magnitude. This provides the theoretical MCD features shown in Figures 2 and 3. They are consistent with the observed MCD signs and magnitudes.

One final comment regards the sign reversal and shift seen in the temperature-dependent MCPL data (Figure 4). This behavior is not evident in a number of other ^{3}LC emitting complexes such as $[Ir(phen)_3]^{3+}$, which show simpler $1/T$ C-term temperature dependence in the 10–100 K range.[23] This can be taken as evidence for the thermal population of a further electronic state $\approx$50–100 cm^{-1} above the ^{3}LC manifold. Luminescence from this state has a shape and quantum efficiency similar to that of the ^{3}LC state, but the MCPL sign, magnitude, and shift (relative to the luminescence) are far more characteristic of a ^{3}MLCT state.[22,24]

Conclusions

The present work clearly shows the great value of Zeeman luminescence line-narrowing experiments in discriminating between a ^{3}LC and a ^{3}MLCT state and in providing valuable information on ZFSs. Analogous Zeeman hole-burning experiments can be envisaged. These have the advantage of not relying on spin–lattice relaxation and could provide information on relative dipole strengths of the ZFS components. Such information can then be used as a basis toward understanding details of more conventional spectroscopic data.

Acknowledgment. We thank Professor H.-U. Güdel for providing the sample of $[Rh(phpy)_2bpy]Cl$. L. W. thanks Celltech for support. We thank Dr. Graham Heath for stimulating our interest in this class of compounds and for his active encouragement.

Registry No. $[IrCl_2(5,6\text{-}Me_2\text{-}phen)_2]^+$, 68842-70-6.

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Role of Charge Transfer in Nucleophilic Substitution Reactions in Clusters of 1-Fluoro-*n*-chlorobenzene Cations with Ammonia Molecules[†]

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The reaction behavior of mixed clusters consisting of fluorochlorobenzene radical cations surrounded by ammonia molecules has been studied by resonant two-photon ionization. The spectral characterization of the neutral precursors allows one to study ion reactions in the cluster with a well-defined microsolvation environment. In addition to charge transfer, two types of nucleophilic substitution reactions take place. In a binary complex chlorine is ejected either in an ipso substitution by radical loss or, for meta and para isomers, by HCl formation, in the latter case by a metastable decay. The reaction efficiency for Cl elimination decreases with decreasing dipole moment of the chromophore. It is rationalized by a σ addition intermediate with an activation barrier due to charge transfer as postulated by the model of Shaik and Pross. The HCl elimination is not rate determined by the formation of a σ intermediate. In ternary and larger mixed complexes mainly substitution of fluorine takes place with HF as leaving group, corresponding to the onset of solvation catalysis.

1. Introduction

Aromatic cations are important reactants and intermediates in condensed phase aromatic substitution reactions. They may be produced by different oxidation methods.[1] Aromatic nitration, for example, occurs via a charge-transfer (CT) reaction step. Recently reactions in mixed clusters of substituted benzene radical cations surrounded by a variable number of polar molecules have been studied by resonant two-photon ionization (R2PI) with a view to a better understanding of the ion chemistry of these species under microsolvation.[2-7] From the dependence of the reactivity on the size and composition of the solvent moiety, the reaction behavior of solvated cations may be investigated from a microscopic point of view and under tailor-made microsolvation. Even for small and simple solute–solvent systems several reaction processes generally compete with each other, with the branching ratio depending on the solvation parameters. Examples of intracluster reactions studied recently are dissociative electron or proton transfer (dET and dPT) between the cation and the solvent[2,4] or nucleophilic ipso substitution (S_N) reactions between halobenzene radical cations and methanol or ammonia.[5] For the latter reactions evidence was provided for the onset of solvation catalysis starting already in small complexes. In the present study S_N reactions of disubstituted halobenzene radical cations YAX^+ with ammonia were investigated to determine the dependence of their efficiency on structural parameters of the radical cation. Of special interest was the transition of reactivity from X to HX or HY displacement and its dependence on the dipole moment of YAX. These intracluster reactions will be compared in the case of binary complexes with analogous ion–molecule reactions, studied recently in an FT-ICR experiment by Thölmann and Grützmacher (TG).[1]

In the present cluster study, the ionic precursors are characterized by resonant two-photon ionization (R2PI). Since only the excitation step in this two-photon process occurs resonantly, the ion-yield curve, measured by tuning the laser, reflects the absorption spectrum of the chromophore (R2PI spectrum). Since

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[†] Dedicated to Professor Dr. H.-Fr. Grützmacher on the occasion of his 60th birthday.

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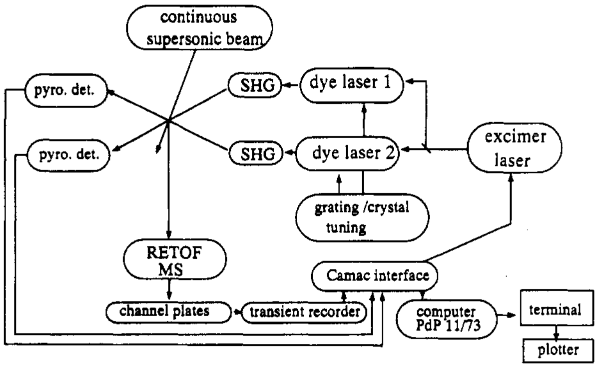


Figure 1. Schematic experimental setup of the R2PI experiment (RETOF MS = reflectron TOF mass spectrometer; SHG = second harmonic generator; pyro det = pyroelectric detector or energy meter). d = 80 μm; p_{He} = 2-3 bar; T_0 = room temperature; dilution ratio of both the solvent and solute 0.1-3%.

a solvated chromophore exhibits a characteristic spectrum, the latter may be utilized as a spectroscopic fingerprint both for the parent and for the product ions of an ionized complex. Hence the reactions may very often be studied with size selectivity. This type of optical mass spectrometry has a great advantage over more traditional photoionization mass spectrometry, since the ionization of weakly bound molecular clusters is very often accompanied by strong fragmentation (evaporation of neutral subunits), making the assignment of the parent clusters a difficult task.

As will be shown in the following, the reactions in (1:*n*) clusters, i.e., in a complex of one cation and *n* solvent molecules, are manifold. In binary complexes reaction channels similar to those encountered in bimolecular ion-molecule reactions in the gas phase are observed[1,8,9] but with much higher efficiency. In clusters however, additional channels open up which obviously are too slow to be observed in more or less short-lived collision complexes.

2. Experimental Section

The experimental setup, described elsewhere in greater detail,[5] is shown schematically in Figure 1. Briefly, mixed clusters are synthesized in a continuous supersonic beam with He as seed gas. After ionization by two photons of either one color (1C-R2PI) or of different colors (2C-R2PI), supplied by excimer pumped, frequency-doubled dye lasers, the ions are analyzed in a reflectron TOF mass spectrometer ($m/\Delta m \approx 1200$). The mass spectra are recorded with a 200-MHz transient recorder and are averaged over 100-400 laser shots. The yield curve of several molecular ions are measured in one run by tuning the laser in the vicinity of the vibrationless $S_0 \rightarrow S_1\ 0_0^0$ transition of the chromophore. The ion-yield curves are normalized to the square of the laser intensity, kept at rather low intensity level ($I < 10^6$ W/cm^2) to avoid absorption of additional photons by the ions.

The disubstituted benzenes of spectral quality, delivered by Aldrich, were used without further purification. For the solvent we used an aqueous solution of ammonia at a concentration of ≈25 wt %. Due to the much higher partial pressure of ammonia at room temperature as compared with water the latter did not interfere.[5b]

3. Results

1-Fluoro-2-chlorobenzene. The R2PI spectrum of the bare 1-fluoro-2-chlorobenzene excited in the vicinity of the $S_0 \rightarrow S_1$ 0-0 transition is shown in Figure 2a. The corresponding spectrum of the 1:1 cluster, shown for comparison in Figure 2d, exhibits a doublet band structure (band 2,3) at very low intensity. At the same resonances (Figure 2c) a new ion mass is observed with m/e = 112 assigned to 2-fluoroanilinium, which is produced in the following S_N reaction:

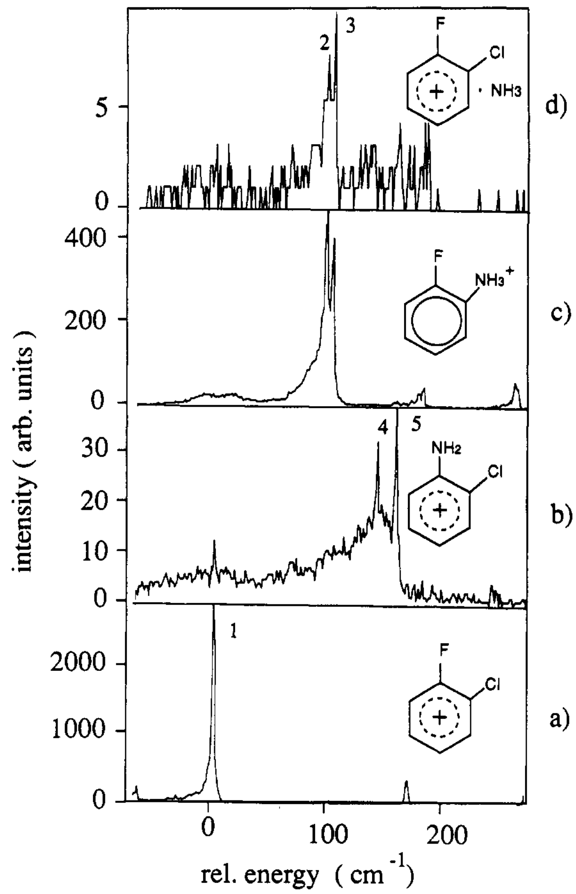
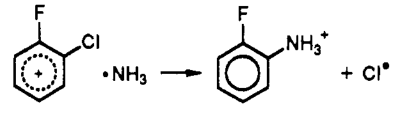


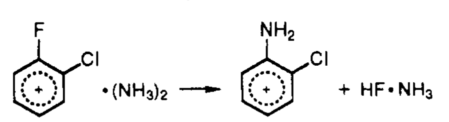
Figure 2. R2PI spectrum of some ions of the cluster system 1-fluoro-2-chlorobenzene (*o*-FClBz)·(ammonia)$_n$. (a) *o*-FClBz$^+$; (b) 2-chloroaniline$^+$; (c) 2-fluoroanilinium; (d) *o*-FClBz$^+$·ammonia. Relative band positions and precursors [1:*n*] in cm^{-1}: ν_{00} = 37040[13] [1:0]; 2 = 96.5, 3 = 102 [1:1], 4 = 142.2, 5 = 158.9 [1:2].



(1)

Since the intensity of the product ions is nearly 2 orders of magnitude larger than that of the remaining (1:1) precursors, the reaction is nearly quantitative. The substitution with the chlorine radical as leaving group is very similar to that found earlier for the chlorobenzene/ammonia system.[3-5] Therefore the reaction behavior is basically not changed by an additional fluorine substituent.

Further product ions appearing at m/e = 127,129 are assigned to the isotopomers of 2-chloroaniline$^+$. Their R2PI spectrum, shown in Figure 2b, shows two fingerprint bands (band 4, 5) which appear at slightly higher energy than those assigned to the (1:1) complex. They are assigned to a (1:2) precursor which reacts according to the following S_N reaction:



(2)

The fingerprint bands do not correspond to those of the actually detected (1:2) or any larger complex found in the mass spectrum. This seems to contradict this assignment. However by decreasing the concentration of ammonia in the expansion this chloroaniline$^+$ peak persists in the mass spectrum up to a degree of dilution, at which no clusters larger than the (1:1) are observed. Therefore its precursor must decay quantitatively and be larger than the

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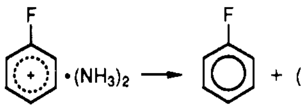
TABLE I: Some Data for Substitution Reactions in 1:1 Complexes of 1-Fluoro-*n*-chlorobenzene:Ammonia Clusters

chromophore	μ/D	IP/eV	eff/% bimol[a]	eff/% 1:1 cl	ΔH°_R/KJ/mol[23-25]	channel
chlorobenzene	1.69	9.06 [17]	13	99	−18	Cl$^\bullet$
			nr	nr	−130	HCl
fluorobenzene	1.6	9.20 [16]	nr	nr	+93	F$^\bullet$
			nr	nr	−151	HF
1-fluoro-2-chlorobenzene	2.41	9.18 [18]	15	88	−35	Cl$^\bullet$
			nr	nr	−117	HCl
1-fluoro-3-chlorobenzene	1.49	9.21 [17]	10	72	−30	Cl$^\bullet$
			nr	11	−104	HCl
1-fluoro-4-chlorobenzene	0.0	9.01 [18]	2.8	7	−9	Cl$^\bullet$
			nr	36	−92	HCl (metastable)
ammonia	1.47	10.16/17				

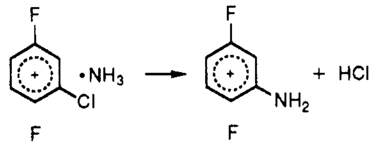
(1:1). The R2PI spectrum of the (1:2) cluster ion, not shown in Figure 2, must then be due to fragmentation of larger complexes. This assignment is supported by earlier measurements with fluorobenzene,[5] where the fingerprint band of the (1:2) complex also shows a similar blue shift relative to the fingerprint of the (1:1) cluster and an analogous S_N reaction. In that case the assignment was further supported by the appearance of an ammonia dimer cation, bearing identical fingerprints, and originating from the following competing intracluster dissociative electron-transfer reaction:



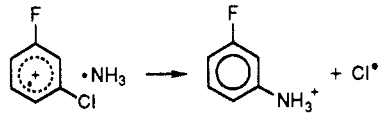
(3)

Thus a disubstituted ortho radical cation behaves in a similar way to the monosubstituted one, i.e., the substitution of chlorine requires only one solvent molecule, that of fluorine at least two. While in the case of chlorine substitution the leaving group is a chlorine radical, in the case of fluorine substitution it is HF.

1-Fluoro-3-chlorobenzene. The spectra with 1-fluoro-3-chlorobenzene are shown in Figure 3. The spectrum of the (1:1) complex (Figure 3c) is strongly adulterated by fragmentation of larger clusters ending up in this channel. The dominant fingerprints are two doublets (1,2) and (3,4) which are blue-shifted relative to the 0–0 transition of the bare chromophore (not shown in Figure 3). These resonances reappear in the spectra of the product ions with masses of fluoroanilinium and fluoroaniline$^+$ (Figure 3b,a). The first doublet (bands 1, 2) is similar to that observed for the ortho isomer (bands 2, 3), but the second doublet (bands 3, 4) is shifted further to the blue. From the appearance of these product ions we propose the following S_N reactions:

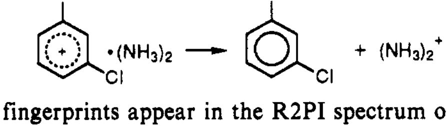


(4)



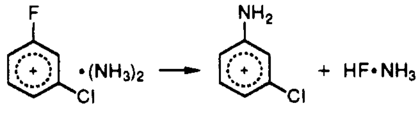
(5)

The bands 5, 6 in the spectrum of the ammonia dimer cation (Figure 3d) are assigned as fingerprints of the (1:2) complex decaying according to the following dET reaction:



(6)

Similar fingerprints appear in the R2PI spectrum of a further product ion with m/e of chloroaniline$^+$ (Figure 3e) assigned to the following substitution reaction:



(7)

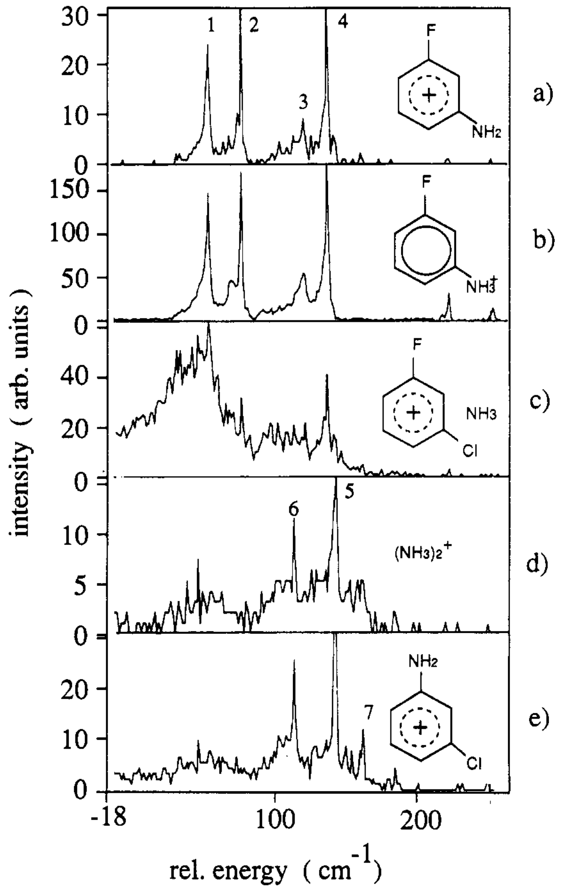


Figure 3. R2PI spectrum of some ions of the cluster system 1-fluoro-3-chlorobenzene (*m*-FClBz)·(ammonia)$_n$. (a) 3-fluoroaniline;$^+$; (b) 3-fluoroanilinium; (c) *m*-FClBz$^+$·(ammonia); (d) (ammonia)$_2^+$; (e) 3-chloroaniline$^+$. Relative band positions and precursors [1:*n*] in cm^{-1}: (ν_{00} = 37 026.95[14] not shown in the Figure 3) 1 = 46; 2 = 69, [1:1]; 3 = 111.8; 4 = 128.5 [1:1]$_{\text{iso}}$; 5 = 134; 6 = 105 [1:2]; 7 = 153.3 [1:3?].

In comparison with the results for the ortho isomer, two peculiarities in the reaction behavior of (1:1) clusters should be noted: (1) HCl abstraction appears as a new reaction channel; (2) the efficiency of chlorine substitution is reduced (Table I). The first finding is particularly remarkable since up to now HCl production has never been observed in either a (1:1) cluster or an analogous bimolecular ion–molecule reaction.[1]

1-Fluoro-4-chlorobenzene. Thölmann and Grützmacher[1] reported a dramatic decrease in the efficiency of chlorine substitution in the para isomer. Similar observations are made with clusters. Part of the TOF mass spectrum is displayed in Figure 4. The most prominent feature, apart from different reaction products, is a broad mass peak from a metastable decay at m/e = 116. Its origin will be discussed below. The R2PI spectra of some ions are depicted in Figure 5. The 0–0 transition in the isolated chromophore is shown for reference in Figure 5a. As with the meta isomer, with 1C-R2PI the para isomer may not be ionized

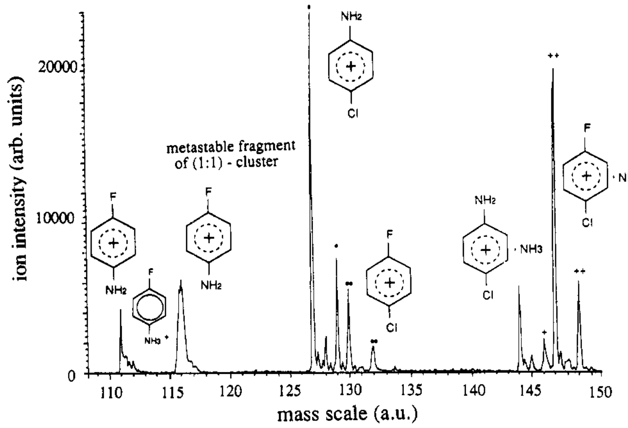


Figure 4. Part of the TOF mass spectrum of the 1-fluoro-4-chlorobenzene·(ammonia)$_n$ system. The broad peak at $m/e = 116$ is a metastable fragment. The laser was tuned to band 2 of Figure 5.

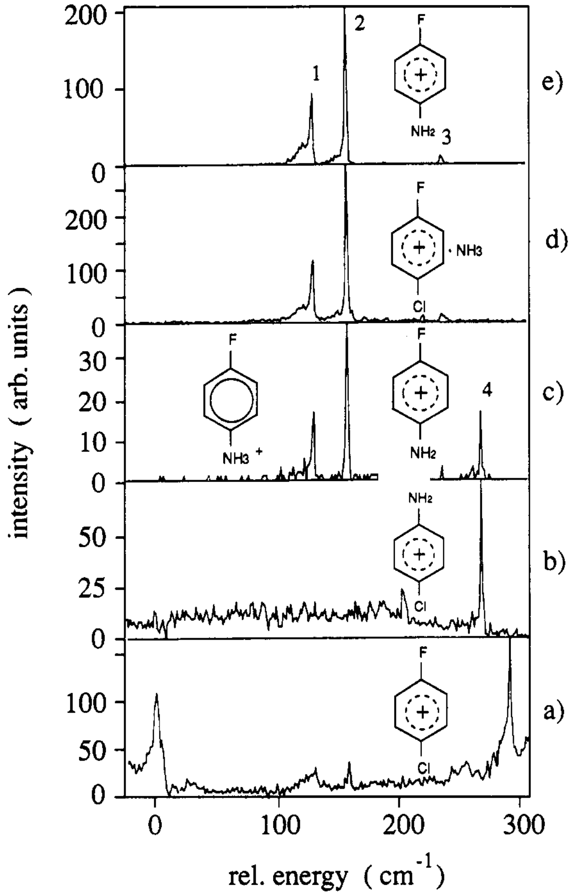


Figure 5. R2PI spectrum of some ions of the cluster system 1-fluoro-4-chlorobenzene (p-FClBz)·(ammonia)$_n$. (a) p-FClBz$^+$; (b) 4-chloroaniline;$^+$; (c) 4-fluoroanilinium and 4-fluoroaniline$^+$; (d) p-FClBz$^+$·(ammonia); (d) metastable 4-fluoroaniline$^+$ fragment. Relative band positions and precursors [1:n] in cm^{-1} 1: (ν_{00} = 36275.1^{15} [1:0]) 1 = 131.2; 2 = 159.0; [1:1]; 3 = 236.6 [1:1]$_{\text{iso}}$; 4 = 268.2 [1:2].

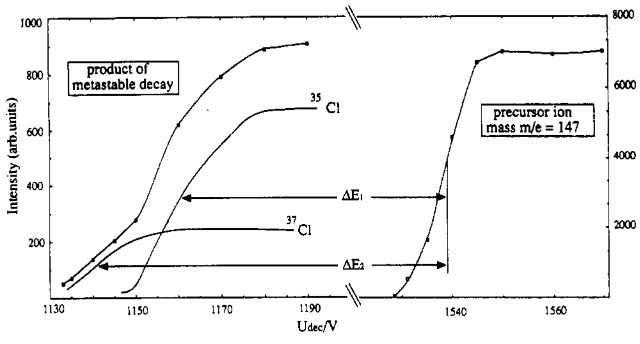
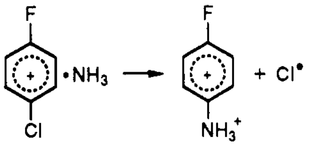


Figure 6. Ion transmission curves of the 1:1 cluster and of the product of metastable fragmentation determined by varying the deceleration field. The laser was focused to decrease the inherent half width of the 1:1 cluster curve.

via the 0–0 transition, as the total energy of the two photons is 20 meV smaller than the ionization potential. But the molecule may be promoted into a high-lying Rydberg state, from which it may be field ionized in the acceleration region. Therefore its intensity is very low. The spectrum of the (1:1) aggregate (Figure 5d) shows one dominant doublet (bands 1, 2) and further to the blue a very tiny band (band 3). Thus, instead of two intense doublets as in the spectrum of the (1:1) cluster of the meta isomer, the para isomer basically shows only one and resembles that of the ortho isomer. Identical fingerprints appear in the spectrum of a reaction product ion corresponding to fluoroanilinium (left part of Figure 5c). They may be assigned to the following S_N reaction:

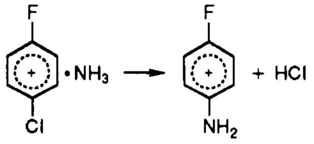


(8)

The very intense metastable product ion in the TOF spectrum in Figure 5 exhibits similar fingerprints (Figure 5e). Its mass was determined in a ancillary measurement. Since its fingerprint suggest a metastable decay of a (1:1) complex, its energy loss ΔE relative to the energy E of the (1:1) precursor allows the determination of the fragment mass $m' = m - \Delta m$ by the following relation:

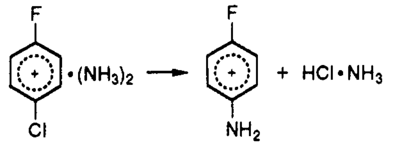
$$\Delta E/E = \Delta m/m$$

To determine the energy E and $E' = E - \Delta E$ we used the ion deceleration region in the ion mirror as high-pass energy filter, by setting the reflecting region to the same potential as the deceleration aperture. Ions with an energy larger than this voltage are not reflected, while those with a lower energy are reflected and detected. The ion intensity of the (1:1) cluster ions and of the metastable ion is shown in Figure 6 as a function of the deceleration voltage. Compared to the sharp onset of the direct ion at about 1538 V, the pass curve of the metastable fragment is shifted to lower energy and considerably broader with a sharp bend in between. The width and sharp bend may be rationalized by the superposition of two different precursor ions fragmenting into one mass channel. Since no isotope splitting appears in the metastable mass peak, one may assume the loss of A^{35}Cl or A^{37}Cl fragment, with an a priori unknown mass A. As shown in Figure 6 one may deconvolute the curve of the metastable by superposition of two curves with an intensity ratio at saturation of 3:1, corresponding to the natural abundances of the chlorine isotopes. From this deconvolution the fragment masses Δm_i are 36 and 38, corresponding to loss of HCl. Since the accuracy of the method is considerably better than half a mass unit, the fragment ion is assigned to the following decay reaction:

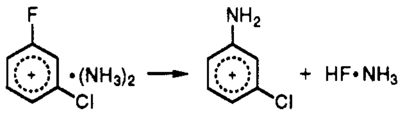


(9)

The product ion with m/e corresponding to fluoroaniline$^+$ exhibits a single fingerprint band (band 4; right part of Figure 5c) which also appears in the spectrum of two isotopes with m/e corresponding to chloroaniline$^+$ (Figure 5b). According to the assignment of the other systems it is assigned to the (1:2) complex, which may decay by nucleophilic substitution according to



(10)



(11)

In summarizing these results two peculiarities in the reactivity pattern of the (1:1) complex are noteworthy: (1) The efficiency of chlorine substitution along the radical channel is much lower than for the other isomers. As summarized in Table I more than 88% of the (1:1) complexes do not react or decay into other channels. (2) The reaction with HCl as leaving group takes place on a microsecond time scale. Its efficiency is much greater than in the case of the meta isomer (Table I). Obviously this slow decay channel is only observable if the rate constant of the competing S_N reaction with chlorine as leaving group is low.

Table I summarizes some relevant data for the systems. In column 4 the efficiencies for chlorine substitution in the collision complex as measured by Thölmann and Grützmacher[1] and the (1:1) clusters after R2PI are compared. The latter are calculated under the assumption that the different fragments have similar detection probabilities. Generally for the intracluster reactions they are a factor of 6–8 larger than for the binary reactions in gas phase collisions.

4. Discussion

1. Reactions in Larger Clusters. For mainly two reasons the present study focused on the reaction behavior of very small mixed complexes: (1) The cluster-specific fingerprints are discrete only for small n, typically for $n < 4$, and are increasingly congested with larger n due to a fast growing number of intermolecular degrees of freedom. The size-specific characterization of the processes is then no longer possible. (2) In larger complexes chemical reactions may get more and more exothermic leading to evaporative cooling, i.e., to fragmentation. In addition, in larger subclusters dET may dominate the reaction behavior. For example, at expansion conditions favoring larger 1:n clusters, the product ions of the S_N reactions studied in this work were never associated with more than one additional solvent molecule. This was surprising since larger precursor clusters were clearly present and solvent subclusters B_n^+ appeared due to dET, with $n = 4$–7. Both the dominance of fragmentation and dET may explain this observation. Since our expansion parameters were optimized for the production of only very small 1:n complexes, the measurements were not sensitive enough to study these reactions in larger cluster. A more systematic investigation of these reactions in larger complexes is still missing.

2. Precursor Assignments. In eq 6 we assigned a 1:2 precursor for the dET product $(NH_3)_2^+$ and due to the identical fingerprints also to *m*-chloroanisole$^+$. On the other hand, larger 1:n complexes with $n > 2$ may possibly decay into the same ionic channel according to the following reaction scheme:

$$(A^+\cdot B_n) \xrightarrow{\text{dET}} A + B_n^+ \xrightarrow{\text{vdWF}} A + B_{n-m}^+ + mB \qquad (12)$$

Since the IP of B_n decreases with n, the dET step should get increasingly exothermic, making subsequent vdW fragmentation (vdWF) more likely. From the ionization and fragmentation energetics of homogeneous ammonia clusters B_n, as reported by Kamke et al.,[12] one may for a B_n precursor derive the following fragmentation appearance potentials (FAP(n)) for a decay into the B_2^+ channel: FAP (2) = 9.19 eV, FAP(3) = 9.34 eV, FAP(4) = 9.56 eV, etc. Hence the fragmentation into B_2^+ from larger clusters requires an increasing amount of energy with increasing cluster size. Since the energies of two photons absorbed in band 5 (Figure 3) add up to 74322 cm^{-1} = 9.21 eV, the overall reaction in eq 12 is endothermic for $n > 2$ and $n - m = 2$.

Further support for the structural assignment may be deduced from a recent IR-depletion spectroscopy experiment by our group[26] for the reactive system of fluorobenzene$^+$ with methanol giving anisole$^+$.[5] The depletion spectrum of the product ion was very similar to that of the free dimer as determined by several groups[19] recently. Since the S_N reactions in eqs 2, 7, 11 with ammonia as nucleophile are very similar to that with methanol, the assignment of a 1:(ammonia)$_2$ precursor for these fluorine displacement reactions is further supported.

We recently assumed for mixed 1:n complexes consisting of an aromatic chromophore and n polar solvent molecules B, a structure with the solvent forming H-bridged subclusters B_n (at least for $n < 5$). By this assumption the reaction behavior of 1:n clusters in dissociative proton-[2] and electron-transfer[4] and nucleophilic substitution reactions[5] could be easily rationalized. Recent results on mixed clusters of benzene with water[20] and methanol,[21] studied by Zwier et al., support this assumption. Breen et al.[22] found differences in the spectroscopic fingerprints of 1:n clusters of phenylacetylene (PA) and ammonia if produced either by solute–solvent coexpansion or by pickup of preformed ammonia cluster in an effusive beam of PA. Although the temperatures were different for a 1:n complex produced by either of these two methods, the clusters exhibited similar spectral shifts for $n = 1$–3 and different shifts for $n > 3$. Therefore the assumption of solvent subclusters seems to be justified at least for $n < 4$. Probably the expansion conditions also play an important role. If the solute is highly dissolved in the solvent a preformation of solvent clusters seems very likely.

The spectra of the product ions from (1:1) complexes of the meta isomer (Figure 3b) exhibit two prominent band groups of similar intensity. For mainly three reasons we tentatively assign each group to a different isomer of the complex: (1) The first group at about 100 cm^{-1} (Figure 3b) strongly resembles a corresponding one in the spectra of the para and ortho isomers. For the second group (bands 3, 4) only very spurious analogous bands may be found in the other cases (Figure 5e (band 3) and Figure 2c, respectively). (2) For the assignment of an intermolecular vibration, the frequency would be unusually large. (3) Fragmentation of a (1:3) complex may be excluded due to the different fringerprints in the dET product ion spectrum in Figure 3d and due to the arguments as given above.

We renounced to calculate possible isomeric structures by simple atom–atom pair potentials as done in our earlier work.[5] In the interaction of an atom with a chlorine substituent, quadrupole contributions may not be neglected, making the usual monopole/dipole model obsolete for an accurate description.

3. Reaction Mechanisms. The intracluster S_N reactions have been recently interpreted by an electron-transfer-induced addition and a proton-transfer-induced elimination step.[4] Shaik and Pross[10] tackled the problem from a more general point of view. In the case of radical cations large activation barriers were postulated, and hence the reactions were classified as "quasi forbidden". In a recent discussion of the model, the factors governing the height of the barriers were considered more carefully. This model was applied very recently by TG to rationalize the reactivity of disubstituted halobenzene isomers with ammonia. In the following the results of the intracluster reactions are also discussed in connection with this model. Qualitative conclusions concerning

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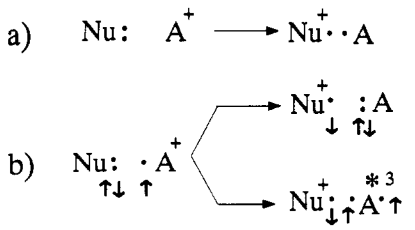

$$\text{a)}\quad \text{Nu:}\ \ A^{+} \longrightarrow \text{Nu}^{+}\cdot\cdot A$$

Figure 7. Nucleophilic attack of a cation according to the arguments of Shaik and Pross: (a) with closed-shell cations, (b) with radical cations. If no additional electron excitation occurs, electron transfer is the only reaction possible.

the nature of the transition states and the reaction energy profile may be drawn.

Before going into details, two salient features of the intracluster reactivity pattern should first be remembered: (1) Chlorine is obviously much more easier substituted than fluorine. This is expected from the strength of the C-F bond, since it is more than 1 eV larger[23] than that of the C-Cl bond. Hence an S_N reaction with fluorine radical elimination is endothermic, while chlorine radical displacement is not. (2) Although S_N reactions of the monosubstituted halobenzenes cations with formation of HCl or HF should be exothermic in bimolecular ion–molecule collisions by about 100–200 kJ/mol (Table I), to the best of our knowledge these reactions have only been observed with I-substituted benzenes. With Cl, F compounds Thölmann and Grützmacher[1,9] found no aniline$^+$ as product ion. While HF elimination similarly was never observed in (1:1) complexes either, HCl elimination obviously occurs if the efficiency of the Cl$^\bullet$ elimination reaction is not high enough. This is evident in the efficiency change in the order from the ortho to the para isomer (Table I). The relative efficiency of the S_N reaction with radical loss decreases in the order (1,2) > (1,3) ≫ (1,4) and increases in the reverse order. In the case of HF elimination although exothermic already in (1:1) clusters, no reaction is observed. Only in (1:2) or larger complexes does this seem to be a very efficient reaction channel. Therefore HF formation in 1:1 complexes must be much more unfavorable than HCl loss, but in the case of a dimer of the nucleophile the reaction efficiency reverses.

As observed for the bimolecular collisions by TG and in the case of (1:1) clusters by the present work, the efficiency of the Cl$^\bullet$ elimination channel strongly depends on the dipole moment of the aromatic chromophore (Table I). This dependence may be rationalized by the Shaik and Pross (SP)[10] model for polar reactions.[1] It is based on the configuration mixing model and usually discussed in the framework of valence bond theory. In the case of nucleophilic attack of cations a charge transfer from the nucleophilic donor (ammonia) to the electrophilic acceptor (cation) is necessary for the formation of a chemical bond in the addition intermediate. As illustrated in Figure 7a and 7b the addition by single electron shift should be different for closed-shell cations and radical cations. Since S_N reactions with closed-shell cations only require a single electron shift, SP postulate low barriers and hence a large reactivity. With radical cations a second electron has to be excited (Figure 7b). Hence higher barriers and lower reactivities are expected. In both cases the barriers are due to an avoided curve crossing of two configurations. With radical cations one is the original $A^+ + Nu$ configuration, the other the $A^{*3} + Nu^+$ CT configuration with the neutral chromophore A excited into the lowest triplet state.

In the case of an aromatic substitution this addition of the nucleophile corresponds to the transition from the relatively weakly bound π complex to the σ intermediate. Thus as illustrated in Figure 8 the height of the first barrier should depend (1) on the energy gap of these two mixing configurations, i.e., on the difference of the IP of the donor and the acceptor plus the energy difference of an S–T transition in A and the difference of the association energies, (2) on the asymptotic energy of the σ complex relative to that of the π complex, and last but not least (3) on the resonance parameter β, which depends on the overlap of the CT-active orbitals.

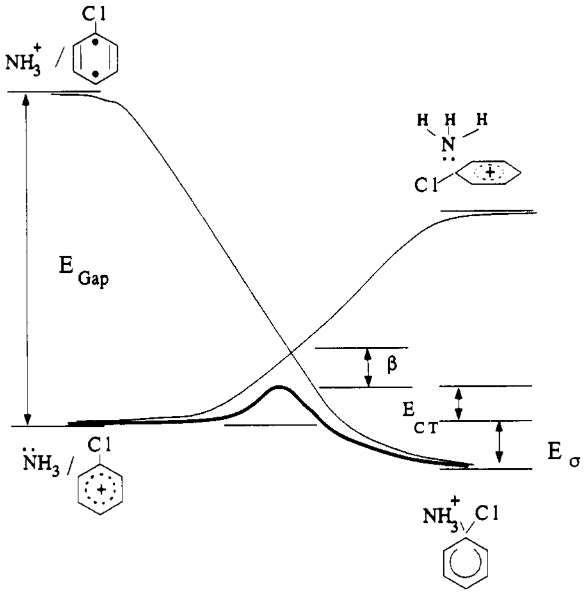

Figure 8. Schematic picture of the origin of the addition barrier for the S_N reaction in chlorobenzene$^+$·ammonia rationalized in the framework of the Shaik–Pross model by configuration mixing.

In the case of bimolecular reactions the π complex, i.e., the dipole adduct, is not stable to back dissociation, while in the cluster it is bound. By the above configuration mixing model, following the arguments of TG, one can easily explain why with increasing dipole moment of the chromophore the reaction barrier is decreased. Since the IPs of the isomers are not very different, the main effect must be due to the lowering of the intermolecular binding energy of the CT configuration. Its nature is a monopole–dipole attraction between the ionized nucleophile and the neutral, electronically excited chromophore in the CT state. Depending on the dipole moment typical values for this energy are 10–30 kJ/mol.

The main difference between the results of TG and of the present cluster work is (1) the >6 times larger efficiency of chlorine substitution in (1:1) clusters as compared to the gas phase reactions and (2) the additional reaction channel with HCl formation. The gas phase reaction with chlorobenzene$^+$ exhibited an efficiency increase at lower kinetic energies.[9] Hence a still stronger increase is expected for a bound reaction system where no back dissociation is possible. The much longer reaction time available in a bound clusters may promote reactions handicapped by entropy. From the high efficiencies in clusters one may deduce barrier heights which are smaller than the binding energy of the π complex, which is a loosely bound ion–dipole adduct with a well depth of 10–50 kJ/mol. From the energetics of the substitution of chlorobenzene$^+$ we determined with 2C-R2PI a rather low activation barrier of $E_a < 5$ kJ/mol.[6] These low barriers seem contradictory to the SP model since the energy gap for an electron shift and an excitation of the chromophore to the lowest triplet state of the aromatics may be estimated at 420 kJ/mol. Hence a rather strong binding energy of the σ complex is necessary to rationalize these low barrier heights. TG calculated with MNDO methods for the substitution in chlorobenzene$^+$ for the σ complex an additional stabilization of 34 kJ/mol relative to the π complex. In a recent study Schöffel[11] calculated with state-of-the-art ab initio methods a much deeper value of 158 kJ/mol. Even with such a large value, the energy splitting in the crossing region due to the resonance

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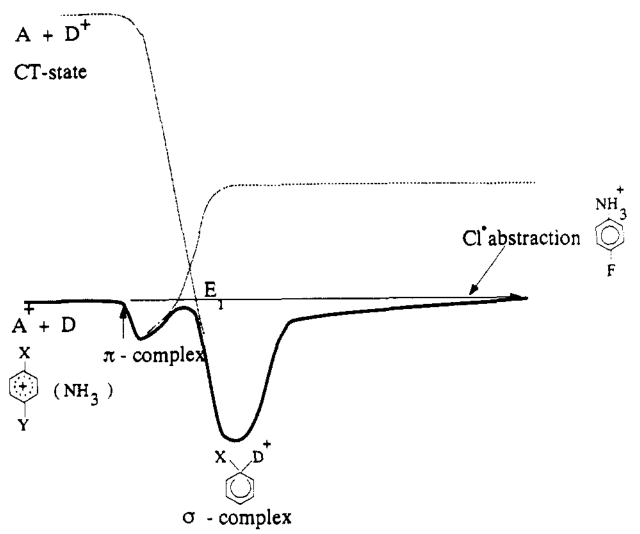

Figure 9. Qualitative reaction profile for the S_N reactions with X• production.

interaction parameter β has to be rather large to give a qualitative explanation for these low barriers. Figure 9 illustrates the general behavior expected for a two-well reaction profile of an S_N reaction.

The HX formation channel is getting dominant when the chlorine abstraction is hindered by an increasing CT barrier. This clearly indicates that a σ complex is probably not a transition intermediate in HX abstraction and not rate determining. We therefore postulate a new decay channel of the π complex, which may compete with Cl displacement only when the barrier for addition is very high. The fact that it is not observed by TG in a bimolecular collision may be explained by a reduced density of states along this reaction coordinate and hence by the dominance of the back reaction for entropy reasons. In a cluster however the latter is not possible, allowing the rearrangement of the complex along this reaction path.

The nature of the transition state is still unclear. One possibility would be a transition state with a temporary three-electron C–Cl bond induced by an electron shift from the nucleophile into the σ^* orbital. The main configuration would be a phenyl cation and Cl^-. An ionized ammonia may easily give away a proton forming an aminyl radical. The latter may be added to the phenyl cation giving aniline$^+$ and HCl. This reaction is believed to take place concertedly, not stepwise. The electrons would be shifted in a cycle. In the case of fluorine substitution this transfer may consume too much energy due to the stronger C–F bond or may be sterically handicapped by the small size of fluorine. In larger clusters electron shift from the nucleophile into the C–X bond may be facilitated due to a reduction of the IP of the solvent subcluster B_n. This decrease of the IP is in the case of an ammonia dimer about 96 kJ/mol.[12] Hence with dimers and trimers of the nucleophile the reaction should be promoted. On the other hand proton transfer should be facilitated by the greater structural flexibility and a greater ease to transfer a solvated as compared to a "free" proton.

If no σ complex is formed, the electron shift may result in the neutralization of the aromatic and the ionization of the subcluster giving $(Nu)_n^+$ cations. The occurrence of each reaction path is controlled by both the reaction enthalpy and entropy. In the case of a (1:1) cluster the elimination of chlorine is the only elimination step energetically allowed (Table I) since the formation of a free ammonia cation is endothermic. In the case of an ammonia dimer both the formation of aniline$^+$ or alternatively of an ionized solvent cluster are exothermic paths. Therefore the occurrence of both a dET and a S_N reaction may be understood from this model very easily.

Surprisingly in (1:2) complexes one generally does not observe radical abstraction, but HX formation with a propensity for HF over HCl. This is possibly due to the much larger endothermicity of these reactions (Table I).

The consequences of this model are the following: (1) The size dependence of the overall efficiency of an S_N reaction should depend on the ionization potential of the nucleophile, if the reaction is of the S_N2 type, i.e., runs via an electron-transfer step. From the size dependence of S_N reactions of disubstituted halobenzenes with ammonia and of other halobenzenes with methanol[5] and with water,[7] it has been found that the minimum size of the nucleophilic subcluster necessary for a substitution increases with increasing difference in the ionization potentials of chromophore and nucleophile. That could explain the recent observation made by Jouvet et al.[7] that with *p*-difluorobenzene$^+$ and water (IP = 12.61 eV) the smallest solvated cluster ion for which a nucleophilic attack is observed is the 1:3 complex. (2) The second rate-determining factor should be the energetics of proton transfer. A transition state determined by proton transfer may be considerably lowered by a polar solvent molecule.

5. Conclusion

The study of S_N reactions of solvated aromatic cations revealed a strong dependence both on the structure of the cation and on the number of solvent molecules. Two types of substitution reaction occur, i.e., either X or HX formation. We tentatively assumed for both reactions transition states determined by an electron shift from the nucleophile subcluster either into the aromatic ring or the R–Cl bond. Simple bond breaking with radical loss is rationalized by an concerted electron shift, the barrier of which was discussed in the framework of the Shaik–Pross model for polar reactions. Depending on the C–X bond strength, either a direct elimination of a halogen radical X or a proton-transfer-assisted, solvent-catalyzed hydrogen halide (HX) abstraction is observed. With the S_N reaction competes a dET reaction. In complexes with a larger solvent moiety the latter process seems to be dominant. While in binary ion–molecule reactions the reactions with HCl elimination are not observed, it occurs in (1:1) clusters if competing processes are not very efficient. Production of HF, on the other hand, is only observed in the (1:2) and larger complexes. From these results a new dimension of cluster ion reactivity in comparison to gas-phase ion–molecule reactions becomes evident, which is due to solvation and due to the fact that the ionic complexes are bound. Thus mixed clusters should be more realistic models for investigating chemistry under microsolvation, i.e., at the very beginning of the condensed phase.

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