Proceedings of the 1995 Workshop on

DISSOCIATIVE RECOMBINATION:

Theory, Experiment and Applications III

Ein Gedi, Israel 29 May – 2 June 1995

editors

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THE EFFECT OF CLUSTERING WATER MOLECULES ON THE RATE AND MECHANISM OF THE $H_3O^+(H_2O)_n+OH^-(H_2O)_m$ REACTION

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ABSTRACT

A dramatic change in the recombination rate and mechanism for the reaction of H_3O^+ and OH^- is observed upon the addition of three solvating water molecules to each reactant. These reactions have been studied by detecting the fast neutral products resulting from electrostatic merging of mass selected beams of oppositely charged cluster ions. The reactions have been studied as a function of clustering, center-of-mass collision energy, and fast neutral spot size.

1. Introduction

Molecules often behave differently at bulk than as free gas phase monomers. To cite just one example, a sodium chloride molecule in water spontaneously dissociates into free aqueous ions, while the same process in the gas phase costs[1] 6 eV. The collective interactions of aqueous solvation produce ion stabalizations greater than typical chemical bond strengths, so condensed phase chemistry in ice or water can be very different than in the gas phase. Clusters provide an opportunity to isolate collective interactions in a finite system whose properties can be studied with powerful and incisive gas phase methods. The cluster approach is applied in this work to study water and aqueous solvation. Our experimental handle is the reaction of oppositely charged, aqueous cluster ions. The rate constants and mechanisms of these reactions are studied to reveal the effect of the clustering solvent molecules.

2. Merged Beam Recombination of Cluster Ions

The ion optical method for the study of cluster ion recombination has been described in detail previously[2,3] and is presented schematically in Fig. 1. An electrostatic quadrupole deflector[4-8] (QD) is used to coaxially merge oppositely charged beams of mass selected cluster ions. Once merged, the ions interact for ~1 μs in a drift region (DR) until a deflector (D) separates the ion beams and directs them to different Faraday cups (FC+, FC-). Any fast neutrals created continue undeflected (dotted line) with keV kinetic energies and are detected by an electron multiplier (EMT) with efficiencies comparable to charged particles. Recombination rates (R) of fast neutral production are determined which relate to the binary recombination rate constant (α_2) by the positive and negative parent ion currents (I_+, I_-) and reactant velocities (v_+, v_-) as

$$\alpha_2 = \frac{R\, v_+ v_-}{I_+ I_- f} \qquad (1),$$

where f is a calibration factor which converts the ion currents to densities and depends on the detector's speed and kinetic energy response to fast neutral products (particularly fragments). The rate constant is studied[9] as a function of center-of-mass (COM) collision energy (W) by applying a voltage (δ) to the drift region (DR) as

$$W = q\frac{m_+m_-}{(m_++m_-)}\left(\frac{(V_{b+}-\delta)}{m_+}+\frac{(V_{b-}+\delta)}{m_-}-2\sqrt{\frac{(V_{b+}-\delta)(V_{b-}+\delta)}{m_+m_-}}\cos\theta\right) \quad (2),$$

where q is the ion charge (assumed the same for each reactant), m is the mass of each ion, θ is the angle between the velocity vectors of reactant ions, and V_b is the absolute value of the beam voltage required at the quadrupole deflector for merging (same for each beam). Each pair of reactants has a specific value of δ which gives the reactants zero average relative velocity (when θ=0) and a small root-mean-squared value due to the angular distributions associated with the geometry of the drift region, so reactions can be studied near room temperature even though the reactants have keV laboratory energies. Fast neutral backgrounds due to parent ion interactions with residual gas in the vacuum chamber are presently ~30 times larger than the recombination signal, so a Fourier transform, double modulation,[10] detection system is employed to pull signal from the background. The fast neutral detector is also positioned far downstream from the drift region to significantly reduce this background.

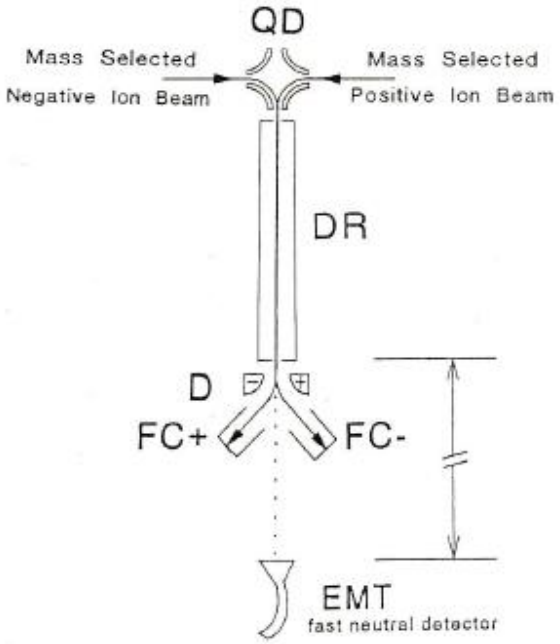

Figure 1. Schematic of the merged beam apparatus for cluster ion recombination studies.

3. Results

The first experiments examined the reactions of $H_3O^+(H_2O)_n$ + $OH^-(H_2O)_m$ with the drift region grounded. This arrangement has the advantage of similar ion optical focussing for each measurement, but the disadvantage of different COM collision energies for each reaction. Under these conditions, reactions with n=m have similar and small COM collision energies (0.4-1.4 eV) and are compared in Fig. 2. The reactions where n=m were studied with two different detectors: a Galileo Channeltron 4750G which is a single channel electron multiplier with a 30 ns output pulse width and a Galileo HOT microchannel plate (6025 HOT MCP) which shows linear response at unusually high input rates and a 3 ns output time constant. The Channeltron data reveal a decrease in the monomer reaction rate upon the addition of a single water to each reactant followed by an increasing trend upon the addition of several more clustering water molecules. It became apparent that the Channeltron could

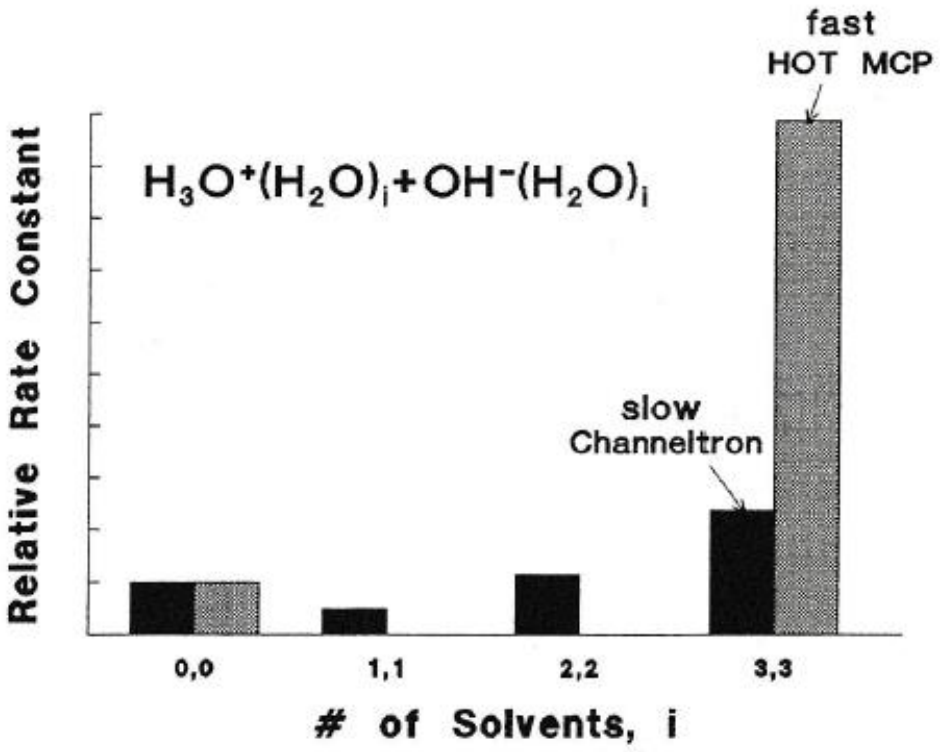

Figure 2. Relative rate constants for the reactions of H_3O^+ and OH^- with equal numbers of solvating waters as determined with a Channeltron (4750G) and HOT microchannel plate (6025) detector.

not respond linearly if multiple fast neutral fragments were created in these reactions, so some of these experiments were repeated with the faster HOT MCP detector. A significantly higher ratio of reaction rates between the n,m=3,3 and 0,0 reactions was observed, while there was little difference in the ratio of the 0,0 reaction to the calibrating reaction of $O_2^+ + O_2^-$.

Recombination rate constant measurements have been made for a few reactions as a function of COM collision energy. The results for $H_3O^+(H_2O)_n + OH^-(H_2O)_m$ with n,m= 3,3 and 1,0 are displayed in Fig. 3. These experiments are more difficult because ion optical focussing changes with each different voltage applied to the drift region. The more heavily clustered 3,3 reaction rate constant is much larger than that of the 1,0 reaction at the lowest COM collision energies and has a different trend with COM collision energy. In Fig. 3 linear fits are given only to help reveal the general trends. Many of the channels for these reactions are highly exothermic, so measurements have been made of the resultant fast neutral spot sizes in order to determine if the products have significant excess kinetic energy. The output

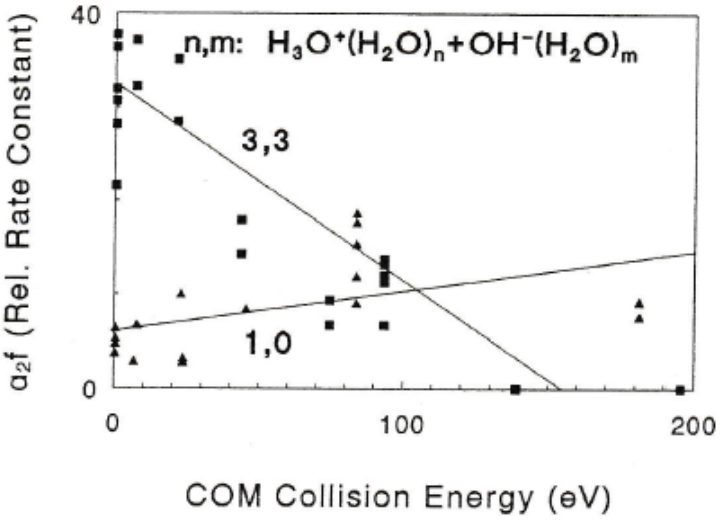

Figure 3. Relative recombination rate constants vs. COM collision energy for the reaction of $H_3O^+(H_2O)_3$+$OH^-(H_2O)_3$ (3,3) and $H_3O^+(H_2O)_3$+OH^- (1,0). The lightly clustered reaction does not vary much with COM collision energy while the more heavily clustered reaction rate is much larger at low COM energy and diminishes with increasing COM collision energy.

electrode of the HOT MCP detector was divided into a linear array of 7 segments and, for a given set of conditions, independent measurements were made on each output segment. The results for the reactions with n,m= 3,3 and 0,0 are given in Fig. 4. The more heavily clustered 3,3 reaction exhibits a width which is twice that of the monomer reaction and about 10% larger than that of the background spot. There is certainly evidence of some excess kinetic energy in the products of the 3,3 reaction.

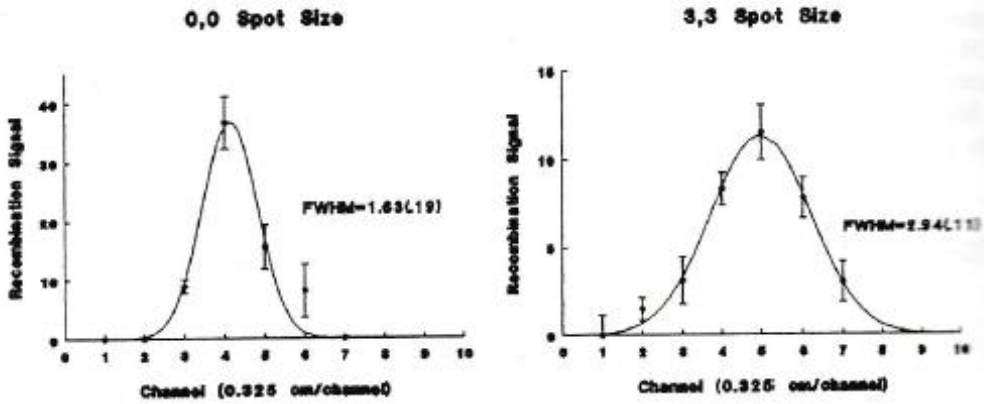

Figure 4. Fast neutral spot sizes for the 0,0 reaction of H_3O^+ + OH^- and the 3,3 reaction of $H_3O^+(H_2O)_3$ + $OH^-(H_2O)_3$. The more heavily clustered reaction produces a spot which is twice as wide as the monomer reaction in spite of the fact that the geometry of the drift region severely vignettes fragments with excess kinetic energy.

The evidence of fragmentation in the products of the 3,3 reaction suggests that several detector issues must be addressed before absolute rate constant measurements can be made. All products in these reactions nominally have the velocity of the reactant ions, so fragment ion products will of necessity have different kinetic energies. Measurements have been made concerning the kinetic energy response of the fast neutral detectors. The fast neutral background produced by a certain current of mass selected ion beam (which is deflected off axis) is measured as a function of beam energy. The OH^- anion is particularly useful in this regard because glancing collisions with residual gas (those which do not knock the products out of the beam) produce primarily detachment, ie. OH radicals. So the resultant fast neutrals have essentially the same kinetic energy as the parent ion beam. The ratio of fast neutral OH signal to OH^- ion current is plotted in Fig. 5 vs. parent beam energy (equals fast neutral kinetic energy) for the two detectors used in this work. The kinetic energy response is distinctly nonlinear in this energy regime and well described by a power law. Extensive fragmentation can result in products with much less kinetic energy eliciting considerably less detector response than unfragmented products.

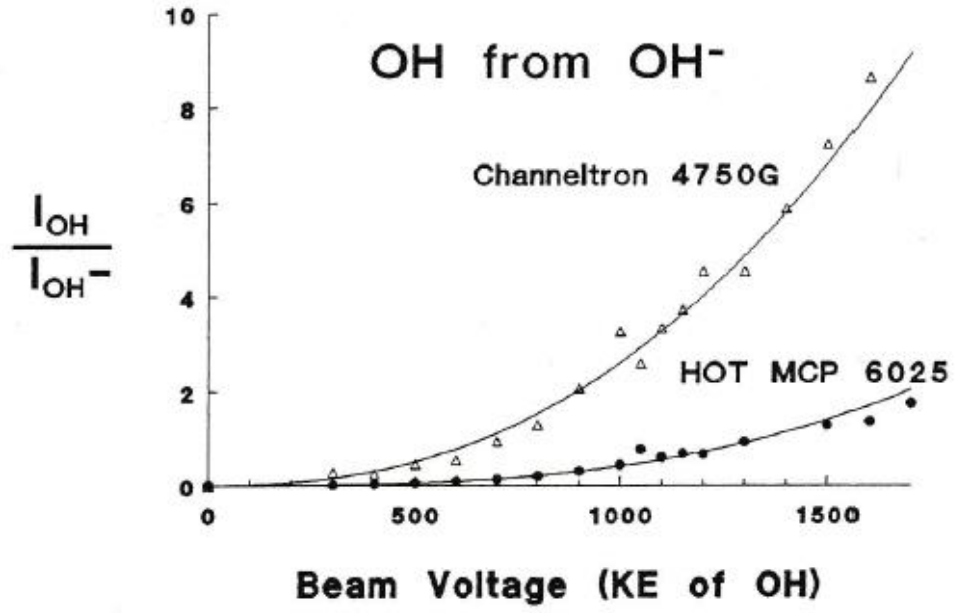

Figure 5. The ratio of the fast neutral detector's output current to the parent ion current producing the fast neutral flux as a function of parent ion beam voltage. Glancing collisions of OH^- with residual chamber gas produces OH almost exclusively. The OH radicals basically have the kinetic energy of the parent ion beam. Product fragments of recombination reactions can produce much less response than unfragmented products.

4. Discussion

Most simple atomic and polyatomic ions recombine by e^- transfer[10] while in bulk water the fundamental ions associated with water, H_3O^+ and OH^-, react by H^+ transfer in an equilibrium which maintains the pH of bulk water at ~7. The trend with cluster size seen in Fig. 2 is similar to that of the collisional attenuation cross sections[11] of $OH^-(H_2O)_m$ that are attributed to an electronic process (detachment) giving way to a more chemical process (dissociation). This suggests a similar explanation for the ion-ion recombination trend, ie. electron transfer gives way to a more chemical interaction such as proton transfer. The n,m=1,0 and 0,0 reactions fit expectations for electron transfer behavior[10,12] by virtue of the

rate constant dependence on COM collision energy and product spot size. Although the 0,0 gas phase proton transfer reaction[14] is 9.71 eV exothermic as compared to the 3.4 eV exothermic electron transfer channel[15], it would be very difficult to dissipate ~10 eV of excess heat in a binary proton transfer reaction, whereas the excess enthalpy of the electron transfer reaction can be readily accommodated as electronic energy in the H_3O^* Rydberg radical[15]. The collision energy trend and product spot size data of the n,m=3,3 reveal a different reaction mechanism than the electron transfer of the monomer reaction. We interpret this as due to a polar cluster enabled trapping, perhaps "tidal trapping"[13], or fusion producing proton transfer which is only efficient at low COM collision energies.

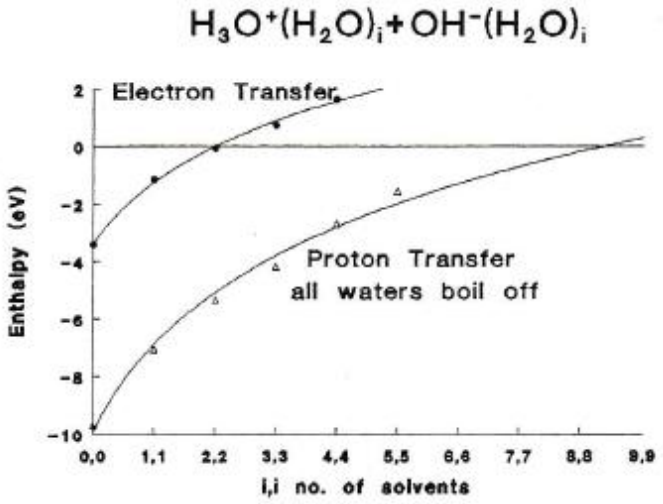

Figure 6. Thermochemical estimates of the effect of clustering on the electron and proton transfer mechanisms. Electron transfer goes endothermic by the addition of three solvating waters on each reactant ion. The proton transfer curve shows that by the addition of about 8 waters to each reactant ion, there is no longer enough excess enthalpy to boil away all of the solvating water molecules - the reaction is, however, still exothermic.

The energetics of electron and proton transfer as a function of cluster size are estimated in Fig. 6 with the aid of cluster thermochemistry from the literature[16-20]. Electron transfer is discouraged with increased clustering for several reasons[10]: ionization potentials decrease, electron affinities increase, charge gets buried in a high dielectric material, reduced mass grows, and polyatomic ions may have geometries different than their corresponding neutrals. The electron transfer process becomes endothermic by the addition of 2 or 3 waters to each reactant ion. Clustering can be expected to increase the likelihood of proton transfer because a large density of states dissipates the coulombic interaction (by rotations and weak bond vibrations of solvent molecules) effectively trapping the reactants at least at low COM

collision energies. Solvent molecules can readily evaporate or be internally excited to dissipate the excess heat of recombination. By the addition of ~8 waters to each reactant ion the proton transfer process no longer has enough enthalpy to boil off all of the waters, although it is still a thermochemically favorable process at all cluster sizes.. The cluster size range between the points at which the electron and proton transfer curves go positive is a region where significant excess kinetic energy can be expected in the product fragments of cluster recombination reactions. For example, the 3,3 proton transfer reaction is 4.07 eV exothermic, so each product water molecule must carry away an average of 0.5 eV as internal or excess kinetic energy. These reactions can be expected to produce fast neutral product spot sizes which are bigger than the spots defined by the geometry of the drift region.

The fast neutral spot size measurements presented in Fig. 4 show a doubling of the full width at half maximum for the 3,3 reaction over that of the 0,0 reaction clearly indicating that the 3,3 reaction products have excess kinetic energy. The output aperture of the drift region in these experiments unavoidably vignettes recombination products having excess kinetic energy with increasing severity upstream of the aperture. The experiment was not optimized for detecting high excess kinetic energy fragments, so modelling of the spot widths reveals only that >5% of the excess enthalpy goes into kinetic energy of product fragments. The fraction could be much higher and further experiments with more favorable geometries are underway.

Absolute calibrations of the reactions studied by merged beam recombination cannot occur until knowledge of the number and type of product fragments is available. Since our experiment determines relative rate constants, we are attempting to calibrate the measurements by comparison to reactions such as $O_2^+ + O_2^-$ with published absolute rate constants[10]. The fast neutral detectors available to us have nonlinear response regarding kinetic energy (see Fig. 5) which can affect the absolute rate constant calibrations by more than an order of magnitude in some cases, such as the 3,3 reaction. If product fragments have significant excess kinetic energies, then many will be attenuated by the drift region's output aperture or perhaps miss the detector. These two effects could easily add two more orders of magnitude to the order of magnitude already observed for the increase in the rate constant of the 3,3 reaction over that of the monomer reaction. If these two effects turn out to be important, then cluster ion-cluster ion recombination rates may be comparable to cluster ion-electron recombination rates and important regarding the chemistry of the D region of the ionosphere[21-23]. Therefore, characterization of products is a critical issue and challenging problem.

5. Conclusion

The advent of merged beam cluster ion recombination studies presents a new arena for the investigation of solvation and cluster dynamics. Comparison of the reaction of $H_3O^+(H_2O)_n + OH^-(H_2O)_m$ with n,m=0,0 and 3,3 shows: 1) an increase in the rate constant by more than a factor of 10 and perhaps as much as 10^3, 2) a change in the reaction mechanism which is interpreted as a change from electron transfer to proton transfer, and 3) excess kinetic energy in the product fragments of the 3,3 reaction. If this interpretation proves

correct, then this result represents a poignant example of the use of clusters to embody bulk-like behavior in finite systems approachable with gas phase methods.

6. Acknowledgements

Thanks to the NSF, CHEM-9204204

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