Dynamics of the Gas-Phase Acid–Base Reaction

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Abstract: Using crossed, seeded nozzle beams, we have studied the detailed dynamics for the reaction of HI with three amines. Reaction with tri-*n*-butylamine and with quinuclidine gives product distributions which are forward peaked in the center-of-mass system, indicating a modified stripping mechanism. Reaction with tetrakis-(dimethylamino)ethylene gives a symmetric distribution, indicating a long-lived complex. However, at high relative energies, a fragment ion is also produced which is forward scattered, suggesting that two different sites can be protonated by different reaction mechanisms.

I. Introduction

The reaction of acids and bases to produce salts has been studied since the early days of alchemy. With the generalizations by Brønsted and Lewis, this reaction plays a central part of much of chemistry. Using crossed molecular beams, we have studied the detailed dynamics of reactions of the type

$$\mathrm{HI} + \mathrm{B} \rightarrow \mathrm{I}^- + \mathrm{HB}^+ \qquad (1)$$

where B is one of three organic amines: tri-*n*-butylamine (TBA), the bicyclic tertiary amine quinuclidine (Qn), or the enamine tetrakis(dimethylamino)ethylene (TDMAE). Even in this small number of systems, the product angular and velocity distributions show a remarkable variety, an indication of rich underlying dynamics.

For all chemical reactions, the dynamics of the reaction depend on the potential-energy surface or surfaces involved in the reaction. In this case, at least two surfaces are needed.[1] The reactants lie on a covalent surface with three-body dissociation products H + I + B. The products, on the other hand, lie on a separate, ionic surface dissociating to $\mathrm{H} + \mathrm{I}^- + \mathrm{B}^+$. There may be still other surfaces involved. The covalent surface cannot form stable products because HB is not bound. On the reactant side, the covalent surface has the lower energy, but it is nearly flat until the reactants come close to each other where it becomes repulsive. The ionic surface is strongly attractive in both the reactant and product regions due to the strong Coulomb attraction between I^- and B^+. Presumably, it intersects the covalent surface on the reactant side, where an electron jumps from B to HI, and the system crosses to the ionic surface. The reaction is thus an example of the "harpoon" mechanism[2] popularized by Dudley Herschbach for the well-studied reactions of alkali atoms and halogen-containing molecules. Following the surface crossing, the system passes through a deep bowl corresponding to an ion-pair complex and then climbs out of the bowl to dissociate as a pair of ions. We expect that the position of the crossing seam is one of the important features in governing the course of the reaction. These reactions have one important difference from the charge transfer in small systems. When the electron jumps as the system crosses from the covalent to the ionic surface, the transition is a rapid, vertical one so that the bond lengths and bond angles in the ion are not in their equilibrium configuration. As the ions move away from the crossing, their structures change. If the system then reaches the crossing seam again, it is almost impossible for it to return to the covalent surface, since this second crossing would create a neutral B molecule with a very large internal energy.

We have previously studied this type of reaction.[3] We did a preliminary study of the reaction of HI and TBA at one relative energy and found that the reaction takes place by way of a modified stripping mechanism. The HI undergoes a grazing collision with the TBA, and a proton is transferred. The product ions are slowed by their Coulomb attraction but separate without a large change in direction. As we shall see, other amines can give quite different results. We have also measured the energy dependence of the total reactive cross section for the reactions of HI,[4] trifluoroacetic acid,[5] and trifluoropentanedione[5] with several amines. In all cases, the cross sections rise rapidly as a function of translational energy, but the observed threshold for the reaction is 0.5–0.9 eV above the thermodynamic threshold for the reaction. This effect was also seen in theoretical calculations on the same reaction.[1] In some cases, we had enough energy to see the cross section drop at energies above 4.5 eV. In the case of HI and TDMAE[4] the cross section rose above the threshold and dropped quickly to zero. At higher energies a fragment ion, due to the loss of dimethylamine, appeared; the cross section peaked and then dropped to zero. At still higher energies smaller fragments displayed similar behavior.

II. Experimental Section

The experimental procedure has been described in detail in previous publications,[3-6] so only a brief description will be given here. The two reactants are each formed in seeded supersonic nozzle beams which intersect at 90° in the center of a vacuum chamber. The detector is mounted on the rotatable lid of the chamber so that we can take the distribution in scattering angles of the product ions. A retarding-potential energy analyzer enables us to measure the distribution in product speed. The experiment then measures the distributions in the

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vector velocity of the products. The data are plotted as a series of contour maps giving the product intensity as a function of the vector velocity.

Each nozzle beam is made in a separately pumped chamber. The carrier gas, He, H_2, or a mixture of 60% He and 40% H_2, is bubbled through the liquid reactant or, in the case of quinuclidine, passed through a plug of small crystals. By controlling the temperature of the bubbler, we can control the vapor pressure of the seed gas. The total pressure is typically 1 atm with 1% or less of the seed gas. The gas mixture then flows through a heated pyrex nozzle into the vacuum chamber. The source chamber is separated from the main chamber by a conical skimmer. The nozzle is wrapped with nichrome heater wire so that we can adjust its temperature between room temperature and about 300 °C. The kinetic energy of the beam is varied by changing the nozzle temperature and by changing the type of carrier gas used. The beam energy can be calculated by using known formulas.[7] It can be measured by ionizing the beam with electrons from a filament mounted on the detector and using the retarding-potential energy analyzer.

The beam of HI is made in a similar fashion, except that the carrier gas is bubbled through *tert*-butyl iodide. The *tert*-butyl iodide decomposes cleanly inside the heated nozzle at 280 °C to produce HI and isobutene.[8] Initially, we had great difficulty in accelerating the HI to the predicted energies.[7] We tried using a mixture of 0.5% HI in H_2 in a gas cylinder rather than the pyrolysis of *tert*-butyl iodide. This gave the same results. We suggested that the small size and high mass of HI make the energy transfer from the carrier gas to HI during the nozzle expansion much less efficient than for our other reagents and, therefore, the final energy is less than it should be. We found that raising the backing pressure of the carrier gas to 2.5 atm increased the energy of the HI by about 0.5 eV, but we never reached the theoretical limit. Of course, we used the measured energies rather than the calculated energies in our analysis.

The detector consists of a grid cage surrounding the beam intersection region.[3–6] The cage is mounted on the first of several ion focusing plates. In these experiments a grid on the first plate is kept at the same potential as the cage so that the region inside the cage has no electric field present. Thus, only ions traveling in the direction of the hole in the first plate reach the detector. The second plate contains the retarding-potential energy analyzer. The voltage is controlled by a computer and is scanned repeatedly over the desired range in order to measure the distribution in the product energy. After the lens, the ions pass through a quadrupole mass analyzer (Extrel) and are detected on a Channeltron electron multiplier (Galileo Electro-optics). A homemade pulse analyzer then amplifies the pulses and passes them on to the computer for counting and data analysis. For experiments measuring the total reactive cross section, all positive (or negative) ions are extracted by making the first grid negative (or positive) with respect to the cage.

III. Results and Discussion

By conservation of momentum, the vector velocity of the center of mass is conserved during the reaction. We can subtract it out, and by applying the proper Jacobian, we then convert the laboratory velocity distributions to Cartesian distributions in the center-of-mass (CM) system.[9] We plot these distributions as a set of contours; note that the x and y axes of the contour diagrams are velocities and not positions. In the CM system, the reactants approach each other with equal and opposite momenta, and the products recede with equal and opposite momenta. Because all the reactant distributions have at least axial symmetry about the relative velocity vector v_{rel}, the product distribution must also have this symmetry. All our distributions are taken in the plane of the two beams, but they show the intensity on either side of v_{rel}. The symmetry (or lack thereof) is a good measure of the accuracy of the experiment. Errors in beam velocity, large spreads in either the beam energies or angles, or poor alignment of the beam machine will cause deviations from this symmetry.

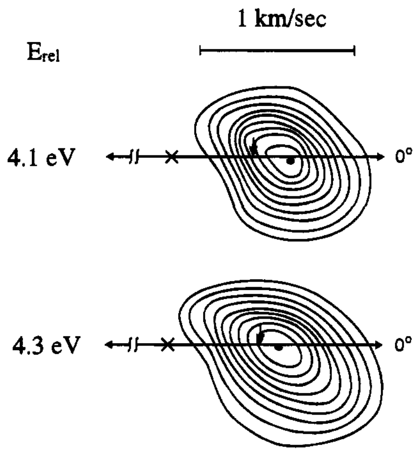

Figure 1. Cartesian product contours for protonated tributylamine (TBA) from the reaction of HI and TBA. The horizontal line is the relative velocity vector; × is the velocity of the center of mass. The maximum in the product distribution is shown by the dark dot. It is surrounded by contours of product intensity at 90%, 80%, ... of the maximum. The relative translational energy is given for each contour, and the line shows the length for 1 km/s. The TBA beam goes to the right and the HI beam to the left. The position of the product predicted by the modified stripping mechanism is shown by the arrow.

Various reaction mechanisms will give very different product distributions. In the modified stripping mechanism, the reactants pass close to each other where the surface crossing occurs and a proton is transferred from HI to B. The product ions continue in the same direction, but the velocity is reduced by their Coulomb attraction. This mechanism produces a distribution strongly peaked around 0° for the cation and 180° for I^-, where 0° is the direction of the B beam in the CM system. The product velocities in the CM system are smaller than the corresponding beam velocities because of the Coulomb attraction between the products. In contrast, a long-lived complex produces product velocity contours that have forward–backward symmetry about the center of mass. The reactants collide and stick together for one or more rotational periods before the products dissociate. The original directionality is lost, but the complex "remembers" its total angular momentum, and so the final distribution need not be spherically symmetric.

Figure 1 shows the product contours for the reaction with tri-*n*-butylamine (TBA) (at two different energies):

$$\mathrm{HI} + \mathrm{TBA} \rightarrow \mathrm{I}^- + \mathrm{HTBA}^+ \qquad (2)$$

The horizontal line is the relative velocity vector; × is the velocity of the center of mass, the CM origin. At 4.1 eV the relative velocity is 3.2 km/s. The right end of the line is the position of the TBA beam, but the full relative velocity vector extends way to the left of the figure. The black dot is at the velocity of the maximum in the product distribution, and the surrounding lines are contours of product intensity 90% of the maximum, 80%, etc. The contours show strong forward peaking and no intensity in the backward direction, confirming our earlier observation that the reaction goes by way of the modified stripping mechanism. In the original spectator stripping model the protonated TBA product carries the sum of the momentum of the TBA and of the proton. Since the proton is light, the product should be distributed roughly at the velocity of the TBA beam, the right end of the relative velocity vector. This is

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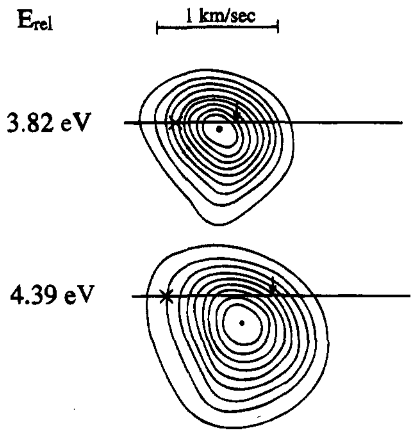


Figure 2. Product contours for protonated quinuclidine (Qn) from the reaction of HI and Qn. See the caption of Figure 1 for details.

clearly not the case. As the products separate, they are slowed down by the Coulomb attraction between the ions. If there is no transfer of translational to internal energy, then the energy loss should correspond to the endothermicity of the reaction. The proton affinity of I^- is 13.64 eV,[10] and the proton affinity of TBA is 10.2 eV so that ΔH = 3.43 eV = 79.0 kcal/mol. The predicted position of the product is shown by the arrow in Figure 1. The modified stripping mechanism then gives a fairly good description of the reaction dynamics, especially when one considers how simple the model is.

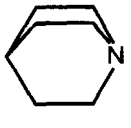
In previous experiments where we measured the total reactive cross section we could move the beam intersection angle to 135° and get to higher energies.[4] We found that, starting at about 6 eV, a fragment ion appeared due to the loss of a butyl radical. Unfortunately, we cannot reach this energy with a 90° beam intersection angle, and we cannot obtain good distributions at 135° because we cannot move the detector over a wide enough angular range and because the LAB energies of the products are so low that the distribution is easily perturbed by stray electric fields.

It is difficult to give a realistic error analysis of the data because of the complexity of the analysis. The best indication of the accuracy of the product contours is to look at the deviations from axial symmetry, since points on either side of the relative velocity vector are independently measured.

Figure 2 shows the product contours for the reaction with quinuclidine (Qn):

$$HI + Qn \rightarrow I^- + HQn^+ \qquad (3)$$

Quinuclidine is a tertiary amine and therefore has a high proton affinity.



Because of the bicyclic structure, the active site, the lone pair on the nitrogen, is not shielded by substituents. The cyclic structure also precludes fragment ions, at least at low or moderate energies, because at least two C−C bonds must be broken to produce the fragment. The contours show some scattering in the backward direction, but the main intensity is forward. The proton affinity of Qn is 10.11 eV[10] so that ΔH = 3.53 eV = 81.3 kcal/mol. As in the case of TBA the modified stripping gives a good description of the dynamics.

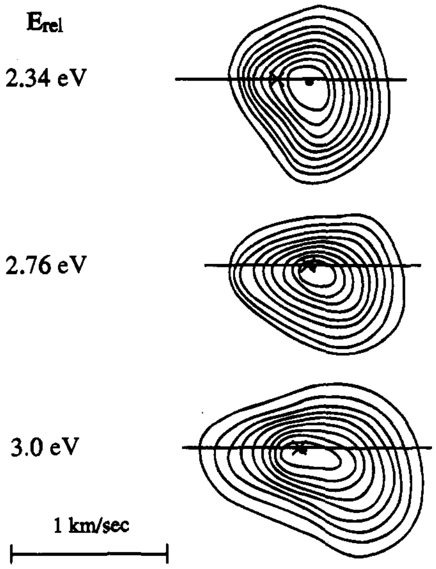


Figure 3. Product contours for protonated tetrakis(dimethylamino)-ethylene (TDMAE) from the reaction of HI and TDMAE at low energies. See the caption of Figure 1 for details.

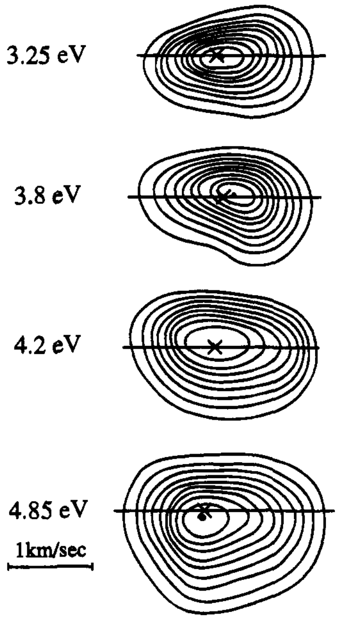


Figure 4. Product contours for the reactions of HI and TDMAE at high energies. See the caption of Figure 1 for details.

Figures 3 and 4 show the product contours for HI reacting with tetrakis(dimethylamino)ethylene (TDMAE):

$$HI + TDMAE \rightarrow I^- + HTDMAE^+ \qquad (4)$$

In this case the relative velocity vector extends beyond each side of the lines in the figures. TDMAE is an enamine with an adiabatic ionization potential of only 5.36 eV,[11] one of the lowest known among organic molecules. The proton affinity has not yet been measured, but from the low threshold energy found in our measurements,[4] it must be at least 11 eV. Given this large proton affinity, one would expect that the reaction would go readily by way of a modified stripping reaction. Indeed, this was our expectation before doing the experiment. Instead, we see that the reaction goes by way of a long-lived complex over the whole energy range studied. The small deviation from the

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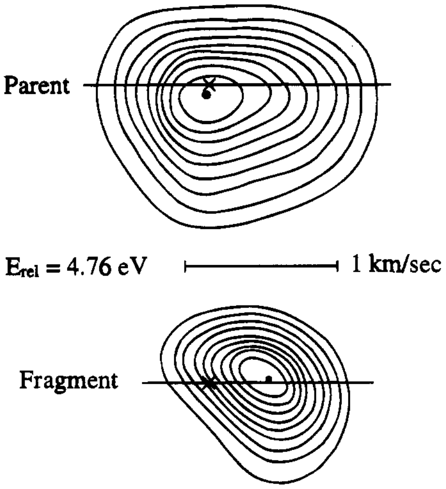

Figure 5. Product contours for the reaction of HI and TDMAE showing the parent and fragment contours.

CM at 2.34 eV is probably an artifact, since this energy is just above the threshold where the intensity is low and the effects of the finite velocity spread of the beams are the largest. At the highest energies, the peak of the distribution remains at the center of mass, but the lower contours seem to bulge out slightly in the direction of the TDMAE beam (the right in the figures). While this feature might easily be dismissed as an artifact, it coincides with the appearance of a fragment ion at mass 157—the loss of dimethylamine. Figure 5 shows the contours for the parent and for the fragment ion at a relative energy of 4.15 eV. Although the contours for the parent are largely symmetric about the center of mass, those for the fragment are clearly forward of the center of mass.

Usually, a fragment is produced when one of the products is formed with enough energy to break a bond. This fragmentation occurs in a time long compared to the duration of the initial reaction by a unimolecular decay process. If this were the case here, then the fragment contours must have forward–backward symmetry with respect to the center of mass because the parent ion distribution has this symmetry. Once the original directionality is lost in the complex, it cannot be regained in a subsequent fragmentation process. Because our fragment distribution is strongly forward peaked, we are forced to conclude that the protonation occurs by two separate mechanisms: one by way of a long-lived complex and the second by way of a modified stripping process, later producing the fragment. We can say nothing about the time scale of the fragmentation reaction, but we do known that the parent, precursor ion does not have forward–backward symmetry and must therefore be formed in a fast, direct reaction. The complex mechanism clearly has the lower threshold, since we see no fragment and no forward peak at low energies. TDMAE has two different sites that can be protonated. The site on one of the four nitrogens is similar to the site protonated on the other two amines that we studied. The molecule can also be protonated on one of the two ethylenic carbon atoms. In this case a very stable cation is produced where the charge is distributed between the unprotonated carbon atom and the two nitrogen atoms bonded to it. Studies of the protonation of tetraaminoethylenes in solution[12] show that both sites can be protonated. Protonation on nitrogen often leads to the loss of the protonated amine, giving, as the other fragment, a stable immonium cation. Protonation on carbon, however, rarely gives rise to fragmentation. Studies on proton exchange in the gas phase using ion cyclotron resonance (ICR)[13] show that the lowest energy site for protonation is the carbon. Although we cannot assign the two mechanisms unambiguously, it seems very likely that the low-energy mechansim is the protonation on carbon. This proceeds by way of a long-lived complex. At higher energies, protonation on nitrogen becomes possible. This reaction goes by way of a modified stripping reaction as it does in the cases of TBA and Qn. The protonation on nitrogen produces fragment ions in most of the reactive collisions, although some of the parent ion appears to be present to produce the bulge in the parent product contours at high energies.

Why should protonation on nitrogen give rise to a stripping reaction and protonation on carbon to a long-lived complex? Protonation on nitrogen requires no change in hybridization, since the nitrogen already has sp^3 hybridization. In other words, the protonation on nitrogen requires little change in bond lengths or bond angles and therefore has a large Franck–Condon factor. This condition then allows the rapid protonation on nitrogen by a vertical, Franck–Condon mechanism. On the other hand, protonation on carbon involves a change from sp^2 to sp^3 hybridization requiring some degree of rearrangement of the large bulky groups. With four bulky groups on the olefinic carbons, there is so much strain energy in TDMAE that the dimethylamino groups on the double bond are actually rotated by 28°.[14] On protonation, this strain energy is probably released as the C–C bond rotates. Thus, protonation on carbon, while energetically favorable, is likely to be a slower, more adiabatic reaction than protonation on nitrogen. Rapid deuterium exchange reactions of NH and OH groups and the much slower exchange of CH acids of similar acidity in solution are related phenomena.[15]

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