# Photoionization-Induced Intracluster Reactions of Chlorobenzene/Ammonia Mixed Complexes

J. R. Grover\*

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

B.-M. Cheng<sup>†</sup>

Synchrotron Radiation Research Center, Taiwan, ROC, and Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

W. J. Herron,<sup>⊥</sup> M. T. Coolbaugh,<sup>‡</sup> W. R. Peifer,<sup>§</sup> and J. F. Garvey

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214 Received: February 14, 1994; In Final Form: April 22, 1994<sup>®</sup>

Complexes of chlorobenzene and ammonia,  $C_6H_5Cl\cdot NH_3$ ,  $C_6H_5Cl(NH_3)_2$ , and  $C_6H_5Cl(NH_3)_3$ , were studied by single-photon ionization. The ionization potentials of these three complexes were measured to be  $8.744 \pm$ 0.022, 8.652  $\pm$  0.013, and 8.555  $\pm$  0.012 eV, respectively. The appearance potential of C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> from  $C_6H_5Cl$ ·NH<sub>3</sub> was found at 8.935 ± 0.004 eV, which, with the known heat of formation of anilinium ion, gives the dissociation energy  $D(C_6H_5Cl\cdot NH_3) = 2.9 \pm 0.5$  kcal mol<sup>-1</sup> (12.0  $\pm 2.2$  kJ mol<sup>-1</sup>). Then, from its onset energy from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub>, the dissociation energy of  $(C_6H_5Cl\cdotNH_3)^+$  is calculated to be  $D[(C_6H_5Cl\cdotNH_3)^+]$ = 10.4  $\pm$  0.7 kcal mol<sup>-1</sup> (43.5  $\pm$  2.9 kJ mol<sup>-1</sup>), unusually large for a heterodimer ion. No production of  $C_6H_5NH_3^+$  from trimers could be detected in the onset region. The ion  $C_6H_5NH_2^+$  has onsets of 8.849 ± 0.009 and  $8.855 \pm 0.029$  eV from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Cl(NH<sub>3</sub>)<sub>2</sub>, respectively. These energies are below the onset for  $C_6H_5NH_3^+$  but far above the thermochemical thresholds for aniline ion, which are near 7.6 eV. Evidently,  $C_6H_5NH_2^+$  is not produced by dissociative ionization of the excited neutral complex. Instead, the complex must first be ionized and excited to at least 0.1 eV. Since the onsets for  $(C_6H_5Cl\cdot NH_3)^+$  and  $C_6H_5NH_2^+$  are lower than for  $C_6H_5NH_3^+$ , then  $(C_6H_5Cl\cdot NH_3)^+$  in its ground state does not spontaneously form  $C_6H_5NH_3^+$ . Kinetic energy release distributions measured for  $C_6H_5NH_2^+$  and  $C_6H_5NH_3^+$  indicate that the formation of both ions is consistent with statistical processes; i.e., no evidence for nonstatistical mechanisms was found, even for photon energies as large as 17.7 eV.

#### Introduction

Dissociative reactions in small mixed dimer ions usually proceed with barrier energies  $(E_b)$  of the order of tenths of an electronvolt to several electronvolts. For example

$$(1,3-C_4H_6\cdot SO_2)^+ \rightarrow C_4H_6SO^+ + O \quad (E_b = 2.3 \text{ eV})^1$$
(1)

$$(C_2H_4 \cdot HCl)^+ \rightarrow C_2H_4Cl^+ + H \quad (E_b = 0.7 \text{ eV})^2 \quad (2)$$

Analogous reactions that do not occur in dimers often take place in trimers, but still with high barriers.<sup>3,4</sup>

$$(C_6H_6O_2)^+ \neq C_6H_6O^+ + O$$
 (3)

$$(C_6H_6)_2O_2^+ \rightarrow C_6H_6O^+ + C_6H_6 + O \quad (E_b = 4.9 \text{ eV})$$
 (4)

$$(C_6H_6\cdot HCl)^+ \not\rightarrow C_6H_6Cl^+ + H$$
 (5)

$$(C_6H_6)_2HCl^+ \rightarrow C_6H_6Cl^+ + C_6H_6 + H \quad (E_b = 2.3 \text{ eV})$$
(6)

(Reactions 5 and 6 afforded the first reported demonstration of the effect of specific microsolvation on an intracluster ionmolecule reaction.<sup>4</sup>) The need to overcome the barriers, and the nonoccurrence of many reactions except in larger clusters, makes it difficult to study most photoionization-induced intradimer reactions.

However, the chlorobenzene/ammonia heterodimer and several related complexes make up a small class of clusters that are exceptions to this general rule. For example, the intradimer reaction

$$(C_6H_5Cl\cdot NH_3)^+ \rightarrow C_6H_5NH_3^+ + Cl$$
(7)

is unusual because it apparently proceeds with little or no barrier.<sup>5</sup> This and certain other convenient characteristics (see below and ref 6) have permitted these special clusters to be extensively studied by resonance-enhanced multiphoton ionization (REMPI). These reactions may be characterized as follows. (1) The cluster ions disintegrate spontaneously and rapidly into reaction products from state(s) that can be reached with available laser photon energies. (2) REMPI requires an intermediate state with special properties, so that, up to the time of this writing, the experiments have been done only on clusters for which one moiety of the dimer or cluster is restricted to simple aromatic compounds.<sup>6</sup> (3) It must be possible to resolve and identify this intermediate level with the target cluster. As the clusters get larger, or as the molecules comprising them get more complex, spectral congestion makes the interpretation of the data difficult or impossible. Another consequence of the above limitations is that the energy range for such studies is confined to energies less than about 11 eV.

Maeyama and Mikami<sup>5</sup> published the first REMPI spectrum of  $C_6H_5NH_3^+$  produced from chlorobenzene/ammonia heterocomplexes. (However, see also the discussion of priority given in ref 78 of ref 15.) Immediately following their report, many

<sup>&</sup>lt;sup>†</sup> 1, R&D Road VI, Hsinchu Science-Based Industrial Park, Hsinchu 30077, Taiwan, R.O.C.

<sup>+ 297</sup> North Illinois Avenue, Apt. E, Oak Ridge, TN 37830.

<sup>&</sup>lt;sup>1</sup> 5025 Northwood Drive, Roanoke, VA 24017.

SLM Instruments, 810 West Anthony Drive, Urbana, IL 61801.

<sup>•</sup> Abstract published in Advance ACS Abstracts, July 1, 1994.

REMPI investigations ensued on this and other halobenzene/ ammonia systems,<sup>9-18</sup> as well as on other aromatic-containing systems.<sup>19-21</sup>

In the laser absorption spectroscopy of  $C_6H_5Cl/NH_3$  complexes, each complex displays an  $S_1$  line that is shifted relative to the  $S_1$ line of uncomplexed  $C_6H_5Cl$ . In this and other systems it is the assignments of the shifted  $S_1$  lines that have caused some controversy, for several reasons. (i) At the outset one does not know what the magnitude, or even the sign, of the shift will be.22,23 (ii) In some expansions the heterodimer can be very dilute compared to larger clusters (e.g., ref 1), so that its shifted  $S_1$  peak could be overlooked compared to a nearby  $S_1$  peak from a different cluster. (iii) The reaction may be very size specific and therefore not occur at all for certain clusters; for example, see reactions 3-6. (iv) Relative nozzle pressure and gas composition dependencies, and "fingerprint band"15 sequences, cannot verify an assignment absolutely but only indicate the size of the cluster relative to other cluster sizes. Thus, independent experiments may be needed for confirmation, especially of the dimer. However, the most common practice is to assign the most conspicuous peak (usually with the smallest shift) to the 1:1 complex. Herein lies the problem. If this key assignment is wrong, then all the assignments that depend on it will also be wrong.

In light of this dilemma, it would be advantageous to verify some of the REMPI results with additional experiments which may provide a broader perspective or, in the case of kinetic energy release measurements, may provide some dynamical information. A promising technique for the tasks outlined above is the use of single-photon ionization, using a tunable VUV source. Although there are several methods of producing tunable VUV radiation, synchrotron radiation from an electron storage ring has both the widest tunability and the highest average intensity. (Line U-11 at the Brookhaven 700-MeV storage ring routinely produces up to 3 orders of magnitude greater intensity than stations at other storage rings.9) This additional intensity has allowed the observation of low-intensity phenomena such as autoionization structure in the threshold region for small van der Waals clusters<sup>1,3,24</sup> and has allowed the practical and general analysis of neutral cluster distributions in free jet expansions.<sup>25,26</sup>

These authors wish to emphasize the complementary nature of the information derived from REMPI, FT-ICR, and single photon ionization techniques. The availability of the three methods allows investigation of a wide variety of systems and photon energies, providing a broad perspective which can significantly enrich our understanding about certain reactions of interest.

The chlorobenzene/ammonia dimer provides a useful arena to show the utility of these distinct techniques to create a selfconsistent picture of the chemistry occurring in this system. It was observed by ICR methods that  $C_6H_5Cl^+$  would undergo an ion-molecule reaction with NH<sub>3</sub> to produce<sup>27–29</sup>  $C_6H_5NH_3^+$ . One question that might be posed is whether this reaction would also occur in the 1:1 heterodimer. The necessary demonstration was provided by the application of the near-threshold method, using single-photon ionization with tuned synchrotron radiation,<sup>25</sup> in which it was seen that  $C_6H_5NH_3^+$  ions arise from the smallest possible mixed clusters, that is, from the heterodimers  $C_6H_5$ - $Cl-NH_3$ .

### **Experimental Section**

The general apparatus and procedures are described in ref 30, and matters specific to this experiment may be found in ref 25. Briefly, the experiments were carried out with a photoionization mass spectrometer that made use of a tunable vacuum-ultraviolet beam provided by the National Synchrotron Light Source at Brookhaven National Laboratory. A sonic nozzle,<sup>31</sup> the orifice of which was 0.0102 cm in diameter, was used to emphasize small clusters. To eliminate second-order radiation, a lithium fluoride filter 0.20 cm thick was used whenever scans were entirely at wavelengths longer than 1100 Å. For scans involving shorter wavelengths, corrections for second- and higher-order radiation were carried out as described in ref 32. Commercial research-grade ammonia and chlorobenzene were used without further purification.

When a given product ion could arise from more than one target cluster (i.e.,  $C_6H_5NH_3^+$  could be formed from either  $C_6H_5$ -Cl·NH<sub>3</sub> or  $C_6H_5Cl(NH_3)_2$  or both), the pressure dependence curves of the neutral clusters (given in ref 25) were used to resolve that ion's parentage.

Kinetic energy release measurements were made as described in ref 33. The apparatus used is an adaptation of the retarding potential method, for use with fast, velocity-focused molecular beams.<sup>34</sup> Unfortunately, this apparatus does not allow resolution of the kinetic energy release distributions according to the excitation energy of the dissociating ion, so that an observed kinetic energy release distribution is the sum over all the excited states that contribute the observed ionic product.

### **Results and Discussion**

The ions studied in this work are  $C_6H_5NH_3^+$ ,  $C_6H_5NH_2^+$ ,  $(C_6H_5Cl\cdot NH_3)^+$ ,  $C_6H_5Cl(NH_3)_2^+$ , and  $C_6H_5Cl(NH_3)_3^+$ . The relative laboratory intensities of most of these ions as a function of nozzle pressure are shown in Figure 2 of ref 25.

Chlorobenzene/Ammonia Heterodimer, Trimer, and Tetramer **Ions.** Although produced only weakly, the ion  $(C_6H_5Cl\cdot NH_3)^+$ displays a convincing onset at  $8.744 \pm 0.022$ , as shown in Figure 1a. However, it is not clear whether this onset is due to  $C_6H_5$ -Cl·NH<sub>3</sub> or  $C_6H_5Cl(NH_3)_2$ . Resolution according to target complex (Figure 1b) suggests that the observed onset represents production from  $C_6H_5Cl(NH_3)_2$ . However, the signal was too weak to permit resolution below 9.2 eV, so the participation of  $C_6H_5Cl\cdot NH_3$  cannot be excluded. Note that the above onset is far below an onset around 9.4 eV that does stem from C6H5Cl- $(NH_3)_2$ . The pressure dependence of the production of  $(C_6H_5-$ Cl·NH<sub>3</sub>)<sup>+</sup> at 21.2 eV (584 Å)<sup>25</sup> reveals that at low pressures it originates from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub>. Fortunately, the REMPI experiments supply an important clue to help show that the 8.744-eV onset refers to the heterodimer. In that work  $(C_6H_5Cl\cdot NH_3)^+$ was observed at 9.21 eV and assumed to arise from the 1:1 complex.<sup>12</sup> According to its "fingerprint band"<sup>15</sup> it is formed, at least in part, from the same precursor that gives rise to the anilinium ion, while results reported below and in ref 25 establish that the latter stems essentially entirely from the heterodimer at this energy. In addition, therefore, any production from trimers seen at 9.21 eV would have a higher onset than 8.744 eV.

For the  $C_6H_5Cl(NH_3)_2$  precursor, three secondary onsets are apparent at 9.4, 11.1, and 14.6 eV. Production of  $(C_6H_5Cl\cdot NH_3)^+$ from  $C_6H_5Cl\cdot NH_3$  increases strongly around 11 eV, and the cross section then overtakes that from  $C_6H_5Cl(NH_3)_2$  near 12.4 eV and exceeds it by a substantial factor by 16 eV. It is difficult to understand this behavior, since one would expect adverse Franck-Condon factors to hold the yield down. Perhaps a metastable state(s) of  $(C_6H_5Cl\cdot NH_3)^+$  is involved.

Onset spectra for  $C_6H_5Cl(NH_3)_2^+$  and  $C_6H_5Cl(NH_3)_3^+$  are presented in Figures 2 and 3. These data are unresolved for parent, but their shapes are independent of nozzle pressure in the ranges shown, suggesting that in each case contributions from larger clusters can be neglected, and the data at different pressures were therefore combined to improve the counting statistics. The resulting onsets are  $8.652 \pm 0.013$  eV for  $C_6H_5Cl(NH_3)_2^+$  and  $8.555 \pm 0.012$  eV for  $C_6H_5Cl(NH_3)_3^+$ .

The sequence of decreasing ionization energies, from that for  $C_6H_5Cl$  (measured to be 9.072 ± 0.005 eV in our apparatus) to the above values for  $C_6H_5Cl\cdot NH_3$ ,  $C_6H_5Cl(NH_3)_2$ , and  $C_6H_5-Cl(NH_3)_2$ , is typical of such cluster studies.<sup>1,35</sup> For homoclusters it is usually understood in terms of the simple independent systems



Figure 1. (a) Onset spectrum of  $(C_6H_5Cl\cdot NH_3)^+$  at a nozzle pressure of 700 Torr. Signal rates were only 0.15 s<sup>-1</sup> at 9.12 eV, over a background rate of 0.10 s<sup>-1</sup> (subtracted). Acquisition of these data required 2 days of beam time. Resolution into production from dimers and trimers was not attempted. Here and in Figures 2, 3, 4b, and 7 the intercept showing the onset is represented by a black rectangle which spans the 68% confidence interval, as evaluated via calculations of chi-square. (b) Broad scan of the spectra of  $(C_6H_5Cl\cdot NH_3)^+$ , resolved into production from dimer (closed points) and trimers (open points). Corrected for secondorder radiation. Although the scale is arbitrary, the cross sections are correct relative to one another. (Note: for all dimer-trimer resolutions, Figures 1, 4, 8, 9, and 10, there are possible small contributions to the trimer points from larger clusters.)

model,<sup>36</sup> which predicts an  $n^{-1}$  dependence, where *n* is the number of molecules in the cluster. Surprisingly, this 1/n plot is nearly parallel to the corresponding plot for NH<sub>3</sub>(NH<sub>3</sub>)<sub>n</sub> for n > 0 (using data from ref 37). Although the resemblance is probably fortuitous, it hints that there may be common structural features.

It is interesting that the IP of  $C_6H_5Cl\cdot NH_3$  is nearly 0.2 eV below the appearance potential of  $C_6H_5NH_3^+$  (see next section). It means that  $(C_6H_5Cl\cdot NH_3)^+$  does not spontaneously self-react in its ground state to produce  $C_6H_5NH_3^+$  but that there is an appreciable barrier.

Also, at the IP for  $C_6H_5Cl\cdot NH_3$  of 8.744 eV, the dissociation energy of  $(C_6H_5Cl\cdot NH_3)^+$  to form  $C_6H_5Cl^+$  plus  $NH_3$  is larger than 7.6 kcal mol<sup>-1</sup> [i.e., IP $(C_6H_5Cl) - IP(C_6H_5Cl\cdot NH_3)$ ] by the dissociation energy of neutral  $C_6H_5Cl\cdot NH_3$ , which one expects to be in the neighborhood of 3–4 kcal mol<sup>-1</sup>.  $D[(C_6H_5Cl\cdot NH_3)^+]$ would then be roughly 11 kcal mol<sup>-1</sup>.

Anilinium Ion. The present work (in ref 25) establishes unequivocally that  $C_6H_5NH_3^+$  is produced by photoionization of  $C_6H_5Cl\cdot NH_3$ .

Spectra, Onsets, and Dissociation Energies. The spectra for



Figure 2. Onset spectrum of  $C_6H_5Cl(NH_3)_2^+$ . Combined data for nozzle pressures of 500 and 700 Torr.



Figure 3. Onset spectrum of  $C_6H_5Cl(NH_3)_3^+$ . Combined data for nozzle pressures of 500 and 900 Torr.

the production of C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> from 8.35 to 16.44 eV are displayed in Figure 4a. The inset shows the region below 11 eV in more detail, where the LiF filter was used to remove second-order radiation. Both spectra reveal that above about 10.6 eV the cross section for production from trimers exceeds that for production from dimers but that the contribution from trimers essentially vanishes at energies below 9.5 eV, where the cross section from dimers is still substantial. A separate scan confined closely to the onset region, from 8.68 to 9.07 eV (Figure 4b), reveals a reasonably sharp straight-line onset at  $8.935 \pm 0.004$  eV (at the 68% confidence level, via a chi-square analysis). This differs somewhat from the value  $8.962 \pm 0.010$  eV reported from Brutschy's laboratory,<sup>11,13,15</sup> indicated by arrow A. The latter's data are coplotted for comparison. Maeyama et al.<sup>17</sup> report a value somewhat smaller than ours,  $8.88 \pm 0.02 \text{ eV}$ , indicated by arrow Β.

The thermochemical threshold<sup>38-40</sup> for the process

$$C_{s}H_{s}Cl\cdot NH_{3} + h\nu \rightarrow C_{s}H_{s}NH_{3}^{+} + Cl + e^{-}$$
 (8)

would be  $8.811 \pm 0.022 \text{ eV}$ , if the neutral complex C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> were not bound. (Here we use  $210.3 \pm 0.4 \text{ kcal mol}^{-1}$ , or  $9.119 \pm 0.019 \text{ eV}$ , for the proton affinity of aniline.<sup>40</sup>) The difference of  $0.124 \pm 0.023 \text{ eV}$  ( $2.86 \pm 0.52 \text{ kcal mol}^{-1}$ ) between the "unbound" threshold and our observed onset therefore measures the sum of the dissociation energy of C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub>, the kinetic



Figure 4. (a) Broad scan of the yield spectra of  $C_6H_5NH_3^+$ , resolved into production from dimer (closed points) and trimers (open points). Corrected for second-order radiation. The inset shows the same spectra measured using a LiF filter to remove higher-order radiation. (b) Onset spectrum of  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$  (open points); the closed rectangle indicates the 68% confidence region of an assumed straightline intercept. The jagged line is the data from Brutschy's laboratory, <sup>11,13,15</sup> normalized to our data for comparison. The arrows A and B show the onsets reported by Brutschy's<sup>11,13,15</sup> and Mikami's<sup>17</sup> laboratories, respectively.

shift,<sup>43,44</sup> and any reaction barrier with respect to the threshold. This may be compared with the expectation, based on other polyatomic heterodimers of comparable complexity, that the dissociation energy would be<sup>1,24,30,32</sup> about 3-4 kcal mol<sup>-1</sup>. One may argue on these grounds that any barrier and kinetic shift are negligible. Also, the linearity and sharp intercept of the production of  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$  are inconsistent with a significant kinetic shift as shown by calculations, and a measurement of kinetic energy release shows that there is no barrier (see next subsection). We therefore believe that the measured onset of 8.935 eV is adiabatic and gives a dissociation energy of  $D(C_6H_5 Cl \cdot NH_3$  = 2.9 ± 0.5 kcal mol<sup>-1</sup> (12.0 ± 2.2 kJ mol<sup>-1</sup>). For comparison, the onsets from Mikami's and Brutschy's laboratories give values for  $D(C_6H_5Cl\cdot NH_3)$  of 1.6 ± 0.7 and 3.5 ± 0.6 kcal mol<sup>-1</sup>, respectively. Note, however, that the cited uncertainties are correlated because of the common uncertainty of  $\pm 0.5$  kcal  $mol^{-1}$  in the heat of formation of  $C_6H_5NH_3^+$ . The agreement of these three values is therefore poor. A prolonged effort was made to measure this dissociation energy by the method of ref 30. Production of  $C_6H_5Cl^+$  from  $C_6H_5Cl\cdot NH_3$  was observable but so weak that an accurate measurement was not possible. Only an



**Figure 5.** Possible potential diagrams considered in the text: shortdashed line, case with one basin; solid line, case with two basins, showing the maximum depth consistent with the data; long-dashed line, attempt to devise a potential consistent with the increased proton affinity recently proposed for aniline.<sup>42</sup> The deepest well results from an *ab initio* calculation.<sup>46b</sup>

upper limit could be determined,  $D(C_6H_5Cl\cdot NH_3) < 3 \text{ kcal mol}^{-1}$ , consistent with the 2.9 kcal mol<sup>-1</sup> reported above. For comparison with theory, an *ab initio* calculated value of 2.3 kcal mol<sup>-1</sup> has recently been published.<sup>46a</sup>

The dissociation energy of the dimer ion may be calculated from the above result as  $D[(C_6H_5Cl\cdot NH_3)^+] = IP(C_6H_5Cl) - IP(C_6H_5Cl\cdot NH_3) + D(C_6H_5Cl\cdot NH_3) = 10.4 \pm 0.7$  kcal mol<sup>-1</sup> (43.5 ± 2.9 kJ mol<sup>-1</sup>). This is an unusually large value for a heterodimer ion<sup>30</sup> and suggests some degree of chemical bond formation.

The Kinetic Energy Release Distribution and the Potential Hypersurface. We discuss the production of anilinium ion in terms of the potential diagram shown in Figure 5 and use measurements of the kinetic energy release distribution to try to sharpen the picture. This diagram is adapted from the triplewell picture postulated by Thölmann and Grützmacher<sup>28</sup> to interpret the results of their ICR study of the ion-molecule reaction between  $C_6H_5Cl^+$  and  $NH_3$ . They suggested<sup>28,45</sup> that the reactants first form a weakly-bound "collision complex", a  $\pi$ -complex, bound mainly by electrostatic forces. This initial complex then rearranges to form an "addition complex", a  $\sigma$ -complex, where the ammonia nitrogen bonds to the carbon attached to the chlorine to form an ipso-substituted chlorocyclohexadienyl radical ion. The addition complex may then disintegrate by expulsion of a chlorine atom to produce the anilinium ion, for which process there is essentially no barrier. Other features of this potential surface are a barrier between the collision complex and the addition complex and no barrier between the collision complex and the original reagents.

To reconcile the Thölmann-Grützmacher diagram with our observations three different adaptations are considered.

(1) The short-dashed curve is drawn using  $H_{\rm f}(C_6H_5NH_3^+) =$ 176.2 kcal mol<sup>-1</sup>, and it is assumed that there is no barrier between the  $\pi$ -complex and the  $\sigma$ -complex, i.e., that the 10.4 kcal mol<sup>-1</sup> for  $D[(C_6H_5Cl\cdot NH_3)^+]$  applies to the  $\sigma$ -complex. This would be consistent with our observation that the dissociation energy of  $(C_6H_5Cl\cdot NH_3)^+$  is unusually high and therefore probably reflects some chemical bonding. However, Thölmann and Grützmacher find an ion-molecule reaction efficiency<sup>28</sup> of only 13%, and this indicates the presence of a barrier between the  $\pi$ - and  $\sigma$ -complexes.

(2) For the solid curve we again use  $H_f(C_{\sigma}H_5NH_3^+) = 176.2$  kcal mol<sup>-1</sup> but retain a barrier between the  $\pi$ - and  $\sigma$ -complexes. The dissociation energy of 10.4 kcal mol<sup>-1</sup> now pertains to the



Figure 6. Kinetic energy release distribution of  $C_6H_5NH_3^+$  from  $C_6H_5$ -Cl-NH<sub>3</sub>, measured at a photon energy of 9.50 eV (points). The three curves are calculated spectra for unimolecular decay, assuming excitation energies of  $(C_6H_5Cl-NH_3)^+$  that are 0.28, 0.56, and 0.88 eV above the minimum energy needed to produce  $C_6H_5NH_3^+$ .

 $\pi$ -complex, while the depth of the potential for the  $\sigma$ -complex is undetermined. A MNDO calculation<sup>28</sup> gives 13.4 kcal mol<sup>-1</sup> for this depth, while one *ab initio* calculation<sup>46a</sup> gives 14.2 kcal mol<sup>-1</sup> and another<sup>46b</sup> gives 37.8 kcal mol<sup>-1</sup>.

If the  $\sigma$ -complex dissociates into products via unimolecular decay, as is most consistent with the triple-well picture, then a potential basin as deep as 37.8 kcal mol<sup>-1</sup> would cause an appreciable kinetic shift. That this reaction is indeed unimolecular is confirmed via the kinetic energy release distribution at only 0.56 eV above threshold (Figure 6), where the points are experimental and the lines are theoretical.<sup>47</sup> The data agree well with an expected average available energy<sup>51,52</sup> of 0.3 eV. Furthermore, in experimental confirmation of the Thölmann-Grützmacher potential, there is no indication of a barrier in the final state, i.e., no evidence for a displacement of the maximum to higher than the theoretical energy.

Estimates of kinetic shift<sup>53</sup> are compared with the experimental onset in Figure 7 assuming a hypothetical excitation function that rises linearly from its appearance potential (short-dashed line). The smooth curves are calculated excitation functions for producing  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$ , assuming unimolecular decay of excited (*ipso*- $C_6H_5Cl\cdot NH_3$ )<sup>+</sup> with well depths of 37.8 kcal mol<sup>-1</sup> (solid line) and 25.0 kcal mol<sup>-1</sup> (long-dashed line). The calculations and the hypothetical straight-line function are normalized together at incident photon energies of 8.965 and 9.065 eV to show the resulting displacement of the thresholds (i.e., kinetic shifts), indicated by arrows. For comparison, the data of Figure 4b are included, normalized to the same two points.

The curve for a well depth of 37.8 kcal mol<sup>-1</sup> is strongly concave, a very different shape than displayed by the data, and has an appearance potential of 8.705 eV. This is an unphysical result because it gives a negative dissociation energy of -2.4 kcal mol<sup>-1</sup> for C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub>. Additional calculations show that the curve shapes are inadmissible for well depths greater than 25 kcal mol<sup>-1</sup>. The linearity and sharp intercept of the onset of C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> are therefore important clues for understanding the reaction hypersurface, for they mean that the kinetic shift is too small for us to detect. Analogous calculations with the simple algorithm of ref 43 lead to a similar conclusion, except to predict that the well depth must be well under 25 kcal mol<sup>-1</sup>.

(3) For the long-dashed curve in Figure 5, a lower value of the heat of formation of anilinium ion,  $H_f(C_6H_5NH_3^+) = 171.7$  kcal mol<sup>-1</sup>, was used, for which the adiabatic appearance potential is 8.616 eV. To maintain an onset of 8.935 eV with a threshold of 8.616 eV, but no exit barrier, the barrier between the  $\pi$ - and  $\sigma$ -complexes must have a higher energy than the products. This



Figure 7. Comparison with the data of Figure 4b of calculated excitation functions for producing  $C_6H_3NH_3^+$  from  $C_6H_5Cl\cdot NH_3$ , assuming unimolecular decay of excited (*ipso*- $C_6H_5Cl\cdot NH_3$ )<sup>+</sup> with well depths of 37.8 and 25.0 kcal mol<sup>-1</sup>, and where the underlying yield function is assumed to be linearly rising. The "shifted" onsets are shown by arrows (see text).

means the kinetic shift is much less important and the well depth for the  $\sigma$ -complex can be significantly deeper than 25 kcal mol<sup>-1</sup>. The measured onset would then only show the height of the intracluster barrier, precluding a measurement of the dissociation energy. However, the kinetic energy release distribution appears to be too soft for this possibility (Figure 6). For this potential curve the maximum and average available energies are 0.88 and about 0.6 eV, respectively,<sup>55</sup> while the data fall systematically to the low-energy side of the line for 0.56 eV.

In summary, of the three possibilities discussed above, only the second is consistent with all of the data. We conclude that the potential surface contains two basins separated by a barrier of less than 4.4 kcal mol<sup>-1</sup> relative to the bottom of the first basin. The first basin has a depth of 10.4 kcal mol<sup>-1</sup> relative to free  $C_6H_5Cl^+$  and  $NH_3$ , and the second is probably deeper than the 13.4 kcal mol<sup>-1</sup> predicted by the MNDO calculation but shallower than about 25 kcal mol<sup>-1</sup>. These conclusions agree remarkably well with the recent *ab initio* calculations of Wassermann and Brutschy.<sup>46a</sup>

The Possible Involvement of Rydberg States. Another route to the production of  $C_6H_5NH_3^+$  could be through Rydberg states. This form of photoexcitation greatly outweighs direct ionization in the 9-eV region<sup>56</sup> and ordinarily leads to dissociation into neutral products, especially for van der Waals clusters. However, ionization always occurs to some extent whenever it is possible, though usually with low yield and broadened lines due to competition with the fast breakup into neutrals. Nevertheless, it is routinely observed in clusters,  $\overline{1,3,24,57-61}$  especially when direct ionization is suppressed, e.g., by adverse Franck-Condon factors.1,3,24,57,58 Dissociation of polyatomic Rydberg states to form product Rydberg states has been observed.<sup>62-64</sup> Here, such a process might be dissociation of the ion core of a cluster Rydberg state  $(C_6H_5Cl\cdot NH_3)^*$  to produce  $Cl + C_6H_5NH_3^*$ , followed by autoionization of the C6H5NH3\* to form C6H5NH3+. Unfortunately, little is yet known about the involvement of Rydberg states in dissociative ionization.

That the threshold excitation function for  $C_6H_5NH_3^+$  is nearly linear is interesting. It resembles the linear excitation functions usually found just above threshold for producing heterodimer parent ions,<sup>1-3,24,30,32</sup> which behavior seems to be connected with the involvement of autoionizing states. The linearity in the production of  $C_6H_5NH_3^+$  may thus be related to linearity in the production of the  $(C_6H_5Cl\cdot NH_3)^+$  intermediate. However, the increasing number of product states and the presence of structure in the Rydberg spectrum could modify this picture as the energy



Figure 8. Kinetic energy release distribution of  $C_6H_5NH_3^+$  from the target beam at a nozzle pressure of 500 Torr and a photon energy of 17.7 eV (solid line). The contribution from  $C_6H_5Cl(NH_3)_2$  was resolved from this spectrum and is shown as points. The dashed lines are the predictions of unimolecular decay calculations, assuming excitation energies of  $C_6H_5-Cl(NH_3)_2^+$  of 2.2 (long-dashed line) and 4.4 eV (short-dashed line) above the minimum energy needed to produce  $C_6H_5NH_3^+$ . In the inset, the contribution from  $C_6H_5Cl(NH_3)_2$ , points, is compared with the data for the production of  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$  at 9.50 eV, solid line. (The same data are shown as points in Figure 6.) Note that the abscissa scale is ion energy, not total energy.

increases, as is often observed for heterodimer parent ions.<sup>1,3,24</sup> The REMPI experiment also gave a linear function<sup>11,13,15</sup> up to 9.01 eV. At higher energies, however, these data display a slight shoulder (Figure 4b), which may be evidence that near-threshold autoionizing resonances are also excited by the two-photon process.

Production at Higher Photon Energies and from Trimers. The cross section for the production of C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> from C<sub>6</sub>H<sub>5</sub>-Cl·NH<sub>3</sub> rises slowly from 9.5 to 14.6 eV (cf. Figure 4a) and then displays a clear onset, beyond which the cross section doubles by 16 eV. Photoelectron spectra of C<sub>6</sub>H<sub>5</sub>Cl show a conspicuous band whose practical onset is 14.0 eV (14.4 eV vertical),68 close to 14.6 eV. Also, the second band in the photoelectron spectrum of ammonia onsets near 14.8 eV,66,67 forming a <sup>2</sup>E' state of configuration  $(1e')^3(1a_2'')^2$ . However, the latter seems to be associated with N-H bonding, which is difficult to reconcile with the expulsion of Cl and retention of H in the final  $C_6H_5NH_3^+$ product. Unfortunately, the 14.4-eV band in C<sub>6</sub>H<sub>5</sub>Cl has not yet been assigned, so we have not attempted an interpretation with respect to its structure. There is a third possibility to consider. At higher energies the cross section from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> is much smaller than it is from  $C_6H_5Cl(NH_3)_2$ , showing that  $C_6H_5NH_3^+$ is only a minor product of the dimer. Thus, the photon energy dependence of the cross section may reflect strong features in another reaction channel, including breakup into neutrals.

 $C_6H_5NH_3^+$  is not detected from the ionization of  $C_6H_5Cl_2^ (NH_3)_2$  until about 9.5 eV. The inset of Figure 4a details the cross sections in this region. The onset from  $C_6H_5Cl(NH_3)_2$  is about 0.6 eV higher than that from  $C_6H_5Cl\cdot NH_3$ , at least twice too high to ascribe to the energy necessary to remove the extra NH<sub>3</sub> solvent molecule, which we estimate to be  $0.1_3-0.3$  eV (3-7 kcal  $mol^{-1}$ ). However, there is little evidence that mechanisms involving Rydberg states dominate the threshold ionization region in trimers,68 so it is reasonable to expect that the kinetic shift43,44 accounts for the difference. Kinetic energy release measurements indicate that after ionization of a van der Waals complex of polyatomic molecules the subsequent depolymerization approaches statistical behavior,<sup>33</sup> so that the present problem can plausibly be treated as unimolecular decay. Estimates of kinetic shift on this basis<sup>43</sup> give values of 0.2–1.3 eV, depending on what mechanism is assumed, i.e., whether loss of NH<sub>3</sub> occurs before or after the intracluster reaction.

The kinetic energy release distribution of  $C_6H_5NH_3^+$  from the photoionization of the raw beam at 17.7 eV (700 Å) and a nozzle



Figure 9. Broad scan of the yield spectra of  $C_6H_5NH_2^+$ , resolved into production from dimer (closed points) and trimers (open points). Corrected for second-order radiation. The inset details the same spectra in the onset region, measured using a LiF filter to remove higher-order radiation.

pressure of 500 Torr is shown in Figure 8 as a solid line. Note that the abscissa gives ion energy, rather than the total energy given in Figure 6. The production of  $C_6H_5NH_3^+$  from  $C_6H_5$ -Cl(NH<sub>3</sub>)<sub>2</sub> was resolved from these data and is plotted as points, showing that most or all of the highest energies come from the trimers. Unfortunately, the data could not support the resolution of the production of  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$ , although this spectrum can be roughly ascertained from the difference between the solid line and the points.

The energy release spectrum of  $C_6H_5NH_3^+$  from  $C_6H_5Cl-(NH_3)_2$  stems from a large range of excitation energies available in the nascent complex ion, from 0 to 8.8 eV, the average of which probably lies in the neighborhood of 4–5 eV. The data are compared with the shapes of the distributions calculated from a statistical model assuming that total energies of 2.2 and 4.4 eV are available (shown as dashed lines). A statistical interpretation appears to be roughly consistent with these data except for a possible dearth of intensity at the lowest energies.

In the inset of Figure 8 the production of  $C_6H_5NH_3^+$  from  $C_6H_5Cl(NH_3)_2$  at 17.7 eV (points) is compared with the production of  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$  at 9.5 eV (line; the same data are displayed as points in Figure 6). The two data sets are arbitrarily normalized to the same peak height. Comparison of the production from  $C_6H_5Cl\cdot NH_3$  at 9.5 eV with the difference between the points and the data for dimer + trimer in the main figure indicates that the spectrum for production from  $C_6H_5Cl\cdot NH_3$  cli-NH<sub>3</sub> changes rather little in proceeding from 9.5 to 17.7 eV of photon energy. This suggests that  $(C_6H_5Cl\cdot NH_3)^+$  ions of high excitation energy produce little or no  $C_6H_5NH_3^+$ .

Aniline Ion. The appearance of  $C_6H_5NH_2^+$  among the photoionization-induced products of  $C_6H_5Cl\cdot NH_3$  was a surprise, since it is not produced in the REMPI work<sup>11,14,16</sup> (see, however, ref 13). The cluster-resolved spectra (Figure 9) reveal that although the yield from  $C_6H_5Cl\cdot NH_3$  is much smaller than from  $C_6H_5Cl(NH_3)_2$  over most of the photon energy range studied, production from  $C_6H_5Cl\cdot NH_3$  becomes comparable in the onset region (cf. inset of Figure 9). Since the ions  $C_6H_5NH_2^+$  and  $C_6H_5NH_3^+$  differ by only one unit of mass/charge ratio, m/e, it was felt important to verify our observation in a separate experiment, the results of which are shown in Figure 10a. Here, mass spectra were collected at three energies across the onset of  $C_6H_5NH_3^+$  and normalized to the intensity of the m/e = 93 peak. The relative intensity of m/e = 94 grows systematically



Figure 10. (a) Comparison of mass spectra in the onset region. The peaks for m/e = 93,  $C_6H_5NH_2^+$ , are normalized to the same height to compare the relative behavior of the peaks for m/e = 94,  $C_6H_5NH_3^+$ , at photon energies below and above the threshold for  $C_6H_5NH_3^+$ . (b) Comparison of the onset spectra for  $C_6H_5NH_2^+$  and  $C_6H_5NH_3^+$ . (b) Comparison of the onset spectra for  $C_6H_5NH_2^+$  and  $C_6H_5NH_3^+$ . The relative intensities are correct, but the curve for  $C_6H_5NH_2^+$  is unresolved for parent cluster. In the inset, the production of  $C_6H_3NH_2^+$  from dimers (closed points) and trimers (open points) is compared.

as the energy is increased. (The small peak at 8.92 eV, which is below the onset of  $C_6H_5NH_3^+$  at 8.935 eV, is due to  ${}^{13}C{}^{12}C_5H_5^ NH_2^+$ .) The excitation functions for  $C_6H_5NH_2^+$  and  $C_6H_5NH_3^+$ in the onset regions of both are compared in Figure 10b.

The difference between the single-photon result and that reported for the REMPI method is stark. It is difficult to understand without more experiments. The two techniques will in general excite different manifolds of Rydberg states, and perhaps this underlies the apparent contradiction. Alternatively, a difference between the two methods in the production of an ion isomeric to  $C_6H_5NH_2^+$ , such as the azepinium ion  $C_6NH_7^+$ , i.e., a seven-membered ring with the nitrogen incorporated, might be responsible.<sup>69</sup>

The onset of  $C_6H_5NH_2^+$  (Figure 10b) is surprisingly linear with a sharp intercept at 8.856  $\pm$  0.003 eV. Such behavior is often evidence that the onset is an adiabatic appearance potential,



Figure 11. The points give the kinetic energy release distribution for  $C_6H_5NH_2^+$  at an incident photon energy of 17.7 eV, from a target beam produced at a nozzle pressure of 500 Torr. The smooth curve is the result of a unimolecular decay calculation, assuming an excitation energy of  $C_6H_5Cl(NH_3)_2^+$  of 3.50 eV above the minimum energy needed to produce  $C_6H_5NH_2^+$ . Note that the abscissa scale is ion energy, not total energy.

but that cannot be the case here, at least for the ground state; the adiabatic threshold from free  $C_6H_5Cl + NH_3$  can be calculated to be 7.543 eV (298 K) from known thermochemical quantities.<sup>39</sup> This barrier of about 1.3 eV is in line with the barriers observed for most photoionization-induced dissociative rearrangements;<sup>1-4</sup> cf. reactions 1 and 2.

The surprise is increased upon resolution into production from dimers and trimers, shown in the inset of Figure 10b. The cross section for production from dimers is somewhat larger than from trimers, but the onsets are identical within experimental uncertainty. They are  $8.849 \pm 0.009 \text{ eV}$  from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> and  $8.855 \pm 0.029 \text{ eV}$  from C<sub>6</sub>H<sub>5</sub>Cl(NH<sub>3</sub>)<sub>2</sub>.

Possible reasons that the onsets are so sharp, and similar to each other, could be the production of a metastable state of  $C_6H_5$ - $NH_2^+$  at 1.3 eV or the need to excite some special state in the neutral complex, or in one of the moieties, to cause the reaction.

In an effort to learn something about the reaction mechanism, the kinetic energy release distribution of C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>+ was measured at a photon energy of 17.7 eV (700 A) and a nozzle pressure of 500 Torr, with the results shown in Figure 11. Under these conditions the number densities of C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Cl- $(NH_3)_2$  are comparable, and there is a significant presence of  $C_6H_5Cl(NH_3)_3$ , but the signal was too weak to permit resolution. However, the cross section for production from trimer is much greater than from dimer (Figure 9), so this spectrum stems essentially from trimers (and tetramers). The excess energy available for product translation ranges from 0 to about 10 eV. A unimolecular decay calculation<sup>47,70</sup> for an excess energy of 3.5 eV, plotted as a smooth line, represents the data reasonably well, indicating that there is no need to invoke nonstatistical processes. It seems reasonable, therefore, to assume that the production of  $C_6H_5NH_2^+$  at lower photon energies is also dominantly statistical, since usually nonstatistical processes are enhanced with increasing energy.

That it is formed slightly above the threshold for the production of  $(C_6H_5Cl-NH_3)^+$  suggests that it is not produced by dissociative ionization of the excited neutral complexes, e.g.

$$(C_6H_5Cl·NH_3)^* \not\rightarrow C_6H_5NH_2^+ + HCl + e^- \qquad (9)$$

but instead represents a disintegration channel of the excited heterocomplex ions,

$$(C_6H_5Cl\cdot NH_3)^{*+} \rightarrow C_6H_5NH_2^+ + HCl \qquad (10)$$

$$C_6H_5Cl(NH_3)_2^{*+} \rightarrow C_6H_5NH_2^{+} + NH_4Cl \qquad (11)$$



Figure 12. Energy diagram consistent with the measurements made in this work. Not drawn to scale. All energies are given in electronvolts.

**TABLE 1: Onsets Observed in This Work** 

product	target	onset energy (eV)	lit.
NH4 <sup>+</sup>	(NH <sub>3</sub> ) <sub>2</sub>	$9.524 \pm 0.002$	$9.59 \pm 0.02^{a}$
(NH <sub>3</sub> ) <sub>2</sub> H <sup>+</sup>	(NH <sub>3</sub> ) <sub>3</sub>	9.073 ± 0.018	$9.15 \pm 0.02^{a}$ $9.15 \pm 0.04^{a}$ $9.14 \pm 0.02^{b}$
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> +	dimer + trimer <sup>d</sup> $C_6H_5Cl\cdot NH_3$	$8.856 \pm 0.003$ $8.849 \pm 0.009$ $8.855 \pm 0.029$	
C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> +	C <sub>6</sub> H <sub>5</sub> Cl·NH <sub>3</sub>	$8.935 \pm 0.004$ $8.935 \pm 0.004$	$8.88 \pm 0.02^{\circ}$ $8.962 \pm 0.01^{f}$
C <sub>6</sub> H <sub>5</sub> Cl (C <sub>6</sub> H <sub>5</sub> Cl·NH <sub>3</sub> ) <sup>+</sup> C <sub>6</sub> H <sub>5</sub> Cl(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> C <sub>6</sub> H <sub>5</sub> Cl(NH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> Cl C <sub>6</sub> H <sub>5</sub> Cl·NH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> Cl(NH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> Cl(NH <sub>3</sub> ) <sub>3</sub>	$9.072 \pm 0.005$ $8.744 \pm 0.022$ $8.652 \pm 0.013$ $8.555 \pm 0.012$	9.06 ± 0.02 <sup>c</sup>

<sup>a</sup> Reference 71. <sup>b</sup> Reference 72. <sup>c</sup> Reference 39. <sup>d</sup> From unresolved mixture. <sup>e</sup> Reference 17 <sup>f</sup> References 11, 13, and 15.

 TABLE 2: Heats of Formation Used in the Discussion<sup>a</sup> (kcal mol<sup>-1</sup>)

		$H_{f}^{\circ}_{0}(g)$	
compound	$H_{\rm f}^{\rm o}{}_{298}({\rm g})$	neutral	ion
C <sub>6</sub> H <sub>5</sub> Cl	$13.0 \pm 0.2$		222*
NH <sub>3</sub>	$-11.0 \pm 0.1$	$-9.3 \pm 0.1$	224.9
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$20.8 \pm 0.2$		198
C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> +			176.2 ± 0.5 <sup>b</sup>
HCl	$-22.1 \pm 0.04$	$-22.0 \pm 0.04$	271.4
Cl	29.0	28.6	328
C <sub>6</sub> H <sub>5</sub> Cl•NH <sub>3</sub>	$-0.8 \pm 0.5^{c}$		$200.8 \pm 0.5^{\circ}$

<sup>a</sup> From ref 39 unless otherwise specified. <sup>b</sup> At 298 K, ref 40. <sup>c</sup> This work.

The agreement of the kinetic energy release distribution with a reasonable unimolecular decay spectrum is consistent with the latter picture.

**Energy Diagram.** A schematic energy diagram consistent with the measurements made in this work is presented in Figure 12. The onsets measured in this work, and pertinent thermochemical information from the literature, are collected in Tables 1 and 2.

Of special interest is the dissociation energy of  $(C_6H_5Cl\cdot NH_3)^+$ . This value, 10.4 kcal mol<sup>-1</sup> (0.45 eV), is unusually large for a heterodimer ion, typical values for which<sup>1-4,30</sup> are in the range 3-5 kcal mol<sup>-1</sup>. In comparison, the collision ( $\pi$ ) and addition ( $\sigma$ ) complexes suggested by Thölmann and Grützmacher were estimated by them via MNDO calculations to be bound by 6 and 13 kcal mol<sup>-1</sup>, respectively.<sup>28</sup>

The dashed line labeled  $(C_6H_5NH_2^+ \cdot HCl)^*$  is meant to call attention to the possible existence of an excited species responsible for the observed sharp onsets of  $C_6H_5NH_2^+$ .

#### Summary

The photoionization and photoionization-induced reactions of complexes of chlorobenzene and ammonia have been studied by single-photon techniques, including the measurement of kinetic energy release distributions. A sharp onset of  $C_6H_5NH_3^+$  from  $C_6H_5Cl\cdot NH_3$  was found at 8.935 ± 0.004 eV, which, when combined with the known heat of formation of  $C_6H_5NH_3^+$ , gives a dissociation energy  $D(C_6H_5Cl\cdot NH_3) = 2.9 \pm 0.5 \text{ kcal mol}^{-1}$ . Production of  $C_6H_5NH_3^+$  from trimers was too weak in the onset region to permit measurement, but at larger energies proceeds with substantially larger cross sections than from dimers. The ion  $C_6H_5NH_2^+$  was also observed, with onsets of 8.849 ± 0.009 and 8.855  $\pm$  0.029 eV from C<sub>6</sub>H<sub>5</sub>Cl·NH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Cl(NH<sub>3</sub>)<sub>2</sub>, respectively, clearly below the onset for  $C_6H_5NH_3^+$  but far above the thermochemical thresholds near 7.6 eV. Except in the immediate region of the onset, its cross section for production from trimer is much larger than from dimers. For the "parent cluster ions"  $(C_6H_5Cl\cdot NH_3)^+$ ,  $C_6H_5Cl(NH_3)_2^+$ , and  $C_6H_5Cl (NH_3)_3^+$  onsets were found at 8.744 ± 0.022, 8.652 ± 0.013, and  $8.555 \pm 0.012 \text{ eV}$ . The above value of the dimer ion onset means that  $D([C_6H_5Cl\cdot NH_3]^+) = 10.4$  kcal mol<sup>-1</sup>, higher than is usual for heterodimer ions. Since the onsets of both  $(C_6H_5Cl\cdot NH_3)^+$ and  $C_6H_5NH_2^+$  are below that of  $C_6H_5NH_3^+$ , the ground state of  $(C_6H_5Cl\cdot NH_3)^+$  does not spontaneously self-react to form  $C_6H_5^ NH_3^+ + Cl.$  No evidence for nonstatistical production processes was found for either  $C_6H_5NH_3^+$  or  $C_6H_5NH_2^+$ . In general, our data support the triple-well potential postulated by Thölmann and Grützmacher, plus the theoretical calculations carried out thereon by Wassermann and Brutschy, and provide evidence for determination of the binding energies of the  $\pi$ - and  $\sigma$ -complexes comprising this potential's main features.

Acknowledgment. It is a pleasure to thank Professor Edward A. Walters for useful discussions and criticism of the manuscript. Phone conversations with Ed Hunter and Dr. Sharon Lias about the proton affinity of aniline were very helpful. The contributions of John Barry, our technician, in keeping the apparatus functioning reliably were crucial to any success we can claim. Also, we thank the NSLS/HFBR Faculty-Student Support Program for travel funds to make this work possible. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported in part by its Division of Chemical Sciences, Office of Basic Energy Sciences, and in part by the Office of Naval Research.

## **References and Notes**

(1) Grover, J. R.; Walters, E. A.; Newman, J. K.; White, M. G. J. Am. Chem. Soc. 1990, 112, 6499-6506.

(2) Walters, E. A.; Grover, J. R.; Arneberg, D. L.; Santandrea, C. J.; White, M. G. Z. Phys. D 1990, 16, 283-292.

(3) Grover, J. R.; Hagenow, G.; Walters, E. A. J. Chem. Phys. 1992, 97, 628-642.

(4) Walters, E. A.; Grover, J. R.; White, M. G.; Hui, E. T. J. Phys. Chem. 1987, 91, 2758–2762. Walters, E. A.; Hui, E. T.; Grover, J. R.; White, M. G. National Synchrotron Light Source Annual Report BNL-52045, 1986, pp 187–189.

(5) Maeyama, T.; Mikami, N. J. Am. Chem. Soc. 1988, 110, 7238-7239.

(6) The REMPI work relies on the presence of a persistent  $S_1$  intermediate state homologous to the  $A^1B_{2u}S_1$  state of benzene. In benzene the vibrationless  $S_1$  state is long-lived because radiation to the  $A^1A_{1g}S_0$  ground state is electric dipole forbidden, there are no intermediate states to provide a pathway of allowed radiations, and the radiationless pathways are also slow. These felicitous properties are reflected to some degree in benzene's vibronic levels and in the homologous states of a number of substituted benzenes, such as

chlorobenzene, so this class of molecules has provided the chromophores for a host of REMPI studies. Several other aromatic and aromatic-like systems (e.g., s-tetrazine<sup>7</sup> and tetracene<sup>8</sup>) have similarly useful states

(7) Young, L.; Haynam, C. A.; Levy, D. H. J. Chem. Phys. 1983, 79, 1592-1604.

- (8) Amirav, A.; Even, U.; Jortner, J. J. Chem. Phys. 1981, 75, 2489-2512.
- (9) Brutschy, B. J. Phys. Chem. 1990, 94, 8637-8647.
   (10) Riehn, Ch.; Lahmann, C.; Brutschy, B. J. Phys. Chem. 1992, 96, 3626-3632.
- (11) Riehn, Ch.; Awdiew, J.; Eggert, J.; Wassermann, B.; Brutschy, B.; (11) Richard J. Mol. Struct. 1991, 249, 33–46.
   (12) Eggert, J.; Janes, C.; Wassermann, B.; Brutchy, B.; Baumgärtel, H.
- Ber. Bunsen-Ges. Phys. Chem. 1990, 94, 1282-1287.
- (13) Awdiew, J.; Riehn, Ch.; Brutschy, B.; Baumgärtel, H. Ber. Bunsen-Ges. Phys. Chem. 1990, 94, 1353-1357.
- (14) Brutschy, B.; Eggert, J.; Janes, C.; Baumgärtel, H. J. Phys. Chem. 1991, 95, 5041-5050.
  - (15) Brutschy, B. Chem. Rev. 1992, 92, 1567-1587.
  - (16) Brutschy, B. Ber. Bunsen-Ges. Phys. Chem. 1992, 96, 1154-1160.
  - (17) Maeyama, T.; Mikami, N. J. Phys. Chem. 1990, 94, 6973-6977.
     (18) Maeyama, T.; Mikami, N. J. Phys. Chem. 1991, 95, 7197-7204.

  - (19) Stace, A. J. Ber. Bunsen-Ges. Phys. Chem. 1992, 96, 1136-1141.
  - (20) Bernstein, E. R. J. Phys. Chem. 1992, 96, 10105-10115.
- (21) Numata, Y.; Ishii, Y.; Watahiki, M.; Suzuka, I.; Ito, M. J. Phys. Chem. 1993, 97, 4930-4935.
- (22) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. J. Phys. Chem. 1981, 85, 3739-3742.
- (23) Gotch, A. J.; Zwier, T. S. J. Chem. Phys. 1990, 93, 6977-6986. (24) Walters, E. A.; Grover, J. R.; White, M. G.; Hui, E. T. J. Phys.
- Chem. 1985, 89, 3814-3818. (25) Grover, J. R.; Herron, W. J.; Coolbaugh, M. T.; Peifer, W. R.; Garvey,
- J. F. J. Phys. Chem. 1991, 95, 6473-6481.
- (26) Walters, E. A.; Grover, J. R.; Clay, J. T.; Cid-Aguero, P.; Willcox,
   M. V. J. Phys. Chem. 1992, 96, 7236-7243.
- (27) Thölmann, D.; Grützmacher, H.-Fr. Org. Mass Spectrom. 1989, 24, 439-441.
- (28) Thölmann, D.; Grützmacher, H.-Fr. Chem. Phys. Lett. 1989, 163, 225-229.
- (29) van der Hart; et al. Org. Mass Spectrom. 1980, 15, 463.
  (30) Grover, J. R.; Walters, E. A.; Newman, J. K.; White, M. G. J. Am. Chem. Soc. 1985, 107, 7329-7339.
- (31) Hagena, O. F.; Obert, W. J. Chem. Phys. 1972, 56, 1793-1802.
   (32) Walters, E. A.; Grover, J. R.; White, M. G. Z. Phys. D. 1986, 4, 103-110.
- (33) Grover, J. R.; Walters, E. A.; Arneberg, D. L.; Hagenow, G.; Clay, J. T.; Willcox, M. V., to be submitted. For a preliminary report see: Kinetic Energy Analyzer for Products of Dissociative Photoionization. In National Synchrotron Light Source Annual Report 1990, BNL 52272, p 141.
- (34) The PEPICO technique would be ideal for this application because it allows specification of the excitation energy. However, we have not tried to adapt this method to the present program for two reasons: (1) product ion rates are only a small fraction of the total ion production rates (e.g., as low as 10-7 for many of the systems being studied), and this precludes the use of coincidence methods because the accidental coincidences would overwhelm the real ones; (2) product ion rates are frequently so small (e.g., 10<sup>-1</sup> s<sup>-1</sup> or less) that any method that lowers the duty factor significantly, as PEPICO does, is precluded.
- (35) Ng, C.-Y. Adv. Chem. Phys. 1983, LII, 263-362. Several examples are given in this review.
- (36) Simpson, W. T. Theories of Electrons in Molecules; Prentice-Hall:
   Englewood Cliffs, NJ, 1962; Chapter 4.
   (37) Kamke, W.; Herrmann, R.; Wang, Z.; Hertel, I. V. Z. Phys. D 1988,
- 10, 491-497.
- (38) Lias, S. G.; Liebman, J. F.; Levin, R. D. J. Phys. Chem. Ref. Data 1984, 13, 695-808.
- 1984, 13, 695-808.
  (39) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. J. Phys. Chem. Ref. Data 1988, 17 (Suppl. 1).
  (40) Lias, S. G.; Hunter, E., Personal communication. These workers now support a value of 210.3 kcal mol<sup>-1</sup> for the proton affinity of aniline at 298 K, in view of recent published results, e.g., refs 41 and 42. One of the support support and the G. Stimutes an uncertainty of ±0.4 kcal mol<sup>-1</sup> (one present authors (J.R.G.) estimates an uncertainty of  $\pm 0.4$  kcal mol<sup>-1</sup> (one

standard deviation) based on a comparison of the scales in refs 38 and 41. The difference between the proton affinity scales of the compilations of Lias et al.38 and of Meot-ner and Sieck<sup>42</sup> stems from the value assigned by the latter for isobutene, used as a reference compound.

(41) Szulejko, J. E.; McMahon, T. B. J. Am. Chem. Soc. 1993, 115, 7839-7848

(42) Meot-Ner, M.; Sieck, L. W. J. Am. Chem. Soc. 1991, 113, 4448-4460.

- (43) Friedman, L.; Long, F. A.; Wolfsberg, M. J. Chem. Phys. 1957, 26, 714-715

(44) Chupka, W. A. J. Chem. Phys. 1959, 30, 191–211.
(45) Thölmann, D.; Grützmacher, H.-Fr. J. Am. Chem. Soc. 1991, 113, 3281-3287

(46) (a) Wassermann, B.; Brutschy, B. J. Mol. Struct. 1993, 284, 107-112. (b) Schöffel, K. Freie Universität Berlin, unpublished result cited in ref 15.

(47) We assumed a "loose" transition state with an r<sup>-4</sup> potential and evaluated the state density via the appropriate subroutine in the Hase-Bunker RRKM program.48 Normal modes of anilinium ion were estimated from those for toluene<sup>49</sup> and aniline.<sup>50</sup>
(48) Hase, W. L.; Bunker, D. L. QCPE 1973, No. 234.

(49) Tasumi, M.; Urano, T.; Nakata, M. J. Mol. Struct. 1986, 146, 383-396

(50) Niu, Z.; Dunn, K. M.; Boggs, J. E. Mol. Phys. 1985, 55, 421-432. (51) That the average available energy is roughly half of the maximum available energy is consistent with the photoelectron spectrum of chlorobenzene<sup>52</sup> in the range 9.0-9.5 eV

(52) Potts, A. W.; Lyus, M. L.; Lee, E. P. F.; Fattahallah, G. H. J. Chem. Soc., Faraday Trans. 2 1980, 76, 556-570.

(53) Standard RRKM calculations48 were used to estimate rate coefficients to compare with the flight time of about 10  $\mu$ s between ionization and entry into the mass spectrometer. Normal modes for the " $\sigma$ " ion *ipso*-C<sub>6</sub>H<sub>3</sub>ClNH<sub>3</sub><sup>+</sup> were estimated from the modes used for anilinium<sup>47</sup> by modification of the benzene-NH3 sensitive modes according to Badger's rule,54 plus inclusion of 842, 350, and 152 cm<sup>-1</sup> for the C-Cl stretch, Cl-C-N bend, and torsion, respectively

 (54) Badger, R. M. J. Chem. Phys. 1934, 2, 128–131; 1935, 3, 710–714.
 (55) The minimum and maximum available energies are 8.935 – 8.616 = 0.32 and 9.50 - 8.616 = 0.88 eV, respectively, to give an average (see ref 51) of 0.60 eV.

(56) Berkowitz, J. Photoabsorption, Photoionization and Photoelectron Spectroscopy; Academic Press: New York, 1979; p 129.

- (57) Dehmer, P. M. J. Chem. Phys. 1982, 76, 1263-1272.
   (58) Dehmer, P. M.; Pratt, S. T. J. Chem. Phys. 1982, 77, 4804-4817.
- (59) Kamke, W.; Kamke, B.; Kiefl, H. U.; Hertel, I. V. Chem. Phys. Lett.

1985, 122, 356-360. (60) Kamke, W.; Kamke, B.; Wang, Z.; Kiefl, H. U.; Hertel, I. V. Z. Phys. D 1986, 2, 159-160.

(61) Kamke, W.; Kamke, B.; Kiefl, H. U.; Wang, Z.; Hertel, I. V. Chem.

 Phys. Lett. 1986, 128, 399–403.
 (62) Appling, J. R.; White, M. G. Decay Dynamics of Autoionizing States in Formaldehyde, National Synchrotron Light Source Annual Report 1986, BNL-52045, Oct 1986, pp 181-182.

(63) Morin, P.; Nenner, I. Phys. Rev. Lett. 1986, 56, 1913-1916.
(64) White, M. G.; Appling, J. R. Manuscript in preparation.
(65) von Niessen, W.; Asbrink, L.; Bier, G. J. Electron Spectrosc. Relat. Phenom. 1982, 26, 173.

(66) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. Molecular Photoelectron Spectroscopy; Wiley-Interscience: New York, 1970; p 356. (67) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S.

Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules;

Halsted Press: New York, 1981; p 42. (68) No such structures had been reported until very recently, when autoionization structure was observed in  $HCl(Ar)_2^+$ ,  $(C_2F_4)_3^+$ , and  $(C_2F_4)_2O_2^+$ in our laboratory (work in progress). We consider the phenomenon to be rare.

(69) Zimmerman, J. A.; O'Malley, R. M. Int. J. Mass Spectrom. Ion Processes 1990, 99, 169-190.

(70) Two-body breakup of C<sub>6</sub>H<sub>3</sub>Cl(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> was assumed.
(71) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T. J. Chem.

(1) Correction (19) Correction (1