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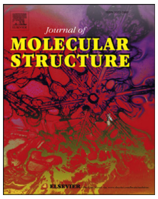

Reactive pathways in the bromobenzene-ammonia dimer cation radical: Evidence for a roaming halogen radical

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ABSTRACT

Photoinitiated reactions in van der Waals complexes provide a means to examine reactive pathways from well-defined initial geometries. In recent work, we re-examined reactive pathways following resonant two-photon ionization (R2PI) of the chlorobenzene-ammonia ($PhCl\cdots NH_3$) dimer. The dimer cation radical reacts primarily via Cl atom loss, and additional channels corresponding to HCl and H atom loss were identified. The structure of the reactive complex was confirmed as an in-plane σ-type, and computational studies of the dimer cation radical potential energy landscape revealed two nearly isoenergetic arenium ion intermediates (or Wheland intermediates). The intermediate produced from *ipso* addition was not stable with respect to either Cl or HCl loss, and the relative branching observed in experiment was well reproduced by microcanonical transition state theory (TST) calculations. Here, we report experimental and computational studies of the related $PhBr\cdots NH_3$ dimer, examined for the first time. We present evidence that the dimer structure is also an in-plane σ-type. However, in contrast to the $PhCl\cdots NH_3$ system, calculations predict that the structure of the reactive intermediate corresponds to a distonic ion-radical complex, where the radical density is largely localized on the bromine atom. The calculated barrier to HBr loss is sufficiently high to render this channel nearly insignificant (less than 1% branching) in TST calculations, yet experiment shows a sizable (37%) branching into this channel. We rationalize these results in terms of a roaming Br radical mechanism for HBr formation.

1. Introduction

The study of van der Waals clusters has provided important insight into the strength and directionality of intermolecular forces, and detailed experimental data (binding energies, vibrational and electronic spectra, etc.) on these systems provide important benchmarks for theoretical validation [1–8]. Additionally, clusters provide a means to initiate reactivity from relatively well-defined initial geometries [9–12]. Prototypical systems in this regard are the dimers of halobenzenes with ammonia (i.e., $PhX\cdots NH_3$) which upon ionization can react via a classic S_N2 mechanism proceeding through an arenium ion (Wheland) intermediate [13–25]. Until recently, it has been thought that the structure of these dimeric complexes were π-type, where the ammonia is located above the plane of the aromatic ring. This was dispelled by studies of the Cockett group [26] (on fluorobenzene-ammonia) and our group [27] (on chlorobenzene-ammonia), which showed, via multidimensional Franck-Condon simulations of the excitation spectra, that the reactive complex corresponds to an in-plane σ-type.

We recently re-investigated the reactive pathways in the well-studied [13–18,25,28] chlorobenzene-ammonia dimer cation radical using resonant two-photon ionization (R2PI) and electronic structure calculations (density functional theory, DFT) [27]. In addition to the well-studied Cl loss channel (producing protonated aniline) [13–18,25,28], a second channel corresponding to HCl loss (producing aniline cation radical) was identified for the first time in R2PI studies of the 1:1 complex, and a third channel, H atom loss, was also identified. The reactive potential energy landscape was extensively characterized by computational methods, and two nearly isoenergetic arenium ion (Wheland) intermediates were found. At the energy accessed experimentally, the intermediate produced from *ipso* addition was not stable with respect to Cl or HCl loss, and the relative observed branching between these channels

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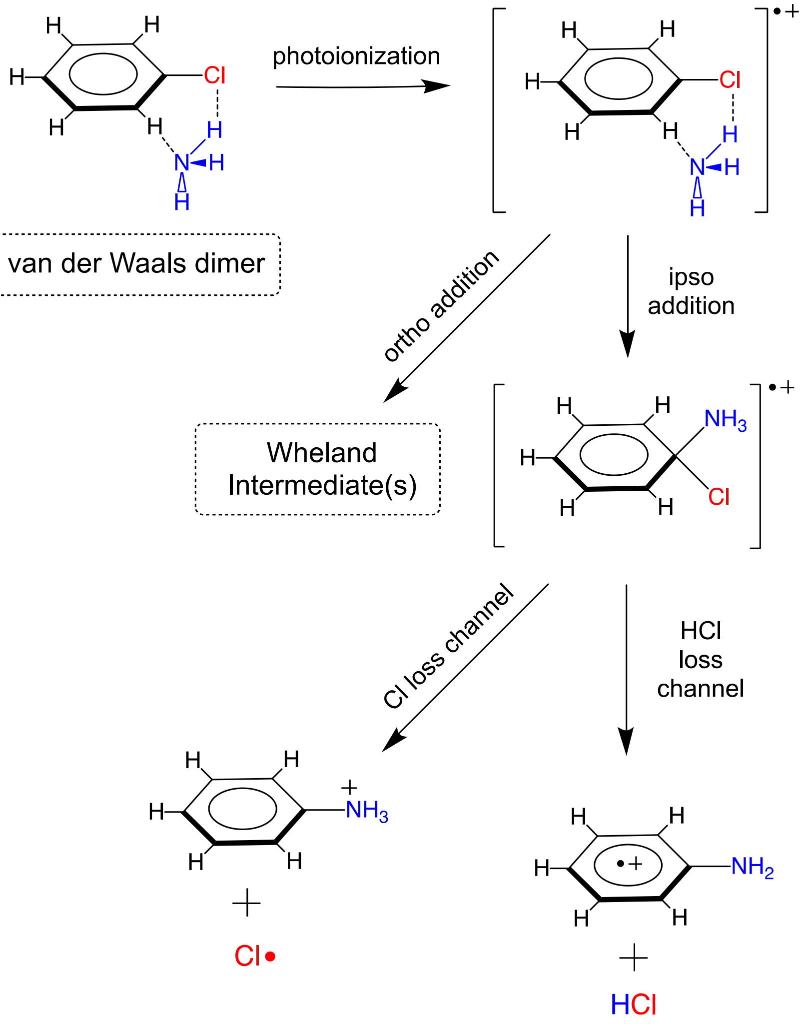
(1:5.6 with Cl loss dominant) was well reproduced by microcanonical transition state theory calculations. The reactive pathways following photoionization in this system are summarized in Scheme 1.

To date, no experimental studies have probed complexes between bromobenzene (PhBr) and ammonia, primarily due to the fact that the S_1 lifetime of PhBr is very short (~30 ps) [29,30] and it is therefore difficult to resonantly ionize with nanosecond lasers [31–34]. Our initial interest in this system stemmed from the possibility of accessing halogen bonded structures. Thus, in the present work, we examine the formation and fate of the ionized complexes of PhBr and NH_3 using one-color R2PI spectroscopy, supported by DFT, time-dependent DFT, and *ab initio* calculations at the explicitly-correlated coupled-cluster level, as well as Franck-Condon simulations. Consistent with other PhX⋯NH_3 (X = halogen) dimers, we find that the observed complex is of a σ-type. However, the structure of the ionic intermediate predicted via theory is very different from that in the PhCl⋯NH_3 system, being a distonic ion-radical complex, where the radical density is largely localized on the Br atom. Calculations predict a sizable barrier to HBr elimination from this intermediate, sufficient to yield very little statistical branching into this channel, yet we observe a branching for the molecular channel (37%) which is significantly *larger* than in the analogous PhCl⋯NH_3 system (15%). Given the structure of the intermediate, and the lower energy exit channel to Br elimination, we postulate the existence of a roaming radical mechanism to explain the increased yield of the molecular channel.

2. Experimental and computational details

The experimental setup has previously been described in detail [27]. Our R2PI setup comprises a linear time-of-flight mass spectrometer (TOFMS) coupled with a supersonic molecular beam source. The expanded mixture was generated by passing a 1–5% NH_3/He premix through liquid bromobenzene (Aldrich, 99%) contained in a stainless-steel bubbler held at 25 °C. The backing pressure was varied between ~2 and 5 bar. Ions were extracted and accelerated using a conventional three-plate stack, and flew through a 1 m field-free drift region prior to striking a dual Chevron microchannel plate (MCP) detector. The detector signal was



Scheme 1. Illustration of reactive pathways in the chlorobenzene-ammonia dimer. Upon photoionization, addition occurs leading to one (or more) Wheland intermediates. Only the structure produced from ipso addition is shown. These intermediates react to give the final set of products: protonated aniline (+Cl) or aniline cation radical (+HCl).

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