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Crossed-Beam Study of the Dynamics of Chemiionization Reactions

R. JAMES CROSS, JR.,* and MARTIN SAUNDERS*

Department of Chemistry, Yale University, New Haven, Connecticut 06520

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Chemiionization reactions—where neutral reagents react to form ionic products—are quite common in solution but have not been studied often in the gas phase. A large difference is due to the solvation energy in solution. The neutral reactants are only weakly bound to the solvent, but the ionic products are strongly solvated. Thus, solution reactions can be more exothermic than the corresponding reactions in the gas phase by as much as 75–100 kcal/mol. Nevertheless, by using molecular beam techniques, we can provide the necessary energy in the reactants and study the reaction in the gas phase. By using beams, we have much greater control over the reactants than by using more conventional methods, and we get more more detailed information about how the reaction occurs. For example, our reactions, like most others, require energy. In a classic kinetics experiment one can only measure the amount of the activation energy, not the type of energy—vibrational, translational, rotational, etc.—that is required. Similarly, in the classical experiment, one can only measure the amount of the product after many subsequent collisions. In a beam experiment, the product is detected immediately after the reactive collision before it has time to collide with other molecules and with the walls of the container. A big advantage of our experiment is that the product ions can be detected and their mass-to-charge ratio measured in the presence of a large excess of neutral reactants. We can measure the distribution of scattering angles and translational energy, which are rapidly scrambled by collisions of the products in a nonbeam experiment. With this additional information we can treat the reaction using more detailed models and theories than before. These reactions are quite different in chemical characteristics from most other reactions studied by beam techniques, and the reactants are much bigger molecules than is typical for this type of study.

Figure 1 shows a schematic of our beam machine.[1,2] Both beams are produced as supersonic nozzle beams. The two beams intersect in the center of the grid cage C, where the reaction takes place. The product ions then pass through grids G_1 and G_2 and an ion lens system into a quadrupole mass filter and are then detected by an electron multiplier. The beam is made by expanding a gas at a pressure of $\sim$1 atm into a vacuum through a small hole $\sim$40 μm in diameter.[3] The expansion is adiabatic in that the internal temperature of the gas drops rapidly as the enthalpy of the gas behind the nozzle is converted into bulk translational energy of the beam. Behind the nozzle the gas is at thermal equilibrium at a temperature of 300–600 K. After the expansion, the velocity distribution can be described by a Maxwell–Boltzmann distribution characterized by a temperature of a few degrees Kelvin superimposed on a constant velocity, which can be calculated by equating the enthalpy lost in the expansion to the gain in bulk translational energy. Because rotational relaxation is not quite as efficient as translational relaxation, the rotational distribution has a somewhat higher temperature. Vibrational relaxation is very inefficient, often requiring thousands of collisions. Consequently the vibrational energy distribution is cooled only slightly, the amount depending on the particular molecule and type of vibration.

A second useful trick is the seeded nozzle beam.[3] When a mixture of 99% of a light gas and 1% of a heavy gas is used, collisions in the beam accelerate the heavy molecules up to the velocity of the light molecules. Because the kinetic energy is $mv^2/2$, the heavy species has up to several electronvolts in kinetic energy. The translational energy can be controlled by varying the nozzle temperature and by changing the type of carrier gas. H_2 produces higher energies at a given nozzle temperature than He because it has the larger velocity. Changing the temperature also changes the vibrational temperature; changing the type of carrier gas has little effect on vibration. The amount of relative energy in a collision is affected by the angle between the two beams: the larger the angle, the more of the energy goes into relative motion. In our beam machine we can use beam intersection angles of 90° and 135°.

Chemiionization reactions offer several advantages over typical neutral reactions and over the study of ion–molecule reactions. The reactants are stable neutral molecules, and we can easily form intense nozzle beams without having to prepare ions, radicals, or excited states. Neutral products, however, are difficult to detect.[4] They can be ionized only at low efficiency (typically 10^{-4}–10^{-3}). The ionization often produces many fragment ions, and there are usually many ions produced by the ionization of background gas. Our

Jim Cross was born in New York, NY, in 1940. He received his B.S. degree from Yale in 1962 and his Ph.D. degree from Harvard in 1966 under the direction of Dudley R. Herschbach. He returned to Yale, where he is now Professor of Chemistry. His research includes the study of reactive scattering with molecular beams and the theory of inelastic scattering.

Martin Saunders was born in Brooklyn, NY, in 1931. He received his B.S. degree from City College and his Ph.D. degree from Harvard in 1956 under the supervision of R. B. Woodward. He has been on the faculty at Yale since 1955. His research includes conformational search methods for molecular modeling and the study of isotope effects on equilibria in stable solutions of carbocations.

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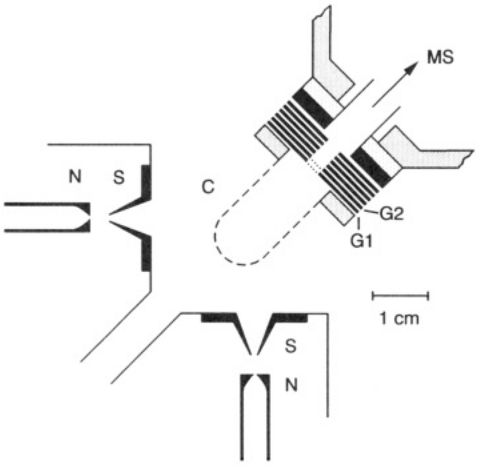

Figure 1. Schematic diagram of the apparatus: N, nozzle; S, skimmer; C, grid cage; G_1 and G_2, grids; MS, mass spectrometer.

experiment avoids all these problems. The products are already ions; there is usually little or no fragmentation, and there is usually no background. We have the added advantage that our neutral reactants are unaffected by the electric fields used to manipulate the products. We can therefore extract the product ions by using an electric field without perturbing the reactants, a trick impossible with either neutral reactions or ion–molecule reactions.

Our detector has two modes of operation. In one, the grid G_1 is at the same electrical potential as the rest of the grid cage. The product ions are thus formed in a region of constant potential (zero field). Only those ions going in the direction of the exit opening will be detected. By rotating the detector about the beam intersection point, we can measure the distribution in scattering angles. The second grid G_2 forms a retarding potential energy analyzer. If an ion has an energy (in electronvolts) greater than the potential on G_2, it will pass through and be reaccelerated on the other side and detected. If the ion has a lower energy, it is repelled and lost. The voltage on G_2 is stepped up and down by a computer, which then collects the data and takes a numerical derivative to get the distribution in translational energies of the product. By measuring both the product angle and translational energy, we are measuring its vector velocity. This measurement of the distributions in scattering angles and velocities of the products is the classic beam experiment for which Herschbach and Lee won the Nobel prize.

In the second mode of operation, the potential on G_1 is set to extract all the product ions of a given charge. We can then vary the initial conditions and measure the relative reactive cross sections as a function of the initial translational energy and vibrational temperature. In both modes we can reverse the sign of the potentials on all the plates and detect either the positive or the negative ions. This information is usually redundant because Newton's laws of motion will tell us where one product is if we know where the other is. Occasionally, it is not clear precisely what reaction is occurring, so that knowing both products is important.

The first reaction that we studied was the halide abstraction by antimony pentafluoride,[2]

$$SbF_5 + RX \rightarrow SbF_5X^- + R^+ \qquad (1)$$

The reaction has long been studied in solution, where it is used to make solutions of stable carbocations.[5] Numerous structures, rearrangement reactions, and equilibria, particularly as perturbed by isotopes, have been studied in these solutions by using NMR.[6] Arnett and Petro[7] have measured the heats of reaction for a number of cases and found the reaction to be thermoneutral to exothermic, depending on the reaction and on the solvent used. Figure 2 shows the distributions in product angular and translational energies for the reaction of SbF_5 with benzoyl chloride (C_6H_5COCl). The horizontal line is a part of the relative velocity vector ($\mathbf{v}_1 - \mathbf{v}_2$). The × is the position of the center of mass (zero relative energy in the two products). The dot is the vector velocity of the maximum in the product distribution. Around this is a set of contours where the product has an intensity of 90% of the maximum, 80%, and so on. A convenient coordinate system is the center of mass (CM) system constructed by subtracting the constant velocity of the center of mass from all velocities. The total linear momentum is then zero; the two reactants approach each other head-on with equal

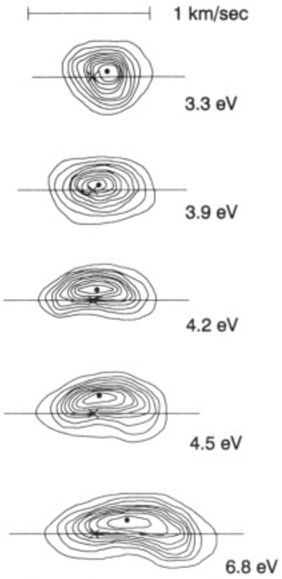

Figure 2. Product intensity contours for the halide abstraction reaction of SbF_5 and benzoyl chloride. The horizontal line is the relative velocity vector, × is the position of the center of mass (zero velocity in the center of mass coordinate system), and ○ is the position of maximum product intensity. The surrounding contours have intensities of 90%, 80%, ... of the maximum. The contours are for the anion product.

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momentum, and the two products recede in opposite directions with equal momentum. Because the initial conditions have cylindrical symmetry about the relative velocity vector, the product contours must also have this symmetry. This is approximately the case in the distributions in Figure 2. The beam velocities and the position of the center of mass are all calculated from the beam conditions, but the product velocities are measured. There is no fit of one to the other, and a 10% change in any of the velocities causes a very noticeable change in the distributions. Similarly, a large spread in beam velocity results in large distortions in the product contours, usually destroying the symmetry.

Those unaccustomed to the CM representation can more easily understand what is happening in the more familiar laboratory coordinates. The reactant beams collide (usually at a 90° angle). In one extreme type of process, called a stripping reaction, a particle (in our cases an electron, a proton, or a halide ion) jumps from one reactant to the other as they approach (and slightly miss) one another. Since relatively little momentum is transferred, the products continue on pathways close to the original paths of the corresponding reactants. Another type of reaction involves a kind of sticky collision where the reactants stay together for a while. After a number of rotational periods, the eventual products separate at random angles. This leads to forward–backward symmetry about the center of mass.

Except for the highest energies, the halide-transfer processes show this feature. The formation of a long-lived complex (~10^{-11} s) is hardly surprising. The products are two ions strongly bound together by the Coulombic attraction, and we would expect an intermediate ion-pair complex. As the initial energy increases, the lifetime of this complex decreases until it becomes comparable to the rotation period of the complex, and the forward–backward symmetry is lost. This appears to be happening at 6.8 eV, but unfortunately, we cannot go to still higher energies to show this unambiguously.

Figure 3 shows the relative cross section as a function of the relative translational energy for this same reaction.[8] The upper panel shows the data at a 90° beam intersection angle, and the lower panel at 135°. Three different carrier gases were used: He (+), H_2 (×), and a mixture of 60% He and 40% H_2 (○). The cross section is obviously very dependent on translational energy. It is also independent of carrier gas. In the region around 7 eV where all three carrier gases overlap, the data for the three carrier gases agree within experimental error. To get the same energy for He as for H_2 the nozzle must be very much hotter: ~400 °C for He as compared to 50 °C for H_2. If a certain amount of vibrational energy is necessary for reaction—translational energy cannot be substituted for it—then simple model calculations[9] show that the cross section should be proportional to an Arrhenius type factor with the required vibrational energy as the activation energy and the vibrational temperature as T. This model predicts an exponential dependence of the cross section on vibrational temperature and clearly does not agree with our data. At the other extreme, we can picture translational and vibrational energies as being interchangeable. Here we do not have the necessary sensitivity to see the effect becasue we are putting much more energy into translation than into vibration. We can then say that vibrational energy is not required for the reaction but may play a role in it.

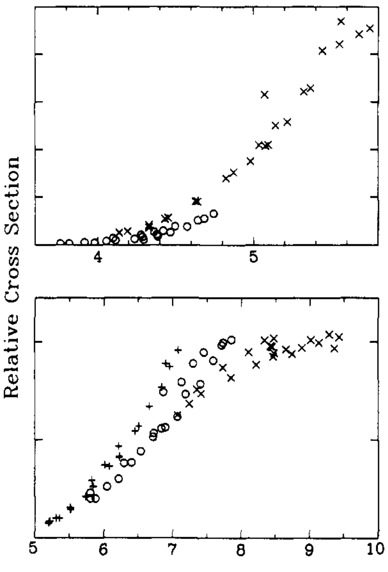

Figure 3. The cross section vs relative translational energy for the reaction of SbF_5 and benzoyl chloride. The top panel shows data with a beam intersection angle of 90°, and the bottom panel for 135°. Three carrier gases are used: He (+), H_2 (×), and a mixture of 40% H_2 and 60% He (○). The energy is varied by changing the nozzle temperature of the benzoyl chloride.

The data in the two panels of Figure 3 seem to be inconsistent. The extrapolated threshold for 90° is 4.3 eV, but the threshold for 135° is 5.1 eV. The reacting molecules have no way of knowing where the beams are in the laboratory, so these two numbers must be the same. There are several explanations for this discrepancy. Vibrational energy may be very important near the threshold. To get a given energy at 90°, we need a hotter nozzle and therefore get more vibrational energy. The determination of a threshold requires an extrapolation and thus assumes some functional form. We have implicitly assumed linear threshold behavior. If the true threshold law is very nonlinear—for example, exponential—the two extrapolations might give the same threshold.

At this point our picture of the reaction is quite simple. There is an initial reaction, probably fast, where the SbF_5 abstracts Cl^- from benzoyl chloride to form a pair of ions. The ion pair sticks together for a few picoseconds and then dissociates to form a pair of separated ions. At low energies the lifetime of this complex is comparable to a few rotation periods, and at higher energies, it gets shorter. Translational energy in the reactants is needed to produce the initial abstraction. Vibrational energy is not needed but may be interchangeable with translation.

We have seen reactions with a number of other halides as well. One of the more interesting cases is pivaloyl chloride, $(CH_3)_3CCOCl$.[7]

$$(CH_3)_3CCOCl + SbF_5 \rightarrow (CH_3)_3CCO^+ + SbF_5Cl^- \rightarrow (CH_3)_3C^+ + CO + SbF_5Cl^- \quad (2)$$

The pivaloyl cation can decompose by eliminating CO

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to form the very stable *tert*-butyl carbocation. We see both cation products. The cross section for total ion formation looks much like that for benzoyl chloride except that the threshold energy is somewhat larger. A plot of the fraction of the ions that fragment vs translational energy shows a strong dependence on the type of carrier gas. Helium, which has the higher nozzle temperature at a given translational energy, gives a much higher amount of fragmentation than H_2. The same data plotted vs nozzle temperature all lie on the same curve. The initial halide abstraction appears to depend on the reactant translational energy, but the fragmentation depends solely on vibrational energy in the pivaloyl chloride. This is quite reasonable. Translational energy causes the initial abstraction. Excess translational energy goes almost completely into translational energy of the product ions with very little ending up in the pivaloyl cation. On the other hand, most or all of the vibrational energy initially contained in the pivalyl chloride remains in the pivaloyl cation, where it is available to break the C–C bond. This second step probably occurs on a larger time scale than the initial reaction, much like a classic unimolecular decay.

There are several interesting problems with this model. If the ion pair sticks together, why does the translational energy between the two ions not rapidly equilibrate with the many vibrational degrees of freedom in the two ions? If this were to occur, the complex would not have enough translational energy to dissociate. The prevailing wisdom tells us that intramolecular vibrational relaxation takes place on a picosecond time scale. Crude calculations using the RRKM theory[10] show that, if this energy relaxation occurs, we will never see any products. The lifetime for dissociation into an ion pair is many orders of magnitude larger than the lifetime for dissociation back into neutral reactants. A closer look at the complex shows that it is bound by a strong Coulombic bond and that the bond has a very low frequency and is very poorly coupled to the faster internal vibrations in the two ions. The situation is similar to the case of van der Waals molecules where vibrational exchange with the van der Waals bond is known to be slow. Near the threshold, many of the complexes formed may be trapped, as energy is transferred to internal vibrations, and they never dissociate into separate ions. The fraction of trapped complexes decreases as energy is increased, and this appears as the rapid rise in the cross section above the threshold energy.

At first, it may seem surprising that vibrational energy plays such a small role in the reaction. We know from the experiments on pivaloyl chloride that vibrational energy is present in the beams and can be controlled. Consider, however, that SbF_5 has 12 vibrational degrees of freedom and benzoyl chloride has 39. Since we are putting the vibrational energy randomly into the normal modes, very little is going into the critical mode or modes responsible for the reaction. Indeed, with molecules of this size, it is impossible to prepare the reactants with more than a small amount of vibrational energy in a specific mode. As the amount of vibrational energy in a mode increases, so also does the coupling to other modes, and the energy is rapidly redistributed to all modes. It is also impossible, in principle, to measure the specific modes in the products that get excited by the reaction. Even as the two product ions separate, intramolecular vibrational relaxation is redistributing the energy to all the modes of the product.

We discovered a second type of reaction by serendipity. An enterprising student made a beam of SbF_5 at the highest energy possible and found ions with no crossed beam. A mass spectrum revealed small peaks separated by 14 amu—the signature of a hydrocarbon—which he supposed was pump oil. The overall reaction is[11]

$$SbF_5 + B \rightarrow SbF_5^- + B^+ \qquad (3)$$

where B is some organic base; amines work very well. The reaction goes with $SnCl_4$ and $TiCl_4$ and probably with many other metal halides of high electron affinity. The product contours are quite different from those in Figure 2. Except at the very lowest energy, they lack the forward–backward symmetry characteristic of a long-lived complex. Instead, the SbF_5^- appears along the SbF_5 beam and the B^+ along the B beam. The reaction appears to go by way of a grazing collision at large impact parameter. The two molecules come close to each other, and an electron is transferred. The products then separate, going in the same direction as before the reaction, but they are slowed down by their mutual Coulombic attraction. The electron transfer should be a fast, vertical, Franck–Condon transition, much like the absorption of a photon. This process forms an ion whose structure is the same as that of the neutral molecule. Because the equilibrium bond lengths and bond angles are different in the ion, the process creates an ion with vibrational excitation. In many cases the vertical ionization potentials and vertical electron affinities are known, so that we can calculate a vertical threshold energy for the reaction (the vertical ionization potential of B minus the vertical electron affinity of SbF_5). Since the reaction is a light, grazing collision, we would expect that very little additional energy transfer takes place. Thus, we predict that translational energy in excess of this vertical threshold will be put into translational energy of the products. In the case of $SnCl_4$ reacting with the base tetrakis(dimethylamino)ethylene, TDMAE, $[(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2$, we know the vertical threshold, and this appears to be the case. For SbF_5 we do not know the vertical electron affinity, but three product distributions for different beam energies give a constant value of 4.84 ± 0.3 eV.

Figure 4 shows the cross section vs energy for SbF_5 reacting with TDMAE.[12] As before, the top panel shows the data for a beam intersection angle of 90° and the bottom for 135°. Near the threshold (top panel), the data look like the data for the halide abstraction reaction: very sensitive to translational energy, but they depend on vibrational energy. The cross sections for He carrier gas (hotter nozzle) are higher than those for H_2, showing that vibrational energy enhances the re-

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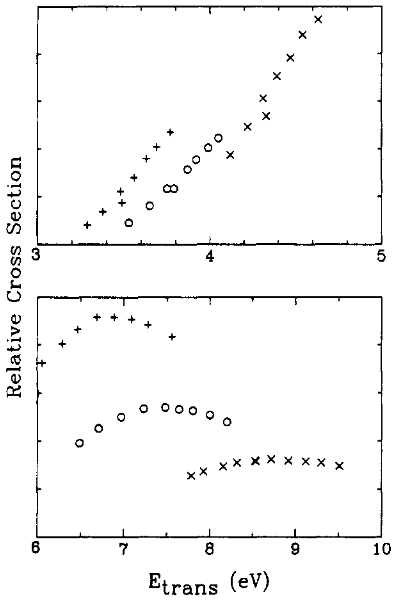

Figure 4. The cross section vs relative translational energy for the reaction of SbF_5 and TDMAE. See the caption of Figure 3 for details.

action. At higher energies (bottom panel), the cross section behaves very differently. Here the data for the different carrier gases differ greatly. At constant nozzle temperature, the cross section drops rapidly as the translational energy is raised (compare the ends of each of the three curves). For a given carrier gas, the cross section is approximately constant as the nozzle temperature is raised, raising both the translational and vibrational energies. Thus the cross section must rise with increasing vibrational energy in the TDMAE.

The behavior with translational energy is expected, and the behavior with vibrational energy[15] is not surprising. Reaction 3 takes place on two potential-energy surfaces: one covalent, corresponding to the reactants, and one ionic, corresponding to the products. At infinite separation, the ionic surface is higher by the adiabatic, thermodynamic threshold energy defined above: it costs energy to remove an electron from B and put it onto SbF_5. As the reactants or products are brought together, the covalent surface is roughly flat until the two molecules touch each other, and the surface becomes repulsive. The ionic surface, however, is strongly attractive due to the Coulombic force until it too becomes repulsive at small distances. The two surfaces cross each other at some point, and this is where the electron jumps from B to SbF_5. This reaction model is a variant on the "harpoon" model used by Herschbach[13] to explain the reactions of alkali atoms and halogen molecules. Because the surfaces have the same symmetry, there are small terms in the Hamiltonian that mix the two surfaces in the vicinity of the crossing, and the electron will jump from B to SbF_5 only in this region. This means that the electron must jump a distance of a few angstroms while the nuclei move through a distance of a few tenths of an angstrom. As the translational energy is increased, there is less time available when the reactants are at the critical distance, and the cross section drops. Since the coupling between the surfaces depends strongly on the vibrational coordinates, we might expect that vibrational energy would play a role in the probability.

We have found similar results by studying three different amines and by substituting $SnCl_4$ for SbF_5.[12] If the ionization potential of B is increased or the electron affinity of the metal halide is decreased, the threshold and the maximum in the cross section with translational energy both move to higher energies as expected.

Finally, we studied the reaction of an acid plus a base to give a salt,[14,15]

$$HA + B \rightarrow A^- + HB^+ \qquad (4)$$

This is one of the oldest known chemical reactions, going back to the days of alchemy. We measured the angular and energy contours for the reaction of HI with tri-*n*-butylamine (TBA),

$$HI + (C_4H_9)_3N \rightarrow I^- + (C_4H_9)_3NH^+ \qquad (5)$$

The reaction behaves very much like the electron-transfer reaction, except that a proton is transferred rather than the electron. The I^- appears in the direction of the HI beam and the protonated amine in the direction of the amine beam.

Measurement of the reactive cross section for the reaction of trifluoroacetic acid and TBA is similar to the halide abstraction.[14] The cross section rises rapidly as a function of translational energy and is independent of vibrational energy in the amine. Unlike reaction 1, where we have no thermodynamic data, and unlike reaction 3, where the data are neither extensive nor accurate, we have very good data from ICR studies on the absolute gas-phase acidities and basicities of a large number of molecules.[16] The measured threshold (based on a linear extrapolation) is ~0.9 eV above the thermodynamic threshold. The possible reasons for this difference are discussed above.

Trifluoroacetic acid, like other carboxylic acids, forms a dimer. The acidic hydrogens each bond to the carbonyl oxygen to form an eight-membered ring. In the gas behind the nozzle there is an equilibrium mixture of dimer and monomer, which is strongly dependent on the nozzle temperature. We know the thermodynamics for the dimerization[17] and that higher polymers are not formed. We can go from a case where the beam is mostly dimers at low temperatures to one where the beam is mostly monomers at high temperatures. Since the dimer has twice the mass of the monomer, it has roughly twice the kinetic energy and so reacts under beam conditions where the monomer reaction is well below the threshold. As we raise the nozzle temperature, the apparent cross section decreases because the fraction of dimer in the beam decreases, and then the apparent cross section rises because the cross section for the monomer reaction rises. The monomer and dimer have the same threshold energies to within our experimental error of ±0.4 eV. The cross sections have roughly the same magnitude as well.

We next studied the reactions of the acid 1,1,1-trifluoropentane-2,4-dione, $CF_3COCH_2COCH_3$ (TFPD). This is a strong acid with ΔG = 322 kcal/mol.[18] We

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chose this acid because it seemed unlikely to form dimers. The cross section appears to rise noticeably as the vibrational temperature of the TFPD is raised. The data for He as a carrier gas are higher than those for H_2. Whereas vibrational energy in the TFPD may enhance the reaction, there is another explanation. TFPD exists as three tautomers: a keto form, $CF_3COCH_2COCH_3$, and two enol forms, $CF_3C(OH){=}CHCOCH_3$ and $CF_3COCH{=}C(OH)CH_3$. The enol isomers are stabilized by the hydrogen bonding of the OH hydrogen to the carbonyl oxygen and, in the first case, to the fluorines. Because of this, the enol isomers are thermodynamically favored at low temperatures,[19] but the equilibrium shifts toward the keto isomer as the temperature rises. Our data can be interpreted by assuming that the keto isomer is more reactive than the enol isomers. This is a dynamic, not a thermodynamic effect. All three isomers form the same anion product. Because the three are in equilibrium, their heats of formation must be very similar, so that ΔH must be very similar for the deprotonation of all three isomers.

As in the case of the electron-transfer reaction, we can guess most of the major features of the potential-energy surface. The reaction must occur on two surfaces, one covalent and one ionic. Consider the reaction of HI and a base B. If the reactants are dissociated, they form $H + I + B$, all neutral. If the products are dissociated, they form $H + I^- + B^+$. The asymptotic separation of the surfaces is often known from thermodynamic data. The covalent surface is unreactive in that neutral HB is not bound. The ionic surface is barely reactive since HI^- is stable but only slightly bound. As in the electron-transfer case, the ionic surface has a deep well in it due to the Coulombic attraction of I^- and HB^+. Presumably, the reactants approach each other along the covalent surface until it intersects the ionic surface near the well. At this point the system crosses over to the ionic surface and emerges as products or is trapped in the Coulombic well and eventually crosses back to the covalent surfaces again.

The dynamics of the three systems of reactions studied here show an overall similarity, but there are obvious differences: not all chemiionization reactions are the same. Most features of the dynamics can be explained in simple terms by using well-known concepts in the field, despite the complexity of the molecules used. From the point of view of organic chemistry, the systems are quite simple; however, we have obtained a much higher degree of detail in understanding the reactive collision than is usual in this field.

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