The same factors as discussed for the fast decay can account for such changes.

At pH 11, our computer simulations predict that the addition of chloride ions to solution up to 4×10^{-2} M produces a negligible change in the behavior of the reaction system for both the fast and slow processes. This is because, even at the highest concentrations of Cl⁻ added, there is only a very tiny fraction in the form of Cl⁻_{ads} due to both the high concentration of OH⁻ in solution and the more than 100-fold difference in the values of the rate constants for adsorption of these ions.

No computer simulations were performed on systems in which nonparticipating adsorbing cations were added to the reaction system (which would equilibrate according to eq 12). However, it is evident from the results obtained above that only at high pH's (where the particles become negatively charged) would one expect to observe large effects on the behavior of the system. Very little adsorption of these cations on the catalyst at the lower pH's would take place due to the already high positive charge that the particle carries in this pH regime.

Conclusion

In this investigation, we have refined the previous model describing the reaction of a reduced acceptor, MV^{*+} , with a colloidal catalyst particle, Pt_c followed by the generation of hydrogen from water. By dissecting the relevant rate constants into their activation and diffusion-controlled components and introducing an electrostatic model based on a good approximate solution for the Poisson-Boltzmann equation for a charged sphere immersed in a mixed electrolyte, we have greatly extended the ability of our mechanistic model to predict the behavior of the reaction system. In particular, the present treatment allows us to reproduce, with an impressive degree of agreement, the experimental results obtained for the reaction system over the pH range 1–11 without the need of internally optimized electrostatic factors. Furthermore, the computer simulation technique has been used to make predictions and interpret data concerning both salt and particle size effects and has also expanded the understanding of deviations from first-order kinetics with respect to Pt concentration.

While our model can still undergo further refinements in order to account for a distribution of sizes of catalyst particles³⁴ and the effects of polymer stabilizer on the system,³³ we believe that our studies have produced for the first time a kinetic model with a high enough degree of sophistication to be incorporated into reaction schemes in which photochemical generation of the reduced acceptor takes place. We intend to carry out simulations of such systems in the near future. Furthermore our kinetic model contains many of the features of simpler models put forward for example by Henglein³⁵ where similar intermediates have been proposed or by Miller and co-workers¹² and Henglein and Lilie³⁶ where platinum and other colloidal particles have been considered as microelectrodes and the charging and discharging processes have been treated from an electrochemical rather than a kinetic point of view. Computer modelling of other colloidal particles where slightly different mechanisms may operate is also currently being undertaken.

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Cluster Beam Chemistry: Adducts of Hydrogen Halides with Ammonia Clusters

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A molecular beam of ammonia clusters $(NH_3)_m$, with n = 1, 2, ..., 20 or more, was generated by expansion from a supersonic nozzle and crossed with a beam of hydrogen halides HX, with X = Cl, Br, or I. This produced adduct complexes $(NH_3)_mHX$ with m as large as 15. No such complexes were observed for scattering from other crossed beams, including Ar, Kr, O_2 , Cl_2 , CH_3Br , CH_2CF_2 , CCl_2F_2 , CF_3Cl , and CH_3CHF_2 . The smallest complexes observed have m = 1 for HCl and HBr but m = 3 for HI. The mass spectra of the complexes also differ noticeably with respect to the regions showing substantial fragmentation; completion of the first solvation shell appears to reduce fragmentation. Together with thermochemical data, these observations suggest that for sufficiently large clusters the complex formation involves proton transfer (more facile as HCl \rightarrow HBr \rightarrow HI) and is driven by solvation of the resulting $NH_4^+X^-$ ion pair by the "extra" NH_3 molecules in the reactant cluster.

Introduction

Much of the molecular beam repetroire developed for study of bimolecular collisions can be applied to processes akin to liquid-phase reactions. This involves simply operating supersonic nozzle sources in a regime that generates large yields of molecular clusters.¹⁻³ Collision experiments with such cluster beams have examined exchange reactions,⁴⁻⁸ inelastic energy transfer,⁹ and electron-transfer processes.¹⁰ This paper describes cluster reactions involving at least partial proton transfer. Whereas mo-

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Figure 1. Mass spectrum of the $(NH_3)_n$ beam; the predominant detected ion is actually $(NH_3)_{n-2}NH_4^+$: (a) low-resolution mass spectrum for n = 4-13; (b) high-resolution mass spectrum for n = 6 and 7.

nomeric ammonia molecules do not react with hydrogen halides, we find clusters of ammonia do react. Solvation by the "extra" molecules in the cluster evidently drives an otherwise endoergic or recalcitrant reaction, as is often the case for reactions in solution.

Although ammonium halides are familar species and form ionic crystals,¹¹ little experimental information is available concerning the structure, bonding, and thermochemical properties of gas-phase NH₄X molecules. Goldfinger and Verhagen observed NH₄Cl in a high-temperature mass spectrometric study of the vapor above the solid.¹² Ault and Pimentel assigned some infrared bands of NH₄Cl in a matrix isolation experiment¹³ and concluded that the bonding involves partial proton transfer, corresponding to $H_3N\cdots H^{\delta+}\cdots Cl^{\delta-}$. This agrees with a theoretical prediction by Clementi¹⁴ who computed a detailed reaction path for $NH_3 + HCl$ \rightarrow NH₄Cl and evaluated the overall reaction enthalpy as $\Delta H \simeq$ 20 kcal/mol. Electronic structure calculations for NH_4F by Kollman and Allen indicate a much more reticient interaction.¹⁵ This complex involves a strong hydrogen bond, H₃N…HF, in which the parent molecules retain their individuality. Further calculations have examined how solvation can induce the hydrogenbonded complex to undergo proton transfer via

$$H_3N \cdots HF + nH_2O \rightarrow (NH_4^+F^-)(H_2O)_n$$

Kollman and Kuntz¹⁶ found that four or more molecules are required, while Noell and Morokuma¹⁷ concluded that about 10 (corresponding to two solvation shells) are needed to enable proton transfer. However, for the H₁N...HI complex, similar calculations by Kollman, Dearing, and Kochanski¹⁸ find that proton transfer may occur even without solvation and conclude that one extra NH₃ molecule should suffice to strongly favor complete proton transfer. More recently Jaisen and Stevens¹⁹ have calculated the structure

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Figure 2. Velocity distributions for various clusters in the (NH₃), beam, with n = 7, 9, ..., 18. The maximum intensity for each distribution is normalized to unity.

of the $NH_3 + HX$ (X = Cl, Br, I) complexes. For both the HCl and HI complexes, they find only a single minimum on the potential surface, in agreement with other work.^{20,21} For the HI complex, they find two minima at the SCF level, one corresponding to a hydrogen-bonded complex A and one corresponding to an ion-pair structure B. Relative to the dissociation limit, B is more stable (8.8 kcal/mol) than A (4.0 kcal/mol). Inclusion of a correlation correction and zero-point effects determined at the harmonic level brings B (now at 1.0 kcal/mol) somewhat above A (4.1 kcal/mol). These theoretical results suggest that the ion-pair structure for NH3...HI lies low enough in energy to be stabilized by solvation and thus facilitate proton transfer.

Experimental Section

The crossed molecular beam apparatus²² is equipped with a quadrupole mass spectrometer mounted on a rotatable platform to permit angular distribution measurements. The ammonia clusters were generated by expansion from a quartz supersonic nozzle with diameter either 0.06 or 0.13 mm and a backing pressure of 1 atm. The reactant beam was generated by expansion from a quartz nozzle with diameter of 0.13 mm and a backing pressure ≤ 150 Torr. Both beams were operated at 295 \pm 5 K and had angular widths of 2° (fwhm). The resolution of the quadrupole mass spectrometer was variable up to $M/\Delta M \sim 100$ and its range permitted detection of $(NH_3)_n$ clusters up to n =22. A mass spectrum of the parent ammonia cluster beam is shown in Figure 1. As in other work with ammonia cluster beams,²³ the intensity distribution exhibited an essentially exponential decrease with cluster size, strongly dependent on the source pressure. Also, the dominant ion produced by electron bombardment (at 30-70 eV) is a solvated ammonium ion, $[(NH_3)_{n-2}NH_4^+]$, corresponding to loss of NH_2^- from the parent

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Figure 3. Low-resolution mass spectra $(M/\Delta M \sim 20)$ of NH₃ clusters scattered by various molecules. Abscissa scales indicate value of *n* for the nominal location of peaks from (NH₃)_n; the predominant detected ion is actually (NH₃)_{n-2}NH₄⁺ and thus the actual mass is given by 17(*n* - 2) + 18. (a) Spectra for scattering with *n* = 7-22 at a laboratory angle of 80° from HI, CCl₂F₂, and Cl₂. (b) Spectra for scattering with *n* = 4-20 at 85° from HBr and Cl₂. (c) Spectra for scattering with *n* = 4-20 at 85° from HCl, Ar, O₂. Progressions of full circles shown for (a) and (b) indicate location of mass peaks for (NH₃)_mX adducts.

 $(NH_3)_n$ cluster. The lower cluster peaks show a doublet with a splitting of 1 mass unit. Temperature- and pressure-dependent studies exhibit the falloff behavior expected for a cluster beam. For temperatures of 300–400 K, the amount of fragmentation for a given cluster is independent of temperature and pressure in the range 570–920 Torr.

To obtain internally consistent mass scans of the scattered clusters, the signal from the ion detector photomultiplier was sent to a lock-in amplifier (Princeton Applied Research 120) and displayed on a chart recorder (Hewlett Packard Moseley 7100 B). A 3-s time constant was used and the mass spectrum was swept at 0.25 amu/s by varying the rf voltage applied to the quadrupole. As in Figure 1, to confirm peak assignments the low-resolution scans thus obtained (typically at $M/\Delta M \sim 20$) were complemented by ion counting of individual peaks at higher resolution $(M/\Delta M \sim 100)$. Time-of-flight analysis of the cluster beam indicated that the velocity of the larger clusters is within 10% of that for the NH₃ monomer component (\sim 1000 cm/s). Sample velocity spectra are given in Figure 2. The relative kinetic energy in collisions of $(NH_3)_n$ with HI is 10 kcal/mol for n = 21and correspondingly less (in the ratio of the reduced masses) for small clusters or lighter reactant molecules.

Results and Discussion

Figure 3 shows mass spectra of clusters scattered from beams of various molecules colliding with the ammonia beam. The scans in (a) were obtained with the 0.13-mm nozzle and pertain to an angle 10° from the ammonia beam; (b) and (c) were obtained

with the 0.06-mm nozzle and pertain to 5° from the ammonia beam. As illustrated by comparison of the data for Cl_2 in (a) and (b), the distribution of scattered clusters does not change significantly with the nozzle diameter, at least for the narrow range of observation angles examined here. As usual in cluster beam experiments,²⁴ interpretation of the data is severely constrained by uncertainties regarding the contributions from fragmentation of the clusters by electron bombardment or collision-induced dissociation, or from van der Waals bond exchange reactions. However, this caveat does not affect the major feature of qualitative interest in Figure 3. For all the molecules examined, except the hydrogen halides, the mass scans show only a regular progression of peaks attributable to scattered ammonia clusters, $(NH_3)_n$. The hydrogen halides produced additional peaks corresponding to adduct clusters, $(NH_3)_m HX$. (Note that *n* refers to the reactant cluster while m refers to the product cluster adducts.)

Even at the low resolution of Figure 3, the contrast between adduct formation and benign scattering is readily discerned. The mass of CCl_2F_2 (m = 121) is similar to that for HI (m = 128). If only elastic scattering were observed, the peak distributions should be very similar. This is clearly not the case as evidenced by the shift in the masses of the peaks and the much higher intensity at higher masses in the HI spectrum. Comparing the HBr spectrum with that for Cl_2 , again one finds higher intensity at higher masses for the HX spectrum even though the masses of HBr (m = 80) and Cl_2 (m = 71) are similar. The pronounced increase in the intensity of higher mass peaks in the HCl (m = 36) mass spectrum as compared to those in the O_2 (m = 32) and Ar (m = 40) mass spectra are again consistent with adduct formation for HCl and benign scattering for O_2 and Ar.

In addition to the reactants shown in Figure 3, experiments were also done with Kr, CH₃Br, CF₃Cl, CH₂CF₂, and CH₃CF₂H as scattering partners. Again there was no evidence for adduct formation in the mass spectra at 80°. Data on CH₃Br was obtained at two angles, 77.5° and 75°. The intensities of the $(NH_3)_n$ clusters decrease and the maximum change from the parent beam distribution shifts to lower size ammonia polymers with decreasing angle.

Hydrogen Halide Complexes. The mass scan for the HI case displays most clearly the adduct complex peaks. The peak from scattered HI (m = 0) is distinct. There is little if any discernible evidence of complexes with one or two ammonia molecules (m = 1, 2) but peaks for adduct complexes containing three or more ammonia molecules $(m \ge 3)$ are apparent. The peaks for $m \ge$ 3 clearly do not fall on the positions expected for $(NH_3)_n$. Rather, they lie between the expected positions for these peaks, where HI(NH₃)_m should be observed. It is also striking that part of the spectrum (m = 3-6 and n = 12-15) evidently suffers more pronounced fragmentation than elsewhere. For the region corresponding to m > 4 and n > 13, the peak heights for the adduct complexes are comparable to or greater than for the ammonia clusters. Thus $(NH_3)_m$ HI complexes with m = 3 up to 14 were readily observed.

For the HBr case, small but distinct peaks appear for adduct complexes with one or two ammonia molecules. Again, the spectrum has a ragged region (m = 2-5 and n = 8-11) indicative of marked fragmentation, and larger adducts give increasingly prominent contributions, eventually becoming the dominant species in the high-mass region. The $(NH_3)_n$ HBr complexes with m = 1-13 were observed.

For HCl, the low-resolution mass spectrum offers no evidence of adduct complexes because the mass of HCl is so close to that of two ammonia molecules. With higher resolution $(M/\Delta M =$ 100), it was possible to discern $(NH_3)_m$ HCl complexes with m= 1, 2, 3. Larger adduct complexes presumably exist, but still higher resolution would be necessary to identify them; only one mass unit separates $(NH_3)_m$ HCl₃₅ from $(NH_3)_{m+1}NH_4^+$. It is noteworthy that for HCl scattering the low-resolution mass scan

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Figure 4. Distribution of $(NH_3)_mHX$ adducts from reaction of (a) HI and (b) HBr with ammonia clusters. For HCl such data (requiring higher resolution) were obtained only for m = 1, 2, 3 and resembled those for HBr. Stick figures constructed from mass spectra shown in Figure 1; relative intensities are estimates of peak areas, without allowance for variations in detection efficiency or fragmentation. Velocity vector diagrams show beam geometry and indicate laboratory scattering angles.

does not exhibit a region of more pronounced fragmentation like those seen for HBr and HI.

Figure 4 compares the intensity distribution of adduct complexes observed for HBr and HI scattering. In terms of the "adduct number", m, the distributions are rather similar except that for HI apparently starts at m = 3 rather than m = 1 and peaks at m = 10 rather than m = 8. Likewise, the intensity is distinctly lower in the regions showing evidence of enhanced fragmentation: m = 3-7 for HI and m = 2-5 for HBr.

In order for the adduct to be detected in the mass spectrometer, kinematic constraints must be fulfilled. The adduct complex must accommodate the collision energy and the reaction exoergicity in some manner. This can happen in three ways: (i) an exchange reaction of HX with part of the parent cluster, with the residual part carrying off some energy; (ii) simple addition of HX to the full cluster, followed by subsequent ejection of NH_3 units to stabilize the adduct complex; (iii) randomization of the excitation energy in the internal modes of the adduct which enables the complex to persist long enough to travel to the detector.

For mode (i) there is no constraint to assess. For mode (ii) we require some energy estimates. The strength of the NH_3 - NH_3 hydrogen bond is 4.1 ± 0.4 kcal/mol.²⁵ The mean relative kinetic energy for $(NH_3)_n + HX$ collisions ranges from about 6 to 10 kcal/mol as *n* and X vary. However, the pertinent kinetic energy is likely to be substantially smaller if the collision is impulsive and involves just part of the parent cluster.¹⁰ Thus unless the exoergicity is large, at most only two NH_3 molecules could be ejected from an adduct complex and more likely one or none. This presumes that an ejected molecule is linked to the parent cluster by only a single hydrogen bond. Since most clusters may involve chains, rings, etc., each NH_3 will probably be linked by at least two hydrogen bonds, so ejection of an NH_3 seems unlikely.

For mode (iii) the adduct coincides with the centroid velocity vector. The minimum lifetime required of the complex is given by $\tau = d/v$ where d is the distance from the scattering center to the detector (14.4 cm) and v is the velocity of the centroid (~1100 m/s). Thus the requisite adduct lifetime for this mode exceeds 10^{-4} s. A very rough estimate of the corresponding potential well depth for the adduct can be obtained from the lifetime formula²⁶ for RRK theory,

$$\tau = \omega^{-1} [E / (E - E_0)]^{s-1}$$

Here ω is an average vibrational frequency, E the total energy

TABLE I: Enthalpy Changes for Proton Transfer

processes (gas phase)	ΔH° , kcal/mol		
	X = I	X = Br	X = Cl
$\frac{(1) \text{ NH}_3 + \text{H}^+ \rightarrow}{\text{NH}_4^+}$	-205 ± 1	-205 ± 1	-205 ± 1
(2) $HX \rightarrow H^+ + X^-$	$+314.4 \pm 0.5$	$+323.5 \pm 0.5$	$+333.5 \pm 0.5$
(3) $NH_4^+ + X^- \rightarrow NH_4^+X^-$	-101 ± 5	-105 ± 5	-111 ± 5
$(4) N\dot{H}_3 + HX \rightarrow NH_4^+X^-$	$>8.4 \pm 6.5$	$>13.5 \pm 6.5$	>17.5 ± 6.5

of the system, E_0 the well depth, and s the number of active vibrations. We estimate $\omega^{-1} \sim 10^{-13}$ s as roughly representative for frequencies (~100-1000 cm⁻¹) associated with a hydrogen bond and take $E \sim 10$ kcal/mol. Then well depths E_0 of 9, 8, 5, and 2 kcal/mol require corresponding values of s to be about 10, 15, 30, and 90, respectively, in order to have $\tau > \sim 10^{-4}$ s. For a (NH₃)_mHX cluster, the number of active modes can be minimally approximated as 3m. Thus the corresponding cluster sizes for these well depths are very roughly 3, 5, 10, and 30, respectively. These estimates indicate that mode (iii) is plausible in our experiments.

The mere detection of these $(NH_3)_mHX$ complexes of course indicates nothing about the nature of the adduct binding. Some likely inferences can be made, however. The minimum cluster size required to permit proton transfer can be estimated from thermochemical data^{27,28} and an empirical correlation of bond strengths for ionic molecules.²⁹ If proton transfer occurs, the ionic ammonium halide salt formed can be expected to suffer drastic fragmentation on electron impact³⁰ unless protected by a solvation shell of ammonia molecules. These considerations provide a rationale for the m = 3 threshold for HI and the regions of enhanced fragmentation seen for HI and HBr but not HCl. Before discussing this rationale, we examine some thermochemical aspects.

Thermochemistry of Proton Transfer. Table I gives the auantities needed to estimate the enthalpy for formation of $NH_4^+X^-$ from NH_3 . The first two processes listed involve the proton affinities for the NH₃ molecule (basicity) and the X⁻ ions (acidity); these are well established.^{27,28} The third process involves the bond strengths for dissociation to an ion pair; these were estimated from a correlation²⁹ with the sum of ionic radii as determined from the extensive data for alkali metal halides.³¹ Since the effective ionic radius³² for the NH_4^+ cation (1.48 Å) is the same as for Rb^+ , the correlation predicts the $NH_4^+X^$ dissociation energy is the same as that for the corresponding rubidium halide. Additional contributions of 2, 2, and 3 kcal/mol were included for the iodide, bromide, and chloride, respectively, to account for the contribution from hydrogen bonding in the ammonium halides.³² Reaction with complete proton transfer corresponds to the fourth process, for which the enthalpy change is the sum of those for the first three processes. The net uncertainty includes a random component of about 5 kcal/mol, due solely to scatter in the empirical correlation.²⁹ There may also be a systematic component, since data for other molecules indicate that the dissociation energies to form ion pairs would be larger than given by the empirical correlation if the bonding is not fully ionic.³³ The enthalpy changes obtained in the bottom line of Table

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I thus are expected to be upper limits, as indicated. According to these estimates, proton transfer in reaction of a single ammonia molecule with a hydrogen halide is endoergic and becomes substantially more so as $I \rightarrow Br \rightarrow Cl$.

The same conclusion may be reached by another route, discussed for the X = Cl case by Ault and Pimentel.¹³ The sum of the first two processes in Table I gives the ΔH° for the gas-phase formation of NH₄⁺ and X⁻ from NH₃ and HX; the values obtained are 106, 116, and 126 kcal/mol for X = I, Br, and Cl, respectively. To offset this endoergicity by Coulomb attraction requires that the ions (treated as point charges) be placed 3.12, 2.86, and 2.63 Å apart, respectively. These distances are about 0.1 Å shorter than the equilibrium bond lengths estimated as noted above from comparison with the rubidium halides; these are 3.17, 2.95, and 2.78 Å, respectively.³⁴ This offers a simple heuristic interpretation of the endoergic character of proton transfer between NH₃ and HX molecules.

In contrast, the calculations of Clementi,¹⁴ and Kollman and Allen¹⁵ show that for the X = Cl case adduct formation with only "half-proton transfer" is excergic, with $\Delta H^{\circ} \simeq -20$ kcal/mol. The subsequent calculations^{18,19} for the X = I case indicate that proton transfer becomes more favorable as Cl \rightarrow Br \rightarrow I, particularly when additional ammonia molecules are present to foster charge transfer via solvation. Considering the error limits, our estimates for the X = I case are consistent with the most recent¹⁹ theoretical results.

Fragmentation and Solvation. Our data for the X = I case may be plausibly interpreted in terms of proton transfer augmented by solvation,

 $(NH_3)_n + HX \rightarrow (NH_4^+X^-)(NH_3)_{m-1} + (NH_3)_{n-m}$

Since measurable yields of the adduct complex are not observed until m > 3, we might infer that at least two solvent NH₃ molecules are required to induce the proton transfer. However, we suspect that this interpretation is not correct. The fact that we see m = 1 adducts for X = Cl and Br suggests that a m = 1 adduct should also be formed for the X = I case. In view of the thermochemical and electronic structure data, we expect the significant difference is that the bonding in the H₃N···HCl and H₃N···HBr adducts is hydrogen bonding and is much less ionic than in the H₃N···HI case. Accordingly, we expect that the latter adduct will suffer more drastic fragmentation on electron bombardment and thus disappear from the mass spectrum. This phenomenon is well-known for ionic molecules A^+X^- such as the alkali metal halides,³⁰ for which electron impact yields the A⁺ fragment almost exclusively.

Supporting evidence was sought in auxiliary single-beam experiments. A beam containing (NH₃)_mHI complexes was produced by vaporizing NH4I from an oven operated at 600 K with an NH₃ overpressue of ~ 100 Torr. The corresponding vapor pressure of NH_4I is estimated to be ~ 1 Torr. This yielded solvated salt clusters, $NH_4I(NH_3)_{m-1}$ with m = 1-6 as illustrated in Figure 5. The dominant peak in the spectrum has m = 0 and comes from I or HI. The m = 1 peak is very weak, but the m = 2 complex is clearly evident. The large peak at m = 3 is due to an obscuring impurity, probably W from the electron emission filament. Although the m = 4 peak is weak, that for m = 5 is stronger. The increase for m = 5 is noteworthy since in view of the relatively low source pressure, the concentration of complexes in the beam is expected to fall off rapidly with increasing size. Thus fragmentation by electron impact indeed appears to be more drastic for smaller clusters. In any case, this experiment shows that the m = 2 complex exists, so only one NH₃ solvent molecule is sufficient to obtain a stable adduct.

The substantial fragmentation seen in the mass spectra for $(NH_3)_mHI$ adducts with m = 3-6 and for $(NH_3)_mHBr$ with m = 2-5, but not for $(NH_3)_mHCl$, is likewise consistent with a marked decrease in the ionic character of the bonding for $X = I \rightarrow Br \rightarrow Cl$. The fragmentation suggests that charge transfer

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Figure 5. Mass spectrum obtained for $(NH_3)_m$ HI in a single beam. The temperature of the $NH_4^+I^-$ salt oven is 600 K corresponding to a vapor pressure of ~ 1 Torr and the overpressure of NH_3 is ~ 100 Torr.

is appreciable for the X = Br case but detection of a m = 1 adduct indicates it is less complete than in the X = I case, at least until more NH₃ solvent molecules are added. The extent of the fragmentation region allows us to estimate the size of the first solvation shell. Until the first solvation shell is complete, the NH₄⁺X⁻ ion pair is not fully protected by solvent and can be expected to suffer substantial fragmentation on electron impact. Once the solvation shell is complete, fragmentation should occur less readily. Taking into account that normal fragmentation of NH₃ clusters involves loss of an NH₂ group, we estimate from the fragmentation regions that the first solvation shell for NH₄⁺Ir⁻ contains about six or seven ammonia molecules and for NH₄⁺Br⁻ about five or six molecules.

For the HCl scattering, the lack of fragmentation is consistent with the large endoergicity for proton transfer. We infer that the solvation required to produce an ion-pair adduct corresponds to completing at least the first solvation shell. Thus, if sufficiently large clusters induce proton transfer, its presence is masked by the protecting solvent shell. By analogy with the X = Br case, this shell should require five or six ammonia molecules, although, because of the endothermicity of proton transfer, a single solvent shell may not be sufficient.

The compound CF_2HCH_3 could also form an ion pair $[CH_3CF_2]^-[NH_4]^+$. The acidity of CF_2HCH_3 is 374 kcal/mol.³⁵ If the energy for the process analogous to step 3 in Table I is roughly estimated as -110 kcal/mol, the corresponding step 4 would be endoergic by about 60 kcal/mol, with X = $[CH_3CF_2]^-$. This large endoergicity is consistent with our failure to observe complex formation for this system.

We note that our evidence for proton transfer in the reaction of ammonia clusters with HI is akin to results of a study of the reaction of alkali metal atoms with van der Waals clusters of methyl iodide by Ureña, Bernstein, and Phillips.⁵ Their study employed surface ionization detection rather than mass spectroscopy, but kinematic analysis of the product angular distribution identified an adduct species of the nominal form $M(CH_3I)_{n-1}$, M = K or Rb and n > 3. In view of the prevalence of electron transfer ("harpooning") in alkali metal atom reactions,³⁶ it seems likely that these adducts correspond to an alkali halide ion pair solvated by extra methyl iodide molecules from the parent cluster.

Registry No. $(NH_3)_3HI$, 61218-86-8; $(NH_3)_4HI$, 12395-74-3; $(N-H_3)_5HI$, 60874-41-1; $(NH_3)_6HI$, 113598-35-9; $(NH_3)_7HI$, 78006-18-5; $(NH_3)_8HI$, 113598-36-0; $(NH_3)_9HI$, 113598-37-1; $(NH_3)_{10}HI$, 113598-

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38-2; (NH₃)₁₁HI, 113598-39-3; (NH₃)₁₂HI, 113598-40-6; (NH₃)₁₃HI, 113598-41-7; (NH₃)₁₄HI, 113598-42-8; (NH₃)HBr, 12124-97-9; (N-H₃)₂HBr, 12010-89-8; (NH₃)₃HBr, 113598-43-9; (NH₃)₄HBr, 12010-90-1; (NH₃)₅HBr, 12010-91-2; (NH₃)₆HBr, 113598-44-0; (NH₃)₇HBr, 78006-02-7; (NH₃)₈HBr, 113598-45-1; (NH₃)₉HBr, 113598-46-2; (N- $H_3)_{10}HBr$, 113598-47-3; $(NH_3)_{11}HBr$, 113598-48-4; $(NH_3)_{12}HBr$, 113598-49-5; (NH₃)13HBr, 113598-50-8; (NH₃)HCl, 12125-02-9; (N-H₃)₂HCl, 113598-51-9; (NH₃)₃HCl, 113598-52-0; NH₃, 7664-41-7; CH₃Br, 74-83-9; CF₃Br, 75-72-9; CH₂CF₂, 75-38-7; CH₃CF₂H, 75-37-6; CCl₂F₂, 75-71-8; HI, 10034-85-2; HBr, 10035-10-6; HCl, 7647-01-0; O₂, 7782-44-7; Cl₂, 7782-50-5; Ar, 7440-37-1; Kr, 7439-90-9; I⁻, 20461-54-5; Br⁻, 24959-67-9; Cl⁻, 16887-00-6.

Models of Electron-Transfer Reactions at a Biological-Membrane-Covered Electrode–Solution Interface

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Three models of electron-transfer processes at a biological-membrane-covered electrode-solution interface are put forward to explain the observed current density-overpotential dependences. The wet protein embedded in the biomembrane is assumed to act as a semiconductor. In model A, the transition of an electron is assumed as due to a transport (diffusion and drift) process in the biomembrane. A direct tunneling of electrons from the underlying metal surface through the barrier in the biomembrane to redox species in solution is assumed in model B. In model C, a resonance tunneling of electron from the metal surface via the resonance states in the band gap of the semiconducting protein in the biomembrane to the species in the solution is assumed. The current density-overpotential dependences from the transport model (model A) agree well with the experimental results. For biomembrane thickness of 70 Å, the results of current density from the resonance tunneling model (model C) agree fairly with the experimental findings. The agreement between the results of theory and experiment suggests that electrons can, in fact, transfer through the biomembrane and react with the redox species in a solution.

I. Introduction

Investigation of electron-transfer reactions at a biological membrane-solution interface has been of considerable concern in recent times.¹⁻⁴ After the hypothesis of Szent-Gyorgy⁵ that electron-transfer reactions across a biological membrane are responsible for many biological processes, several experimental investigations have been carried out to determine the electrical conductivity of wet proteins in biomembranes.⁶⁻⁸ It was found that a wet protein behaves as a semiconductor and this behavior is in agreement with the solid-state mechanisms of charge transfer in a protein as suggested by Cope.⁹ Though wet proteins are considered to behave as a semiconductor its conductivity values¹⁰ are the boarder line values of that of a semiconductor and an insulator. However, the solid-state behaviors of semiconductors and insulators in terms of band structure and band bending are similar.¹¹ The only difference is in the magnitude of band gap and consequently in the magnitude of conductivity.

Williams¹² portrayed the biological reactions as involving charge transfer between solid and liquid phases. However, this treatment

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Recently, some experiments have been carried out by Habib and Bockris to explore the electron-transfer processes and the corresponding redox reactions across a biomembrane^{1,2} and also at a biological-membrane-covered solid electrode.^{3,4} In the former,^{1,2} it was found that a current density across a bilayer lipid membrane varied exponentially with the potential applied across the membrane, as expected if this membrane potential were controlled by redox processes involving electron-transfer reactions at two membrane-solution interfaces. In the latter^{3,4} a layer of lipid membrane (with or without a protein) have been absorbed on a metal electrode and the current-potential dependences were measured after the electrode was brought into contact with an aqueous solution of redox species. From the observed currentpotential dependences it was pointed out that the electron exchange occurred between the protein-containing membrane surface and the redox species in the solution.^{3,4}

In this paper we have made a theoretical analysis to unravel the mechanisms or channels by which electrons could possibly transfer across a protein-containing membrane covered electrode (Figure 1) and give rise to the observed current potential dependences.^{3,4} For this we have formulated expressions of current density as a function of electrode potential considering three possible mechanisms of electron-transfer processes through the protein-containing biological membrane to redox species in so-

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