

# Binding Energy of $\text{Al}(\text{C}_6\text{H}_6)^+$ from Analysis of Radiative Association Kinetics

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**Abstract:** Analysis of radiative association kinetics is a new and promising approach to estimating absolute metal–ligand bond energies for gas-phase metal ions. The method is illustrated using previously published data to estimate the binding energy of aluminum cation to benzene and several deuterium-substituted benzenes. A formulation of radiative association theory is applied which is valid at low association efficiency, and is independent of assumptions about the transition state. Photon emission rates from the complex are derived from McMahon-type analysis of collisional and radiative association data, and alternatively from *ab initio* calculations of IR radiative intensities, with excellent agreement for all four isotopomers. Analysis of the radiative association data gives a binding energy of  $1.53 \pm 0.10$  eV ( $35.2 \pm 2$  kcal mol<sup>-1</sup>), which is concordant with, but has a smaller estimated uncertainty than, an interpolated thermochemical estimate based on data from other methods. For this system the semiquantitative “standard hydrocarbon” estimate of photon emission rate is a good approximation, but it is shown that in order to give valid predictions of the radiative association rate this scheme requires a correction for the fact that one of the reactants is an atomic ion.

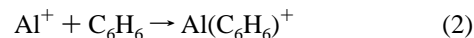
## Introduction

There is considerable interest in solidifying the thermochemistry of binding of ligands to gas-phase metal ions. Such bond dissociation energies have traditionally been measured by ligand dissociation approaches and by ligand exchange methods. It has recently been recognized that an independent approach to estimating absolute binding energies exists through the *association* process,



The rate of formation of stabilized  $\text{M}(\text{L})^+$  complexes is extremely sensitive to the  $\text{M}^+ - \text{L}$  binding energy, and our understanding of the kinetics of this process has advanced to the point that this is an attractive new source of thermochemical information on binding energies.

The kinetics of such associations are a potentially useful source of information in the case of either collisional or radiative stabilization of the collision complex. However, there is considerable uncertainty about the efficiency of collisional stabilization, whereas, as will be seen below, it is becoming possible to estimate the rate of radiative stabilization with fair confidence. Accordingly, recent emphasis has been on quantitative analysis of the *radiative* association component of the overall association kinetics.<sup>1</sup> The present work illustrates this approach through a careful analysis of the association reaction of aluminum ion with benzene,



As a consistency check, the analysis was carried out for the four isotopic variants  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{D}$ ,  $[1,3,5]\text{-C}_6\text{H}_3\text{D}_3$  and  $\text{C}_6\text{D}_6$ . A new value of the binding energy of this complex will be derived which seems worthy of reasonable confidence.

An established and fruitful source of relative binding energies is ligand-exchange equilibrium methods,<sup>2</sup> as illustrated by the existing relative binding energy scale measured by Uppal and Staley<sup>3</sup> for aluminum cation with a number of organic molecules (not including benzene). For determining absolute binding energy values, dissociation approaches (threshold photodissociation,<sup>4</sup> time-resolved photodissociation,<sup>5</sup> and threshold collision-induced dissociation<sup>6</sup>) are increasingly recognized as quantitatively useful when carefully interpreted. Dalleska *et al.*<sup>7</sup> used threshold collision-induced dissociation to determine the aluminum ion–water binding energy, which provides one absolute anchor for aluminum ion thermochemistry.

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**Table 1.** Parameters for the Complexes from the *ab Initio* Calculations<sup>a</sup>

<b>Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup>:</b> 3415 (1.5), 3409 × 2 (1.3), 3397 × 2 (0), 3389 (0), 1759 × 2 (0), 1639 × 2 (45), 1508 (0), 1380 (0), 1293 × 2 (0), 1242 (0), 1146 (0), 1133 × 2 (0), 1130 × 2 (0), 1101 (0), 1065 (12), 1011 × 2 (1.5), 829 (184), 729 (0), 653 × 2 (0), 430 × 2 (0), 198 (118), 138 × 2 (2.9); rotation constants 0.0952, 0.0803, 0.0803
<b>Al(C<sub>6</sub>H<sub>5</sub>D)<sup>+</sup>:</b> 3413 (1.4), 3409 (1.4), 3403 (0.7), 3397 (0), 3391 (0), 2520 (0.5), 1753 (0.2), 1750 (1.2), 1633 (44.7), 1604 (37.3), 1474 (1.6), 1368 (0.1), 1294 (0), 1258 (0), 1182 (0.1), 1142 (0), 1134 (0), 1126 (0.1), 1097 (0), 1082 (4.7), 1055 (9.9), 1011 (1.4), 943 (0.7), 924 (52), 767 (92), 700 (26.5), 650 (0), 646 (0), 430 (0), 410 (0.6), 198 (118), 138 (3.0), 136 (3.0); rotation constants 0.0920, 0.0799, 0.0776
<b>Al([1,3,5]-C<sub>6</sub>H<sub>3</sub>D<sub>3</sub>)<sup>+</sup>:</b> 3403 × 2 (0.7), 3403 (0.8), 2520 × 2 (0.1), 2519 (1.3), 1733 × 2 (1.5), 1562 × 2 (35.7), 1447 (0), 1322 (0), 1199 × 2 (0.3), 1095 (0), 1087 × 2 (0.4), 1059 (35.2), 1028 (2.0), 1006 (0), 915 × 2 (0.7), 836 × 2 (1.0), 756 (0), 639 × 2 (0), 626 (64.5), 403 × 2 (0), 197 (116), 134 × 2 (3.0); rotation constants 0.0862, 0.0763, 0.0763
<b>Al(C<sub>6</sub>D<sub>6</sub>)<sup>+</sup>:</b> 2434 (2.6), 2526 × 2 (0), 2513 × 2 (0), 2504 (0), 1700 × 2 (0), 1457 × 2 (30), 1331 (0), 1172 (0), 1058 (0), 1015 (8.8), 949 × 2 (0), 925 (0), 914 × 2 (0), 911 (0), 890 × 2 (1.1), 785 × 2 (1.2), 637 (0), 623 × 2 (0), 613 (121), 377 × 2 (0), 195 (114), 130 × 2 (3.1); rotation constants 0.0787, 0.0729, 0.0729

<sup>a</sup> Frequencies (unscaled) (cm<sup>-1</sup>); IR intensities (in parentheses; intensity per individual degree of freedom for degenerate modes) (km mol<sup>-1</sup>); rotational constants (cm<sup>-1</sup>).

Spectroscopic approaches have the potential for providing the most precise binding energies. Some vibrationally resolved photodissociation spectra of metal ion complexes with triatomic ligands can now be measured and assigned (refs 8 and 9, for example), and Mg<sup>+</sup>L complexes (L = CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>) have been analyzed via Birge–Sponer extrapolation to estimate binding energies.<sup>9</sup> As such approaches are refined and applied to larger systems they will provide increasingly reliable and useful thermochemical information.

Analysis of radiative association kinetics has been used to estimate and compare binding energy values in some systems.<sup>10</sup> However, these efforts have been recognized as very approximate, based on estimates of the radiative properties of the complex and on highly approximate modeling of the redissociation kinetics. An important conceptual advance is exploited in the present paper, with the realization that for the appropriate (low efficiency) association conditions the nature of the transition state and detailed modeling of the complex formation and redissociation kinetics are irrelevant. The association kinetics can be completely predicted using properties of the reactants and of the ion–ligand complex which can be confidently estimated from other sources, or calculated with sufficient accuracy by *ab initio* methods. This model-independent kinetic analysis should put association kinetics on a solid conceptual foundation as a quantitative route to ligand-binding thermochemistry. This approach has been used recently to measure the binding energy of Ag<sup>+</sup> to benzene, with results in satisfactory agreement with other recent determinations.<sup>11</sup>

The recently reported measurement in Berlin<sup>12</sup> of the association kinetics of Al<sup>+</sup> with several D-labeled benzenes, along with the results of *ab initio* calculations of the Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> complex, gives an outstanding opportunity to illustrate and try out the capabilities of detailed kinetic analysis for gaining insight into the binding energy and other properties of the complex.

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Two properties of the complex can be explored by consideration of the radiative association results, namely the binding energy and the rate of IR radiative emission from the energized complex. This system offers the opportunity to address both of these questions. We will be concerned here first with estimating the IR emission rate of the complex from both experiment and theory, and then with further analysis of the experimental kinetic results to derive the Al<sup>+</sup>–C<sub>6</sub>H<sub>6</sub> binding energy in this complex.

## Results

**Quantum Chemical Methodology and Results.** The implementation of the kinetic analysis requires estimated vibrational frequencies and moments of inertia for both the Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> complex and C<sub>6</sub>H<sub>6</sub>, and also for each of the corresponding isotopomers to be considered here. For the Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> complex the infrared intensities are also required. For consistency in this work, all of these quantities were evaluated via *ab initio* calculations implementing the GAUSSIAN 92 program suite<sup>13</sup> at the HF/6-31G(d) level of theory.<sup>14</sup> The resulting frequencies and intensities for the various isotopomers of Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> are reported in Table 1. For use in the kinetic calculations, each of the vibrational frequencies shown in Table 1 was scaled by a factor of 0.89 to correct for the known systematic error at this level of theory. As in the earlier work,<sup>12</sup> frequency calculations for the optimized geometry indicated that the C<sub>6v</sub> symmetrical structure corresponds to a true minimum on the potential energy surface.

In ref 12 a reoptimization of the Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> and C<sub>6</sub>H<sub>6</sub> structures at the MP2/6-31G(d,p) level of theory was carried out in order to give a better estimate of the stabilization energy of the complex. In this reoptimization, (i) the core electrons (1s of carbon and 1s, 2s, 2p of aluminum) were kept frozen in the correlation energy calculation and (ii) based on the SCF results the optimization was performed within the C<sub>6v</sub> symmetry group. The optimized structure looks as follows: *d*(Al–C) = 2.710 Å, *d*(C–H) = 1.082 Å, *d*(C–C) = 1.405 Å, with the hydrogen atoms bent away from the carbon plane by 0.5°, in the opposite direction from the Al atom.<sup>12</sup> While this level of theory cannot be expected to give highly accurate absolute energies, the *ab initio* calculated dissociation energy is still

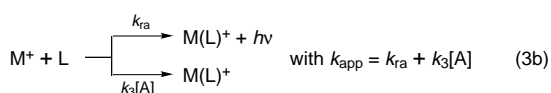
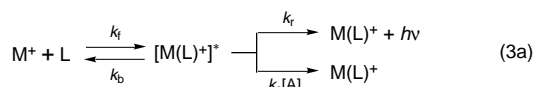
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(14) Comparative calculations indicated negligible difference between the HF/6-31G(d) calculations described here and the earlier calculations (ref 9) at the HF/6-31G(d,p) level.

interesting. The combination of this MP2/6-31G(d,p)//HF/6-31G(d,p) evaluation of the dissociation energy  $D_e$  with HF/6-31G(d,p)-based evaluation of the zero-point corrections provides an estimated zero-Kelvin bond dissociation energy of 1.69 eV, as reported in ref 12.

With the modest basis sets and limited corrections for correlation which are currently feasible for molecules of this size, the infrared intensity calculations are certainly not highly accurate. Unfortunately, the accuracy of quantum-chemical estimates for the infrared intensities for ionic species is difficult to ascertain due to the paucity of experimental data. However, for representative neutral organics (including benzene), HF/6-31G(d) calculations have been shown generally to predict the absolute absorption intensities to within about a factor of 2<sup>15</sup> (at least for those modes whose intensities are not too weak, and can accordingly be expected to make a reasonable contribution to the radiative relaxation process.). More comparisons with experiment for ionic species are needed, and providing another such comparison is one purpose of the present analysis.

**Kinetic Analysis.** The kinetic analysis of the association reaction 1 is based on the kinetic scheme



where  $k_f$  is the rate constant for formation of metastable collision complexes  $[M(L)^+]^*$ ,  $k_b$  is the rate constant for redissociation of the metastable complexes,  $k_r$  is the rate constant for stabilization of complexes by IR photon emission, and  $k_c$  is the rate constant for stabilization of complexes by collision with neutral molecules of concentration  $[A]$ . Equation 3b expresses the idea that at a given pressure (given  $[A]$ ), the association reaction has the kinetics of a simple bimolecular process, where the apparent bimolecular rate constant  $k_{app}$  is a linear function of pressure. Then  $k_{ra}$ , the bimolecular radiative association rate constant, is the limit of  $k_{app}$  at vanishing pressure, or in other words the zero-pressure intercept of a plot of  $k_{app}$  versus  $[A]$ .  $k_3$  is the rate constant for three-body collision-stabilized association.

All four of the microscopic rate constants  $k_f$ ,  $k_b$ ,  $k_r$ , and  $k_c$  are in principal functions of the reactant energy  $E$ . However, since the internal temperature of the complex is primarily determined by the relatively large ion-neutral binding energy and depends only slightly on the reactant thermal energy, and since  $k_r$  is not strongly  $E$ -dependent in any case,<sup>16</sup> it is an excellent approximation to assume that  $k_r$  is independent of  $E$ . In making the McMahan-type data analysis below we will also make the less secure assumption that every collision with a neutral benzene molecule stabilizes the metastable complex against redissociation, so that  $k_c$  is independent of  $E$  and is equal to the Langevin collision rate of complexes with benzene.

Solution of the kinetic scheme 3 gives the relations

$$k_{ra} = k_f k_r / (k_b + k_r) \quad (4a)$$

$$k_3 = k_b k_f k_c / (k_b + k_r)^2 \quad (4b)$$

Kofel and McMahan<sup>17</sup> suggested the analysis of association

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kinetics results to derive the rate of radiative emission, along with an average unimolecular dissociation rate for the metastable complex. For this purpose, eqs 4 can be reformulated as

$$k_r = \frac{k_{ra} k_c}{k_3} \left( 1 - \frac{k_{ra}}{k_f} \right) \quad (5a)$$

$$\cong \frac{k_{ra} k_c}{k_3} \quad (5b)$$

$$k_b = \frac{k_f k_c}{k_3} \left( 1 - \frac{k_{ra}}{k_f} \right) \quad (6a)$$

$$\cong \frac{k_f k_c}{k_3} \quad (6b)$$

where the last set of approximate equalities (eqs 5b and 6b) are valid under conditions of low radiative association efficiency where  $k_{ra} \ll k_f$ . In deriving  $k_r$  and  $k_b$  in this way, we are essentially using the collisional stabilization process as an internal clock. By assuming that each collision results in stabilization of the metastable complex, and taking the collision rate to be given by the Langevin orbiting collision rate, we use the collisional stabilization part of the kinetics as a known rate standard against which the unknown  $k_r$  and  $k_b$  processes can be calibrated. This calibration is expressed by eqs 5 and 6.

In general, McMahan's analysis<sup>17</sup> is unsatisfactory in one respect: it is based on a picture of each pair of reactants coming together with the same energy, so that  $k_r$  and  $k_b$  are true microcanonical rate constants. In reality the reactants possess a wide Boltzmann distribution of kinetic and internal energies and angular momenta, so that the population of complexes is far from a uniform microcanonical population, and one must think of a picture in which the observed results represent a convolution over a spectrum of  $k_r$  and  $k_b$  values.  $k_r$  is only weakly dependent on reactant energy, and can be safely considered constant, but  $k_b$  is a very strong function of energy, and the assumption of a single constant value for  $k_b$  seems to be a severe approximation. The more exact approach to calculating fully canonical kinetics used in the present work avoids this approximation and represents a full convolution over the Boltzmann distribution of reactant energies and angular momenta. However, in the limit of low association efficiency ( $k_{ra} \ll k_f$ ) these considerations are unimportant, since eq 5b becomes approximately valid for all reactant energies, and is thus correct for the canonical as well as the microcanonical case. (This is most easily seen by noting that taking the ratio  $k_{ra} k_c / k_3$ , obtained by dividing eq 4a by eq 4b and taking the low efficiency limit, results in cancellation of  $k_b$ . Since  $k_b$  is the only strongly energy-dependent quantity in these relations, the origin of the approximate energy-independence of eq 5b is evident.)

The association ( $k_f$ ) and redissociation ( $k_b$ ) aspects of the kinetics can be treated by transition state theory. If the reactant energies and angular momenta are taken as having a Boltzmann probability distribution, transition state theory gives the canonical bimolecular rate of formation of stabilized complexes from reactants as

$$k_{app} = \frac{\sigma^\ddagger}{\sigma^\ddagger h Q_{react}} \int dE \int dJ N_{EJ}^\ddagger e^{-E/kT} \frac{k_r + k_c[A]}{\frac{\sigma^\ddagger N_{EJ}^\ddagger}{\sigma^\ddagger h \rho_{EJ}^\ddagger} + k_r + k_c[A]} \quad (7)$$

Here  $\sigma^\ddagger$  and  $\sigma^\ddagger$  are symmetry numbers for reactant and transition

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**Table 2.** Photon Emission Rates for Complexes<sup>a</sup>

	Al(C <sub>6</sub> H <sub>6</sub> ) <sup>+</sup>	Al(C <sub>6</sub> H <sub>5</sub> D) <sup>+</sup>	Al([1,3,5]-C <sub>6</sub> H <sub>3</sub> D <sub>3</sub> ) <sup>+</sup>	Al(C <sub>6</sub> D <sub>6</sub> ) <sup>+</sup>
<i>k<sub>r</sub></i> ( <i>ab initio</i> )	17.5	13.5	13.5	10.2
<i>k<sub>r</sub></i> (expt, McMahon analysis)	16	13	13	11
<i>k<sub>r</sub></i> (expt, canonical analysis via eq 8)	17	13	13	11
standard hydrocarbon <sup>b</sup>	25			

<sup>a</sup> Values derived from *ab initio* IR radiative intensity calculations, from kinetic analysis of association rate data, and from the generic “standard hydrocarbon” estimation scheme. (Total photon emission rate, s<sup>-1</sup>, for complex with 1.7 eV of internal energy.) <sup>b</sup> References 16 and 19.

**Table 3.** Calculated Association Rates Using Eq 8 with *ab Initio* IR Intensity Values for a Series of Assumed Binding Energies

<i>E<sub>0</sub></i> (eV)	Al(C <sub>6</sub> H <sub>6</sub> ) <sup>+</sup> ( <i>k<sub>r</sub></i> = 17.5 s <sup>-1</sup> ) <sup>a</sup>		Al(C <sub>6</sub> H <sub>5</sub> D) <sup>+</sup> ( <i>k<sub>r</sub></i> = 13.5 s <sup>-1</sup> ) <sup>b</sup>		Al([1,3,5]-C <sub>6</sub> H <sub>3</sub> D <sub>3</sub> ) <sup>+</sup> ( <i>k<sub>r</sub></i> = 13.5 s <sup>-1</sup> ) <sup>c</sup>		Al(C <sub>6</sub> D <sub>6</sub> ) <sup>+</sup> ( <i>k<sub>r</sub></i> = 10.2 s <sup>-1</sup> ) <sup>d</sup>	
	<i>k<sub>ra</sub></i> <sup>e</sup>	<i>k<sub>3</sub></i> <sup>f</sup>	<i>k<sub>ra</sub></i> <sup>e</sup>	<i>k<sub>3</sub></i> <sup>f</sup>	<i>k<sub>ra</sub></i> <sup>e</sup>	<i>k<sub>3</sub></i> <sup>f</sup>	<i>k<sub>ra</sub></i> <sup>e</sup>	<i>k<sub>3</sub></i> <sup>f</sup>
1.3	0.16	0.11	0.18	0.15	0.30	0.25	0.55	0.61
1.4	0.48	0.32	0.52	0.44	0.96	0.79	1.8	2.0
1.5	1.4	0.9	1.5	1.3	2.8	2.3	5.5	6.0
1.6	3.7	2.5	4.2	3.5	8.1	6.6	16	18
1.7	10	6.7	11	9.4	22	18	46	50
obsd	1.7	1.2	1.8	1.5	3.5	3.0	6.2	6.2

<sup>a</sup> A polarizability of 10.55 Å<sup>3</sup> was used for benzene, giving the following Langevin collision rate constants (10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>): (Al<sup>+</sup> + benzene), 1.69; (complex<sup>+</sup> + benzene), 1.14. <sup>b</sup> Langevin: 1.69, 1.13. <sup>c</sup> Langevin: 1.69, 1.12. <sup>d</sup> Langevin: 1.68, 1.10. <sup>e</sup> Rate constants *k<sub>ra</sub>* in units of 10<sup>-12</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>. <sup>f</sup> *k<sub>3</sub>* in units of 10<sup>-22</sup> cm<sup>6</sup> molecules<sup>-2</sup> s<sup>-1</sup>.

state,  $Q^{\text{react}}$  is the partition function for reactants,  $N_{EJ}^{\ddagger}$  is the number-of-states function for the transition state, and  $\rho_{EJ}^{\text{c}}$  is the density-of-states function for the complex. In the limit where complex stabilization is very inefficient, and  $k_b \gg (k_r + k_c[A])$ , this simplifies greatly, giving

$$k_{\text{app}} \cong \frac{\sigma^{\text{r}}}{\sigma^{\ddagger}} \frac{1}{hQ^{\text{react}}} \int dE \int dJ \rho_{EJ}^{\text{c}} e^{-E/kT} (k_r + k_c[A]) \quad (8)$$

Note in particular that in this limit the properties of the transition state have all dropped out, and only quantities involving state densities of reactants and complex remain. These quantities can be obtained by state-counting procedures using estimated or calculated geometries and vibrational frequencies of the reactants and the complex. In the present case the low-efficiency condition is well obeyed, and eq 8 was evaluated to predict the association rate constant as a function of the varying parameter  $E_0$ , the critical energy for dissociation. These calculations were done in the rigid-rotor-harmonic-oscillator approximation, using the Beyer–Swinehart algorithm for state counting.<sup>18</sup>

**Radiative Rate.** The infrared radiative intensities of ionic species, which are interesting in their own right and are also needed to assign  $k_r$  in the kinetic analysis which follows, are accessible by three main approaches; in this section we consider the information about the aluminum–benzene ion complex available from approaches 2 and 3.

**(1) Absorption intensity measurements:** Such data are available for only a very few gas-phase ionic species, not including metal ion–benzene complexes, and need not be considered further here as a useful source of information.

**(2) Radiative cooling rates of internally hot ions:** Such rates can be measured by direct ion thermometry techniques, as has been described for several cases,<sup>15(b),19–21</sup> or they can be derived less directly, as in the present work, from ion–neutral association kinetics.<sup>1,17,19</sup>

**(3) Quantum chemical calculations:** Available *ab initio* programs, like the GAUSSIAN package used here, calculate

doubly harmonic IR intensity values for all the normal vibrations.

**(a) Radiative Rates from Association Results (Approach 2).**  $k_r$  is derived from the simple McMahon analysis by applying eq 5. This was carried out in ref 12, and the results are reproduced in Table 2. As discussed above, the microcanonical approximation inherent in the simple McMahon analysis<sup>17</sup> is removed by using the present canonical formulation of the kinetics, but for the present case where the low-efficiency approximation is applicable, eq 5b should give the same result whether evaluated by simple McMahon analysis or by using eq 8 to calculate canonical values of  $k_{ra}$  and  $k_3$ . This was indeed found to be the case, as indicated in Table 2. The main uncertainty left in these values derives from the assumption that the collisional stabilization rate constant  $k_c$  is equal to the Langevin collision rate constant.

**(b) Calculation of Radiative Rates from *ab Initio* Infrared Intensities (Approach 3).**  $k_r$  can be predicted theoretically using *ab initio* IR intensity values like those listed in Table 1. The procedure for doing this has been described in detail.<sup>19,22,23</sup> It proceeds by summing up the photon emission probabilities from each quantum level of each normal mode of the molecule, weighted by the probabilities of occupation of the levels. As usual, we carried this out in a harmonic oscillator picture of the normal modes, using the internal-temperature formalism as a convenient and fully accurate way to evaluate the emission probabilities.<sup>23</sup> (For example, the internal temperature of the energized complex was calculated to be 1225 K, assuming a binding energy of 1.53 eV.) These results are also given in Table 2.

**Bond Strength Determination.** Having satisfactory values for  $k_r$ , we can return to consideration of  $k_{ra}$ , with  $E_0$  as the adjustable parameter which is to be fixed by comparison with experiment. Equation 8 was used to calculate the values of  $k_{ra}$  and  $k_3$  shown in Table 3 as a function of  $E_0$ . As shown graphically in Figure 1, the calculated curve of  $k_{ra}$  versus  $E_0$  can be used directly to derive the value of  $E_0$  corresponding to the observed radiative association rate. In order to assess the extent of error made in using eq 8 instead of the more exact eq 7, a trial calculation for Al<sup>+</sup> + C<sub>6</sub>H<sub>6</sub> was made using eq 7 with

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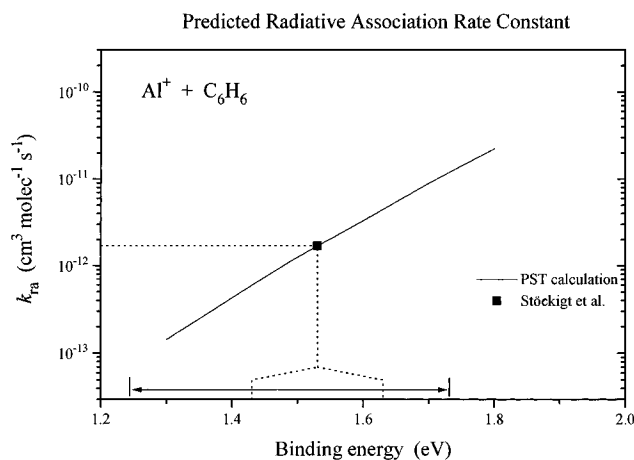
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**Figure 1.** Fitting procedure using the calculated curve (solid line) of association rate versus  $E_0$  to convert the observed  $k_{ra}$  ( $1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), given by Stöckigt et al.,<sup>12</sup> to a value of binding energy ( $1.53 \pm 0.10 \text{ eV}$ ). The interval on the  $x$ -axis delimited with arrows is the range of binding energy values estimated in ref 12 from prior measurements.

**Table 4.** Comparison of Binding Energy Assignments from Various Approaches

method	derived binding energy at 0 K	
	eV	kcal mol <sup>-1</sup>
full TST calculation from $k_{ra}$ (eq 7)	$1.53 \pm 0.10$	$35.2 \pm 2$
low-efficiency TST from $k_{ra}$ (eq 8)	$1.52 \pm 0.10$	$35.0 \pm 2$
standard hydrocarbon estimation from $k_{ra}$ (ref 16)	1.83	42
<i>ab initio</i> (MP2/6-31G(d,p)) thermochemical estimate <sup>a</sup>	1.69	39
BDE <sup>298</sup> (corn of 0 K value, 35.2 kcal mol <sup>-1</sup> , to $\Delta H_{\text{diss}}$ at 298 K)	$1.52 \pm 0.10$	$34.9 \pm 2$

<sup>a</sup> Estimated as described in the text by interpolation using data in refs 3 and 7.

**Table 5.**  $E_0$  for Isotopic Species Derived from Radiative Association Efficiencies (Eq 8, with 0.01 eV Correction according to Eq 7)

	$\text{Al}(\text{C}_6\text{H}_6)^+$	$\text{Al}(\text{C}_6\text{H}_5\text{D})^+$	$\text{Al}([1,3,5]\text{-C}_6\text{H}_3\text{D}_3)^+$	$\text{Al}(\text{C}_6\text{D}_6)^+$
$E_0$ (eV)	1.53	1.53	1.54	1.52

the orbiting transition state for assigning values of  $N_{EJ}^\ddagger$  (i.e. phase space theory). The calculations using eq 7 gave association rate constants of the order of 10% lower for the relevant range of parameters, which is equivalent to a change of 0.01 eV in the binding energy. Accordingly, we corrected all the fitted binding energies by this small amount, and made the final assignments of the binding energies shown in Tables 4 and 5.

## Discussion

The aluminum–ring bond strength determined from this analysis ( $35.2 \text{ kcal mol}^{-1}$ ) is in excellent agreement with the estimate made in ref 12 ( $36 \text{ kcal mol}^{-1}$ ), which was derived from experimental data in refs 3 and 7 by interpolating experimental values assuming a linear correlation of proton affinities with aluminum ion affinities. The latter estimate was realistically considered uncertain within  $\pm 7 \text{ kcal mol}^{-1}$ , and the present directly determined value, with an estimated uncertainty of  $\pm 2 \text{ kcal mol}^{-1}$ , should be more accurate and reliable.

The 0 K binding energy can be converted to a 298 K bond dissociation energy (BDE<sup>298</sup>), which is the same as the 298 K dissociation enthalpy. The conversion is

$$\text{BDE}^{298} = E_0 + \Delta E_{\text{trans}} + \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + RT \quad (9)$$

where  $\Delta E$  quantities refer to the changes in energy content of the indicated degrees of freedom upon dissociation of the complex. Here  $\Delta E_{\text{rot}} = 0$ ,  $\Delta E_{\text{trans}} = 0.90 \text{ kcal mol}^{-1}$ , and  $\Delta E_{\text{vib}}$  is calculated to be  $-1.2 \text{ kcal mol}^{-1}$ , giving  $\text{BDE}^{298} = E_0 - 0.3 = 34.9 \text{ kcal mol}^{-1}$  (see Table 4).

The *ab initio* bond strength calculated as described above was  $39 \text{ kcal mol}^{-1}$  (1.69 eV). The level of theory used is not expected to give highly accurate absolute binding energies, and the agreement of this calculated value with our experimentally derived value of  $35.2 \text{ kcal mol}^{-1}$  can be considered entirely acceptable.

There has been some interest in the analogous complexation of  $\text{Si}^+$  with benzene and other aromatic hydrocarbons.<sup>24–26</sup> At a comparable level of theory, the  $\text{Si}^+$ /benzene  $\pi$  complex was calculated<sup>25</sup> to have a bond strength of  $44.1 \text{ kcal mol}^{-1}$  (1.92 eV). Experimental evidence was found<sup>25</sup> for the formation of a  $\text{Si}^+$ /benzene insertion structure in addition to the  $\pi$  complex, but the latter structure was calculated to be less stable by  $5.5 \text{ kcal mol}^{-1}$ .

The IR photon emission rates from the  $\text{Al}^+$ /benzene complex, as determined here, are in line with magnitudes observed for other hydrocarbon systems (as indicated by the accord between the actual values and the generic “standard-hydrocarbon” estimates<sup>16,19</sup> shown in Table 2). A remarkable feature of the results is the quantitative agreement between the *ab initio* derived rates of IR photon emission ( $k_r$ ) from the metastable complex (first row of Table 2) and the  $k_r$  values derived by the McMahon-type reduction of the experimental data (second and third rows of Table 2). Realistically neither the experimental nor the calculated values should be considered reliable to an accuracy as good as 10%, which might be inferred from this near-perfect level of agreement. Still, this agreement, consistent for all four isotopomer cases, is a gratifying validation of the soundness of our understanding of how to treat the kinetics, and of the utility of the *ab initio* IR intensity values using this relatively modest level of theory.

The last row of Table 2 notes the “standard hydrocarbon” estimate of  $k_r$ , which is a generic value expected for a “typical” hydrocarbon ion complex of this size and binding energy. Such generic estimates of radiative intensities are useful as a summary of typical experience, and have been found to have semiquantitative utility in some comparisons with specific systems.<sup>19</sup> It is good to find that the directly determined  $k_r$  values for this particular case are actually quite close to the generic estimate, differing by a factor of 1.4. (Factor-of-2 agreement might be considered quite reasonable.)

The present study also gives a useful opportunity to test the generic “standard hydrocarbon” approach to deriving semiquantitative bond strengths from radiative association observations.<sup>1a,16</sup> It is disconcerting to find that the binding energy (1.83 eV) obtained by applying the standard hydrocarbon estimation to this system is in poor agreement with the accurate kinetic treatment (1.53 eV), meaning that the standard hydrocarbon estimate of  $k_{ra}$  is substantially lower than it should be. The problem is not with the  $k_r$  estimate, since, as noted above, the generic estimate of  $k_r$  is quite close to the value used in the full kinetic analysis. It must be that the generic model gives a poor treatment of the complex redissociation ( $k_b$ ) part of the problem,

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and in fact it must be predicting  $k_b$  too high by a factor of at least 20. Actually, it is expected that the association of an atomic ion with a molecule will be substantially faster than an otherwise similar association of a diatomic or polyatomic ion with a corresponding neutral, because of the additional reactant rotational degrees of freedom in the polyatomic case. A test was made for the present system using eq 8, and it was found that with other factors being similar, the fact of the present system being an atomic-ion case makes its calculated association *faster* by roughly a factor of 50 than it would be if the reactant ion were diatomic. This atomic-ion effect is entirely sufficient to explain the high  $E_0$  value estimated from the standard hydrocarbon scheme. In summary, the standard hydrocarbon scheme, as presented in ref 16, is inappropriate for predicting  $k_{ra}$  in systems where one of the reactants is an atom, and consequently gives a poor estimate of  $E_0$  for the present system. It will be necessary to introduce a correction factor in the standard hydrocarbon estimation scheme for the special case of atomic ions.

In considering radiative association kinetics analysis as a useful method for future applications, it is of interest to note how sensitive the results are to the parameters needed as input. The uncertainty range of  $\pm 0.1$  eV ( $\pm 2$  kcal mol<sup>-1</sup>) given here for the derived binding energy corresponds to multiplying (or dividing) all of the radiative intensities (or, similarly, the overall photon emission rate) by a factor of 3. Alternatively, for the assignment of the vibrational frequencies to the ion–ligand complex, this uncertainty range corresponds to a 50% change in the lowest three vibrational mode frequencies. (That is, if the three lowest frequency modes in Table 1 are changed by  $138 \rightarrow 207$ ,  $138 \rightarrow 207$ ,  $198 \rightarrow 297$  cm<sup>-1</sup>, the derived binding energy increases by 0.1 eV.) Since we are confident that we can assign the IR intensities and the complex vibrational frequencies with better accuracy than these limits, we consider that the overall uncertainty of  $\pm 0.1$  eV in  $E_0$  is realistic.

Another potential source of error is the use of the Langevin orbiting rate for  $k_c$  in the McMahon derivation of  $k_r$ . Note first that this McMahon analysis was only one of two approaches used to obtain  $k_r$ , with the *ab initio* calculations providing the other, independent, approach. Determination of the bond strength from the low-pressure  $k_{ra}$  measurements via eq 8, using the *ab initio* derived  $k_r$ , involves no assumptions about the value of  $k_c$ . The agreement of the two approaches gives some support to the validity of the assumptions made in the McMahon analysis.

Considering the McMahon-type derivation of  $k_r$ , we consider that, since benzene is nonpolar and is not large enough for significant hard-sphere effects at thermal kinetic energies, the Langevin estimate of the orbiting collision rate should be quite good. The assumption that  $k_c$  is equal to the orbiting collision rate also seems reasonable, since it is physically sensible to assume that each orbiting collision with a benzene molecule removes at least the small increment of energy from Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> necessary to stabilize the complex.

The analysis of association kinetics as described here has the attractive feature that it is independent of any assumptions about the kinetics of the association and dissociation reactions represented by eq 2, other than the fundamental statistical assumption that energy is randomized among the internal degrees of freedom of the complex between the time of its formation and the time of its redissociation. The remarkable property of eq 8 is that any features of the transition state which lead to unpredicted behavior affect  $k_f$  and  $k_b$  equally and cancel out in the final  $k_{app}$  relation. By removing the guesswork aspect of applying simple RRKM theory or (to a lesser extent) phase

space theory, the use of eq 8 begins to make radiative association kinetics appear viable as an accurate thermochemical tool. In this sense it is less model dependent, and has less arbitrary parameter choices, than the threshold-law assumptions necessary to interpret threshold dissociation data.<sup>6</sup> When this approximation is valid, it also removes the need to estimate  $k_f$  (or to measure it directly by high-pressure methods, as has been done for some radiative association analyses.<sup>1,27</sup>) It does, however, require assignment of the radiative and vibrational properties of the complex from *ab initio* calculations or other sources, and is thus more dependent on uncertain quantities than equilibrium measurements of ligand exchange thermochemistry,<sup>2,3</sup> which continue to be the most reliable source of dissociation thermochemistry when the ligand-exchange approach is applicable.

A final reassurance of the validity of the kinetic analysis is the fact that all four isotopomers give the same binding energy, despite having quite different photon emission rates and association kinetics. There is also excellent agreement between the *ab initio* calculations and the McMahon analysis for assessing the isotopic substitution effects on photon emission rates (as seen in Table 2), which gives a significant boost to our confidence in the accuracy of the calculations of IR radiative intensities.

## Conclusions

Kinetic analysis of the radiative association kinetics of Al(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup> formation gives a quantitatively consistent and convincing picture of the association process. The range of possible binding energies consistent with the observed kinetics is tightly constrained, and leads to the estimation of the Al<sup>+</sup>–benzene binding energy as  $35.2 \pm 2$  kcal mol<sup>-1</sup> (at 0 K), corresponding to a 298 K BDE of 34.9 kcal mol<sup>-1</sup>.

The rates of IR photon emission from the energized complex have been derived from both *ab initio* calculations and the kinetic analysis of the experimental data, showing excellent agreement between experiment and theory. The radiative rates are of the order of 20 s<sup>-1</sup>, with some variation depending on deuterium content of the benzene. The generic “standard hydrocarbon” prediction of the radiative rate is in good semiquantitative agreement with this value.

The kinetic analysis illustrates the convenience and accuracy of an approximate formulation of the association/dissociation kinetics (valid at low association efficiency) which is model independent, in the sense of having no dependence on the nature of the transition state or on uncertain assumptions about the nature of the association/dissociation process. In the present case, the low-efficiency calculation was shown to agree (within 10%) with specific phase-space-theory calculations. The low-efficiency formulation will be particularly interesting for application to more sterically hindered associations, since steric hindrance to complex formation is inherently taken care of in this model-independent approach, but presents formidable problems in trying to apply transition-state theory to such associations. However, we would caution that the analysis rests on assumptions and approximations which might be less valid in other systems than they appear to be in the present case. It would be premature in general to consider unsupported binding energies from this new and little-tested approach to be as reliable and accurate as we believe the present favorable case to be.

The semiquantitative “standard hydrocarbon” estimation<sup>16</sup> for relating radiative association rates to binding energies fails quite seriously in this case. It is pointed out that this special case of one of the reactants being an atomic ion leads to a significant

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increase (by a factor of the order of 50) of the radiative association rate relative to corresponding values for polyatomic reactants. This leads to an overestimate by about 0.3 eV in the binding energy. The standard hydrocarbon approach should be semiquantitatively useful in metal-ion–ligand systems like this, but only if this atomic-ion effect is corrected for by lowering the estimated bond strengths by several tenths of an electronvolt. This question will be addressed in more detail in future work.

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