C_7H_8)$, the methyl carbon is bent away from the ring plane (away from the Cr) (Chart 1 and Table 2). An *ab initio* calculation of the geometry of toluene neutral at the HF/6-31G* level[42] gave two low-energy configurations of toluene (eclipsed−staggered and orthogonal). Since the orthogonal configuration was found to have a lower energy than the eclipsed−staggered one, the orientation of the methyl group on the toluene was set to be orthogonal to the benzene ring in carrying out the present $Cr^+-(C_7H_8)$ calculations. (While the methyl orientation motion would probably be best represented as an internal rotor, the representation used here as a low-frequency torsion should be a reasonable approximation.) Table 2 is a partial summary of bond lengths and bond angles from the present *ab initio* calculations. Table 3 gives the vibrational frequencies and infrared intensities from the present calculations. For $Cr^+-(C_8H_{10})$, $Cr^+-(C_9H_{12})$, and all Cr^+-L_2 systems, the vibrational frequencies and IR intensities were estimated from $Cr^+-(C_6H_6)$ and $Cr^+-(C_7H_8)$. A sandwich geometry was assumed for Cr^+-L_2 systems.
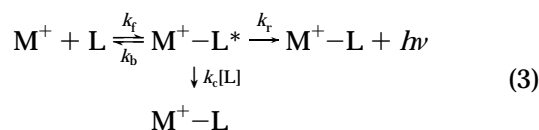
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Table 3. Vibrational Degeneracy, Frequencies (cm^{-1}), and Intensities (km mol^{-1})

species	frequencies (IR intensities)
Cr$^+$(C$_6$H$_6$)[a]	2 × 55.4(0), 125.5(20.42), 2 × 406.5(0), 2 × 597.7(0), 688.3(0), 725.4(227.27), 2 × 891.5(0.20), 936.2(3.53), 986.5(0), 2 × 995.2(0), 2 × 1002.1(5.64), 1016.1(0), 1123.2(0), 2 × 1168.2(0), 1222.3(0), 1352.8(0), 2 × 1450.7(26.48), 2 × 1562.9(0), 3029.8(0), 2 × 3037.6(0), 2 × 3051.8(4.06), 3061.5(0)
Cr$^+$(C$_7$H$_8$)[a]	51.4(0.53), 61.6(0), 127.6(19.04), 84.2(0.7), 209.9(7.7), 328.1(0.3), 410.1(0), 471.6(14.2), 504(2.22), 610.4(0.13), 690.7(8.3), 750.2(0), 770.3(150.03), 892.5(0.31), 929.8(1.41), 962.6(2.94), 976(0.22), 993.7(1.17), 998(0.04), 1008.4(0.61), 1059.4(8.57), 1065.6(6.75), 1136.9(0.35), 1171.2(1.9), 1186.8(0.9), 1214.6(0.05), 1328.2(0.14), 1410.2(10.7), 1417.4(6), 1458.7(15.2), 1463.9(30.1), 1465.7(26.2), 1551.9(1.3), 1577.3(12), 2861.3(18.3), 2936.2(13.5), 2943.3(18.7), 3025.6(2), 3026.7(0.8), 3037.8(1.13), 3044.9(4.9), 3056.7(1.54).
C$_7$H$_8$[b]	20.5(0.2), 204.1(2.1), 326.5(0.3), 405.6(0), 462.6(7), 501.1(0.9), 607.2(0.1), 688(11.4), 733.1(60.4), 758.3(1.4), 851.1(0), 905.2(0.8), 965.6(0), 969.8(0), 976.5(0), 998(0.06), 1007.1(1.6), 1053.8(3.38), 1098.1(0.07), 1159(0.32), 1179.1(0.46), 1194(0), 1317.5(0.08), 1394.5(0.5), 1431.7(1.34), 1456(4.4), 1463.9(12.34), 1488.4(16.5), 1565.4(1.1), 1613.5(7.6), 2848.8(38.2), 2898.2(33.1), 2917.5(25.4), 2978(9.92), 2980.6(5.7), 2992(14.59), 3000.6(60.15), 3012.6(22.8).

[a] HF/LANL2DZ//HF/LANL2DZ with frequencies scaled by 0.89. [b] HF/6−31G*//HF/6−31G* with frequencies scaled by 0.89.

Kinetic Modeling. Mechanism and Kinetics. RA kinetics have been discussed in detail in various places.[19,22,25−28,33,34,43] Equation 3 lays out the detailed kinetic scheme for an ion−molecule association reaction, where the individual rate constants are those for complex formation (k_f), redissociation (k_b), collisional stabilization (k_c), and radiative stabilization (k_r).[28] An

$$M^+ + L \underset{k_b}{\overset{k_f}{\rightleftharpoons}} M^+ - L^* \overset{k_r}{\longrightarrow} M^+ - L + h\nu$$
$$\downarrow k_c[L] \quad\quad (3)$$
$$M^+ - L$$

apparent bimolecular rate constant (k_2) is often derived assuming that the collisional complex [M$^+$−L*] is at steady state:[33,34,43]

$$k_2 = k_f \frac{k_r + k_c[L]}{k_b + k_r + k_c[L]} \quad\quad (4)$$

However, the individual rate constants appearing in this equation are actually functions of energy and angular momentum, and a more exact formulation using a canonical average over E and J should strictly speaking be used. Such an average is included in the kinetic modeling methodology summarized in the next section.

Kinetic Modeling. The details of the modeling approach used here were developed and described by Klippenstein *et al.*[28] In brief, a thermal distribution of reactants was assumed and the effective bimolecular rate constant k_2 was obtained within the framework of transition state theory by integrating the efficiency of complex stabilization over all possible E and J values, as shown in eq 5, where Q_r is the partition function of the reactants and $N_{EJ}{}^{\ddagger}$ is the number-of-states function of the transition state. $k_c(E,J)$ is the collisional rate

$$k_2 = \frac{1}{hQ_r}\int dE\,dJ\, N_{EJ}{}^{\ddagger}\exp(-E/KT) \times$$
$$\frac{k_r(E,J) + k_c(E,J)[L]}{k_b(E,J) + k_r(E,J) + k_c(E,J)[L]} \quad (5)$$

constant for which the Langevin model was used. A dipole correction was applied to $k_c(E,J)$ for the toluene system.[44] $k_r(E,J)$ is the rate constant for photon emission, whose derivation from the vibrational frequency/

intensity values of Table 2 is described in detail in ref 30 or 45. $k_f(E,J)$ and $k_b(E,J)$ are the complex formation and redissociation rate constants, respectively. It can be noted that the binding energy E_b does not appear explictly in the equation, but it is present implicitly because $k_b(E,J)$ is a very strong function of E_b and k_r-(E,J) is also a weak function of E_b. $N_{EJ}{}^{\ddagger}$, $k_f(E,J)$, and $k_b(E,J)$ were calculated by the variable reaction coordinate transition state theory (VRC-TST) methodology described in ref 28. A long-range forces approximation was used, in which only the ion-induced dipole attraction and the ion-permanent dipole interaction were considered to be significant ion−neutral interactions in the transition state. For neutral molecules without a dipole moment (i.e., all of the present systems except Cr$^+$/toluene), this approach is exactly equivalent to phase space theory (PST).[46−48]

In the present approach, the effective bimolecular rate constants (k_2) calculated from the present modeling were equated to the k_{a1} or k_{a2} values derived from experiment, using the ligand/metal-ion bond energy, E_b, as an adjustable parameter. The computer code used in the present calculations was provided by Klippenstein.

A potentially important systematic error must be considered in the radiative association measurements of the ML$^+$ + L → ML$_2{}^+$ reactions (following the sequential kinetic scheme of eqs 1 and 2). The ML$^+$ reactant ion, after it is stabilized by emission of one IR photon, still contains excess internal energy on the order of 1.5 eV, which was liberated by the formation of the M$^+$−L bond. During the time before this excess energy dissipates into the surroundings, any ML$_2{}^+$* complex formed by an ion/neutral encounter will contain and be destabilized by this excess energy, which will inhibit radiative stabilization of the ML$_2{}^+$ product complex. The result will be an erroneously low observed k_{a2} rate constant for dimer complex formation and an erroneously low binding energy inferred from it. This will be a serious error if the dimer-formation rate is comparable to the rate at which the initially excited ML$^+$ ions thermalize. In typical cases where the association is inefficient (as for instance in the Al$^+$/benzene system[25]), the reactant ions will thermalize by undergoing numerous collisions with neutral reactants before association occurs, but in the present cases where the reaction is quite efficient, such collisional cooling is not sufficient

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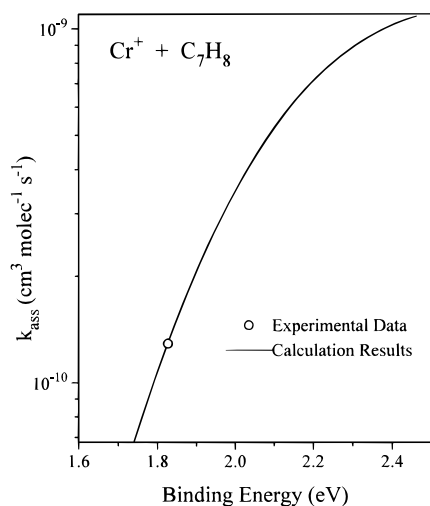(48) Herbst, E. *Astrophys. J.* **1987**, *313*, 867.

Figure 3. Rate−energy curve calculated for the Cr$^+$/toluene association. The experimental point is plotted, showing the basis for the assignment of 1.83 eV for the binding energy.

Table 4. Summary of Bond Energies (eV)

ligand	Cr$^+$−L	LCr$^+$−L
benzene	1.70 ± 0.15	2.2 ± 0.4
toluene	1.83 ± 0.15	2.3 ± 0.4
p-xylene	1.87 ± 0.20	2.2 ± 0.3
mesitylene	2.0 ± 0.3	2.2 ± 0.4

to eliminate the problem and radiative cooling of the complexes must be relied upon. In all of the present cases, the rate of radiative thermalization was faster than the rate of dimer complex formation. In particular, for the benzene case, calculation[30] using the data of Table 3 shows that it takes about 1.5 s for the excess internal energy of ML^{+*} to fall from 1.5 eV to a low level (<0.1 eV), while the time scale (inverse reaction rate) for the dimerization reaction was ∼4 s at the pressures used. Similarly, for toluene, the time for radiative cooling is about 0.5 s, while the time scale for dimerization at the pressures used was about 3 s. However, the strong temperature sensititvity of the radiative association rate makes it hard to rule out some effect on the reaction rate, and we estimate that the observed rates for the benzene and toluene cases might have been depressed by as much as a factor of two by this mechanism. This would correspond to an underestimate of the ML$^+$−L bond energies by as much as 0.2 eV. We have raised the estimated bond energies by 0.1 eV to take this possibility into account, as well as increasing the already large uncertainties in these numbers. The pressure in the xylene and mesitylene cases was so low that radiative cooling was expected to be highly efficient on the reaction time scale, and no effect on these measurements was expected.

For each of the reactions studied, the experimental rate constant was fitted to the calculated rate−energy curve using the binding energy as the adjustable parameter, as illustrated in Figure 3. Table 4 is a summary of the bond strengths derived from the present kinetic modeling.

Discussion

Competitive complex stabilization by collisions and by photon emission is often observed in the pressure regime around 10^{-7} Torr and above, but Figure 2 illustrates the pressure-dependence results indicating the absence of collisional effects for the present systems. This observation indicates that the metastable complexes are stabilized by emitting photons.

In the present studies, the accuracy in determining the ligand/metal-ion bond energy is greatly dependent on the measurements of absolute neutral pressures. A factor of two uncertainty in pressure gives an uncertainty of 0.05−0.2 eV for the ligand/metal-ion bond energies, depending on the particular case. The uncertainties in bond strengths arising from this factor are greater for the faster reactions, for which a small rate constant error translates into a relatively large binding energy error. Another significant source of uncertainty is the *ab initio* values of the vibrational frequencies and intensities, which may contribute an uncertainty on the order of 0.1 eV for the benzene and toluene associations. The other reactions, for which these parameters were estimated, have a larger uncertainty from this source. An overall uncertainty of ±0.15 eV was assigned to the ligand/metal-ion bond energies for Cr$^+$−(C$_6$H$_6$) and Cr$^+$−(C$_7$H$_8$) and larger uncertainties to the other reactions, as shown in Table 4.

The bond energies of Cr$^+$−(C$_6$H$_6$) and Cr$^+$−(C$_6$H$_6$)$_2$ have been determined by threshold collision-induced dissociation (CID) by Armentrout *et al.*[6] A comparison between the bond energies derived from the present method and from CID results should be of interest, as displayed in Table 5.

The CID approach becomes increasingly difficult for larger systems, when the unimolecular dissociation rate of the near-threshold parent ions becomes slow compared with the residence time of the ions in the apparatus. This is the kinetic shift, which acts to increase the apparent threshold above the true value. Armentrout's group has used RRKM kinetic theory to correct their thresholds for kinetic shifts,[5−7] which, although convincing, still suffers from the well-known uncertainties of RRKM parametrization. Table 5 illustrates results from this approach (reproduced from ref 6). In addition to the uncorrected CID thresholds, corrected values are shown using two different RRKM parametrizations. It is seen that for the smaller Cr$^+$-(C$_6$H$_6$) parent ion, the kinetic shift is calculated to be quite small and is quite similar using the two different RRKM parametrizations. For this case, the present RA kinetics value is in excellent agreement with the corrected CID value and a best value assignment of 1.73 ± 0.10 eV would seem worthy of confidence.

On the other hand, it is seen from Table 5 that the Cr$^+$(C$_6$H$_6$)$_2$ system is large enough to run into severe kinetic shift effects in the CID experiment. The kinetic shift correction is large and very sensitive to the RRKM parametrization used. Thus, the value for this complex obtained by threshold CID is substantially uncertain, just as is the value from the present work. The two values are mutually consistent but do not fix this bond strength very closely. It will be possible in the future to improve the RA kinetics determinations of these dimerization binding energies substantially, chiefly by working in a high-temperature cell where the reactions will be less efficient.

Generous error limits have been assigned in Table 4, reflecting the uncertainties in the absolute pressure

Table 5. Bond Energies (eV) of $Cr^+-(C_6H_6)$ and $(C_6H_6)Cr^+-(C_6H_6)$

	threshold CID[a]			present results[b]	theory[c]
	uncorrected[d]	loose TS[e]	tight TS[f]		
$Cr^+-(C_6H_6)$	1.85	1.76 ± 0.10	1.70	1.70 ± 0.15	1.62
$(C_6H_6)Cr^+-(C_6H_6)$	3.26	2.40 ± 0.19	2.04	2.2 ± 0.4	

[a] Reference 6. [b] Phase Space Theory (loose) transition state. [c] Reference 41. [d] Assuming no kinetic shift. [e] RRKM kinetic shift correction (loose transition state model). Note that Meyer *et al.* adopt these values as their best assignments of the final bond strengths. [f] RRKM kinetic shift correction (tight transition state model).

measurement and in the modeling, particularly the assignment of the vibrational intensities. These are probably realistic errors for the absolute uncertainties of the bond strength values. However, many of the possible systematic errors in these determinations are common to all the species, and comparisons at least among the Cr^+-L values in Table 4 are probably legitimate with relative uncertainties of the order of ±0.1 eV.

Tables 4 and 5 suggest that bonding of the second ligand is somewhat stronger than bonding of the first ligand. Other examples of first- versus second-ligand binding energies for delocalized π ligands show no simple trend. For example, $D^\circ(Co^+-C_5H_5)$ is 3.7 eV, increasing to 5.1 eV for $D^\circ(Co(C_5H_5)^+-C_5H_5)$.[49] On the other hand, for the Fe^+ and Ni^+ metallocene cases,[10,14] the second ligand is less tightly bound, so that $D^\circ(Fe^+-C_5H_5)$ is 4.3 eV while $D^\circ(Fe(C_5H_5)^+-C_5H_5)$ is 3.7 eV; and $D^\circ(Ni^+-C_5H_5)$ is 4.0 eV while $D^\circ(Ni(C_5H_5)^+-C_5H_5)$ is 3.2 eV. For the bonding energies of the transition-metal/benzene complexes,[6,41,50] Meyer *et al.* have rationalized the wide variation in relative first- and second-ligand energies on the basis of regular periodic trends combined with varying spin-pairing effects.[6] In a study of the binding of several ligands (including benzene) to Ag^+, it was found that the second ligand was slightly more strongly bound than the first, although the differences were generally not significant within experimental uncertainty.[51]

Table 4 shows a small but consistent and perhaps real increase in bond strength for Cr^+-L with the addition of methyl groups to the benzene ring. This increase on the order of 0.1 eV per methyl group is within the order of magnitude that could be attributed to the increase in a purely electrostatic attraction between the ion and the neutral ligand with the increasing polarizability of the neutral ligand. For Cr^+L-L, no effect of the methyl groups on the bond strength can be discerned within the large experimental uncertainties.

For the determination of binding energies of large systems in particular, the RA kinetics approach has attractive advantages over dissociative methods like CID, photodissociation, or dissociative photoionization. This is because the problem of kinetic shifts does not complicate the RA kinetics analysis to the extent that it does for dissociation techniques. In common with other approaches (with the exception of ligand exchange equilibrium), RA kinetics analysis involves an assumption about the nature of the transition state for associa-

tion/dissociation (in the present work taken to be the loose PST transition state, modified in the case of a permanent dipole). However, two considerations make the RA kinetics approach less susceptible to errors associated with slow dissociation and the attendant kinetic shift relative to most dissociation techniques. One is that in the RA kinetics formulation, the association/dissociation kinetics need not be convoluted with a broad, imperfectly known energy deposition function for the parent ions.[19,21,52] The other is that in RA kinetics, the same transition state governs both association and redissociation so that the errors introduced by an inappropriate choice of transition state tend to cancel. In fact, in the limit of low association efficiency, it has been pointed out that the RA kinetics become entirely independent of the nature of the transition state.[28]

Conclusions

The present set of RA kinetics data allows the assignment of bond energies of chromium-ion/ligand complexes, both monomer complexes and sandwich dimers, for the series of methylated benzenes from zero to three methyls. Although the observed association rate constants vary over a wide range, the analysis taking into account the varying number of degrees of freedom leads to quite similar binding energies for each series. For the monomer complexes, at least, there appears to be a small increase in binding energy with increasing methyl substitution, which can be attributed to the increasing polarizability of the ligand, but in general, the effect of methyl substitution on the binding energies is small. The second ligand is more tightly bound than the first by several tenths of an electron volt in each case, and there is no resolvable effect from methyl substitution on the second ligand binding energies.

The bond energies of $Cr^+-(C_6H_6)$ and $Cr^+(C_6H_6)-(C_6H_6)$ obtained from the present study are consistent with values from threshold collision-induced dissociation work by Meyer *et al.*[6] For $Cr^+-(C_6H_6)$, the consonance of the two techniques, as well as the reasonable agreement with the *ab initio* calculated value of Bauschlicher *et al.* (Table 5), gives considerable confidence in a binding energy in the vicinity of 1.7 eV for this complex, with a best value of perhaps 1.73 ± 0.10. For $Cr^+-(C_6H_6)-(C_6H_6)$, the uncertainty introduced into the CID analysis by the kinetic shift correction seems substantial and it is encouraging that the present estimate of 2.2 eV from the association measurement, while not very

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(52) This advantage is shared by several energy-specific dissociation-based techniques, including time-resolved photodissociation (ref 19) and photoelectron photoionization coincidence (Refs 20 and 21), which have been successfully used to give accurate bond strengths for larger ions.

precise, is in consonance with the assignment of 2.4 eV by Meyer *et al*.

The present work represents an apparently successful application of RA kinetics analysis to metal-ion/ligand bond energy determinations. This is an approach worthy of serious consideration for measuring bond energies in the 1.5−2 eV region at room temperature and it can be extended to weaker bonds or stronger bonds by, respectively, lowering or raising the temperature of the ion trap.

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