Proc. Int. Conf. Lasers '88, 618 (1989)

STEPWISE SOLVATION OF REACTIVE ANILINE CATIONS

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Abstract

Single molecules of aniline were stepwise solvated with solvent shells M_n consisting of either NH_3, N_2H_4, CH_3OH, or H_2O and studied by mass-resolved one- and two-color resonance-enhanced multiphoton ionization (REMPI) and electron impact (EI) ionization. The influence of microsolvation was investigated for the processes of unimolecular dissociation and intracluster dissociative proton transfer. Dissociative proton transfer from aniline to M_n to form H^+M_n was strongly dependent on M_n proton affinity, which for a particular solvent generally increased with n. Consequently, a solvent size threshold for formation of H^+M_n was observed for NH_3 ($n \geq 3$), N_2H_4 ($n \geq 2$), CH_3OH (not seen, $n > 4$), and H_2O (not seen, $n > 4$). Calculated enthalpies of these reactions, using a model that accounts for the energetics of stepwise solvation, displayed excellent correlation with the observed results. In a second experiment, the solvation of the well-known $C_6H_5NH_2^+ \rightarrow C_5H_6^+ + HNC$ dissociation revealed a striking electron transfer mechanism whereby solvation with N_2H_4 led to extensive formation of $HNC{\cdot}M_n^+$. Although all the solvents studied have ionization potentials above that of aniline, only N_2H_4 has a value less than that of the fragment C_5H_6.

Introduction

One of the fundamental issues in reaction dynamics is understanding how solvent molecules influence the properties of a chemical reaction. This has traditionally been investigated by comparing the kinetics of gas phase reactions to that in solvents of varying viscosity.[1] In a recent study, we have refined a technique to sequentially solvate single reactive molecules with one or more solvent molecules.[2] The technique relies on the ability to form molecular clusters in a supersonic expansion. Clusters of solvent molecules, seeded with a single reactive solute molecule, can be formed under the appropriate expansion conditions and sample mixtures.

We present results for an investigation of the reactivity of a single aniline cation seeded within a solvent shell M_n of varying size (typically n = 1-10) consisting of either NH_3, N_2H_4, CH_3OH, or H_2O.[2] The reactivity of cations was chosen because the microsolvated reactant cation and the subsequent formation of charged products could be monitored by time-of-flight (TOF) mass spectrometry in the molecular beam apparatus. The cations were formed with specific initial energies by resonance enhanced multiphoton ionization (REMPI). We also compared these results to the chemistry of microsolvated aniline formed by electron impact (EI) ionization.

There are only a handful of studies in the literature that focus on the reactivity of large aromatic molecules in microsolvent shells. Most of these tend to deal with so called "soft" chemistry (e.g., charge transfer and intermolecular vdW bond dissociation. However, a few notable studies of hydrogen bond dissociation,[3] proton transfer reactions,[4,5] and microcluster crystallization[6] deserve citing. In the present investigation, emphasis was placed on how sequential solvation promotes or quenches "hard" chemistry (e.g., fragmentation and rearrangement). Aniline was chosen for this work because its unimolecular ion fragmentation properties have been extensively studied.[7,8] The molecule also permits a study of intracluster acid-base type chemistry such as dissociative hydrogen transfer from solvent to form protonated aniline cation and dissociative proton transfer from aniline cation to solvent to form protonated solvent. Our success in stepwise solvation provides us with the opportunity to systematically observe a gas phase reaction evolve toward solution phase behavior (i.e., "dissolve") on a molecule-by-molecule basis.

Experimental

The supersonic molecular beam time-of-flight (TOF) mass spectrometer has been described before[2,9] and is illustrated with a few recent modifications in Fig. 1. The vacuum system consists of differentially pumped source and ionization chambers. A temperature-controlled magnetic solenoid pulsed nozzle in the source chamber is used for the supersonic expansion which enters the ionization chamber through a 1-mm-diam skimmer. The extent of clustering is very sensitive to the relative delay between the excitation source (laser or e^- beam) and the pulsed valve firing is illustrated in Fig. 2. By exciting at the extremities of the gas pulse, it is possible to suppress larger clusters and still form a high yield of the singly solvated dimer. This should prove important in photodissociation experiments by helping to remove interferences from dissociation of larger clusters.

The acceleration grids for the TOF mass spectrometer consist of the standard three-grid configuration. We use 1-cm grid spacings, a 1-m drift tube, and typical extraction and acceleration fields of 100-200 V/cm and 1500-2000 V/cm, respectively. Deflector plates are used near the ion source to compensate for the forward velocity of the molecular beam. Ion signals are collected by measuring current versus ion TOF using a microchannel plate detector. Mass spectra are recorded using a 125-MHz bandwidth transient digitizer interfaced to an IBM AT computer.

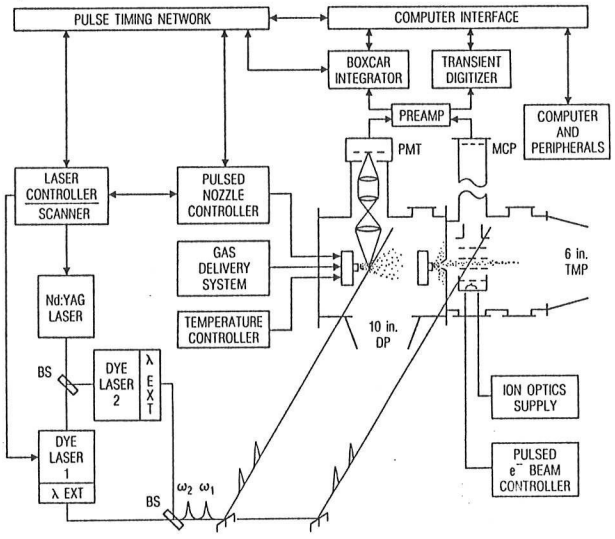

Fig 1. Schematic of the experimental apparatus. In the present work, 2-C excitation was achieved using a single dye laser and the 2nd, 3rd, or 4th harmonic of the Nd:YAG laser. Symbols are defined as follows: MCP = microchannel plate detector; PMT = photomultiplier tube; TMP = turbomolecular pump; DP = diffusion pump; BS = beamsplitter; λ EXT = wavelength extension components. Free jet fluorescence detection was not used in the present study.

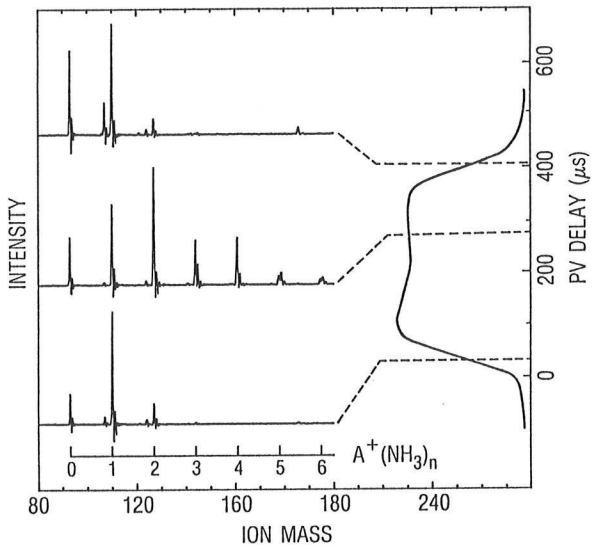

Fig. 2. 1-C REMPI TOF mass spectra (MS) of aniline-$(NH_3)_n$ clusters as a function of the overlap of the laser pulse with the temporal profile of the pulsed valve (PV) output. Conditions were ω_1 = 294 nm, 0.05 mJ/pulse, 50 psi He.

The laser pulses were mildly focused by using a 30-cm focal length spherical lens positioned to bring the light to a focus about 3-5 cm before crossing the molecular beam. For the 2-color (2-C) REMPI experiments, the ω_2 pulse was typically delayed (optically) by 3 ns from the ω_1 pulse. The laser pulse widths are about 4-6 ns. A pulsed EI ion source with scanning electron energy capabilities[10] was also employed for these studies.

Chemistry in Microsolvents

We investigated two reactions involving microsolvated aniline cation; the proton or acid dissociation reaction

$$C_6H_5NH_2^+ \longrightarrow C_6H_5NH + H^+ \qquad (1)$$

which is energetically unfavorable in the gas-phase, and the dissociation

$$C_6H_5NH_2^+ \longrightarrow C_5H_6^+ + HNC \qquad (2)$$

which is a well-known gas-phase reaction.[7,8]

Dissociative Proton Transfer

The first reaction is particularly interesting because it can become favorable in the presence of solvent molecules of sufficient basicity. The interesting question is how large a solvent shell is required to observe an acid-base reaction.

A thermodynamic cycle appropriate to reaction (1) can be written that gives the gas phase reaction enthalpy

$$\Delta H_g = I_p(H) - I_p(A) + D_H(A\{-H\}) - D_{H^+}(M) \quad (3)$$

The I_p values are ionization potentials, and the D values are bond energies which are written to be interpreted as a hydrogen affinity (D_H) and a proton affinity (D_{H^+}). The addition of terms to include the energetics of stepwise solvation has been derived previously[2], and is given by

$$\Delta H_{s,n} = \Delta H_g + \sum_{i=1}^{n} \Delta E_{i,i-1}(A^+M_i) - \sum_{i=2}^{n} \Delta E_{i,i-1}(H^+M_i) \quad (4)$$

Here, the ΔE terms are solvation energies for successive addition of M to A^+ or H^+, respectively.

The appearance of the product H^+M_n in the REMPI mass spectra for M=NH_3, N_2H_4, and CH_3OH is presented in Fig. 3. From these and other spectra, the following observations are reached; (i) H^+M_n formed from $A^+ \cdot M_n$ precursor was observed for NH_3 and N_2H_4 with a solvent size threshold of $n \geq 3$; (ii) no protonated solvent H^+M_n was observed for CH_3OH or H_2O up to values of $n = 5$, representing the limit to acceptable signal-to-noise for these solvents.

As expected, proton transfer from aniline to M_n to form H^+M_n was strongly dependent on M_n proton affinity, which for a particular solvent generally increased with n. A small solvent threshold size for formation of H^+M_n was observed for the more basic solvents NH_3 ($n = 3$) and N_2H_4 ($n = 2$). The less basic solvents CH_3OH and H_2O, however, did not induce an acid-base reaction for solvent shell sizes up to $n = 4$. Qualitatively, it was found that as the solvent basicity increased, the number of solvent molecules required to initiate an acid-base reaction decreased.

Brutschy *et al.*[5] recently reported evidence for a threshold solvent size effect in the dissociative proton transfer involving toluene and p-xylene solvated with NH_3, CH_3OH, and H_2O. The relative ordering of the n threshold values for the various solvents was consistent with that observed in the present work, although the absolute values in the former work were shifted to smaller n. These results are in accord with the model for stepwise solvations developed above. Calculated microsolvation enthalpies $\Delta H_{s,n}$ are represented in Fig. 4.

A notable feature of the calculated results is the predicted increase in enthalpy at the first level of solvation $n = 1$ due to stabilization of the reactant side of reaction (9) without an offseting stabilization of the products. Subsequent solvation, however, stabilizes the products to a greater extent than the reactants so that the overall influence of solvation is to increase K_{eq} relative to the gas phase. A second feature is that the ordering of exothermicities, $NH_3 > CH_3OH > H_2O$, is in agreement with the present results and those of Brutschy *et al.*[5] This trend is most strongly correlated with the proton affinity $D_{H^+}(M)$.

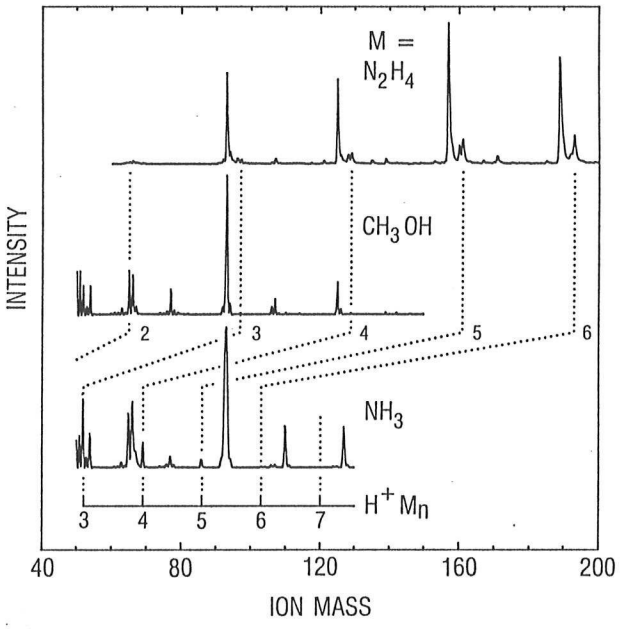

Fig. 3. 1-C REMPI/MS of A^+M_n clusters showing evidence for a critical solvent size in various solvents for dissociative proton transfer to form H^+M_n. Pulse energies were about 1.0 mJ (295 nm) for M = NH_3 and CH_3OH, and 0.40 mJ (233 nm) for N_2H_4.

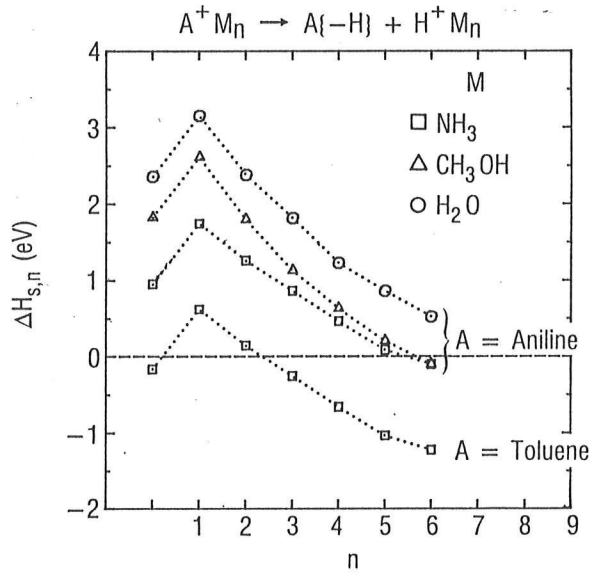

Fig. 4. Calculated stepwise solvation enthalpies as a function of solvent and shell size n for dissociative proton transfer. Calculated results are compared for A = aniline and toluene. The lefthand most data are for the gas phase reactions.

A third feature is that the calculated solvation enthalpies $\Delta H_{s,n}$ are more exothermic for A=toluene, thus explaining the smaller threshold values of n reported by Brutschy *et al.* for that system. The calculated curve for the reaction involving toluene-$(NH_3)_n$ is plotted in Fig. 4, although the calculated curves for all solvents are shifted in energy from the aniline-$(NH_3)_n$ data by essentially a constant representing the differences in the I_p and hydrogen bond dissociation energy $D_H(A\{-H\})$ of the aromatic cations.

Dissociation Induced Electron Transfer

The second reaction was studied with the original intent of examining solvent quenching of known gas-phase dissociation. In the course of this work, we observed a striking electron transfer mechanism that was strongly dependent on the properties of the solvent. This is diagrammed schematically in Fig. 5. The aniline cation is represented by AB^+ which dissociates as indicated above to $C_5H_6^+$ and HNC, represented by A^+ and B, respectively. Two different product pathways were observed, depending on the solvent molecule M. When solvated by NH_3, CH_3OH, or H_2O, AB^+ was observed to dissociate to the usual uncomplexed gas-phase products $A^+ = C_5H_6^+$ and higher threshold energy ions. When solvated by N_2H_4, the positive charge was observed to jump to a solvent molecule in the course of the dissociation. The dissociation-induced electron transfer can be very efficient as shown by the mass spectra in Fig. 6. For REMPI excitation at 233 nm, the electron transfer occurs with near unit probability, as evidenced by the strong $HNC{\cdot}N_2H_4$ signal at mass to charge ratio m/q = 59 and the near absence of the $C_5H_6^+$ signal at m/q=65. These results occur because the aniline cation suddenly dissociates into two fragments that have larger ionization potentials (I_p). The solvent molecule N_2H_4 has a lower I_p than C_5H_6 and is in effect ionized by the product $C_5H_6^+$. The NH_3, CH_3OH, and H_2O solvent molecules, on the other hand, have higher values of I_p and hence electron transfer to these solvents is not energetically favorable. An interesting sidelight is that these results demonstrate that the bonding site for the first few solvent molecules is the amine group and not the aromatic ring of aniline.[2]

Summary and Conclusions

The influence of microsolvation was investigated for unimolecular dissociation and intracluster bimolecular hydrogen transfer and proton transfer. The solvation of unimolecular dissociation revealed a striking mechanism for electron transfer from fragment to solvent that depended strongly on the properties of the solvent molecules. For acid-base type reactions, distinct evidence for critical solvent size effects was obtained that correlated well with characteristic properties of the solvent (e.g., ionization potential, proton affinity, bond energies, etc.). These results systematically illustrate how a gas-phase reaction evolves toward solution-phase behavior (i.e., "dissolve") on a molecule-by-molecule basis.

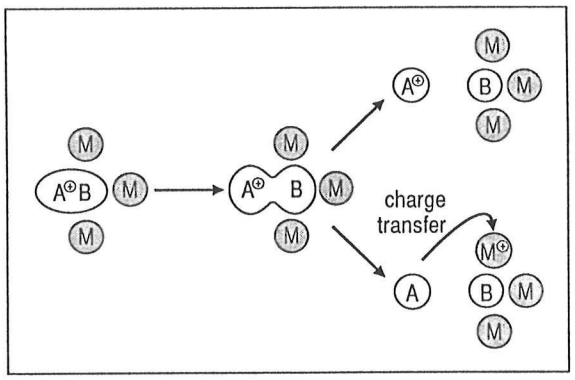

Fig. 5. Pictorial view of the process of dissociation and or electron (or charge) transfer in microsolvated molecular clusters. AB^+ represents the aniline cation dissociating to C_5H_6 (A) and HNC (B). The solvent molecules M are shown preferentially bonded to B as determined experimentally.

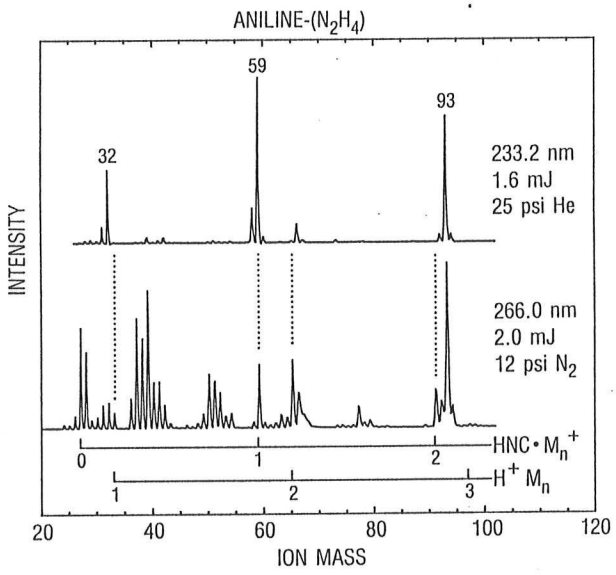

Fig. 6. 1-C REMPI/MS of A-$(N_2H_4)_n$ clusters for different excitation conditions. The appearance of the fragment clusters $HNC{\cdot}(N_2H_4)_n^+$ is evidence for a dissociation-induced charge transfer mechanism. Numbers over peaks denote amu.

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