3774 J. Am. Chem. Soc. 1990, 112, 3774-3778

Crossed-Beam Study of the Acid-Base Reaction

Y. D. Huh, R. J. Cross,* and M. Saunders*

Contribution from the Department of Chemistry, Yale University, Box 6666, New Haven, Connecticut 06511. *Received November 20, 1989*

Abstract: We have used crossed seeded nozzle beams to study the reaction of a neutral acid and a neutral base to produce the separated ions of a salt. Two acids were used: CF_3COOH and trifluoropentanedione (TFPD). Three bases were used: tri-*n*-butylamine, tri-*n*-propylamine, and tetrakis(dimethylamino)ethylene (TDMAE). In all cases the cross section rises rapidly as a function of relative translational energy. The observed thresholds are about 0.9 eV above the thermodynamic thresholds. The cross sections appear insensitive to vibrational energy in the base. In the case of TDMAE, however, the protonated base ion fragments, and the amount of the fragmentation depends on the vibrational energy in the TDMAE. In the case of CF_3COOH the cross section depends on the nozzle temperature of the acid because CF_3COOH dimerizes, and both monomer and dimer react. Similar effects are observed for TFPD; either the reactive cross section depends strongly on vibrational energy in the TFPD or we are seeing the reactions of both the keto and eenol forms of TFPD.

The reaction of an acid and a base to produce a salt is surely one of the oldest known chemical reactions. It is also one of the most fundamental since the concepts involved have been broadened by Brønsted and later by Lewis to include a large fraction of Chemistry. Here we use crossed molecular beams to study the detailed dynamics of proton transfer from an acid to a base

$$HA + B \rightarrow A^- + HB^+ \qquad (1)$$

where HA is the acid and B is the base, an amine. Ultimately, we want to know how the chemical bonds are broken and made, where in the reactants the energy must be put for maximum effectiveness, and where it goes in the products.[1] It is difficult to get this kind of information by using conventional chemical kinetics. The use of molecular beams, however, enables greater control and selection of the reactant energies and states and provides more information about the products. In a static gas, the distribution of velocities follows a broad Maxwell-Boltzmann distribution that is dependent on only one parameter, the temperature, and this can be varied only over a narrow range. In contrast, the velocity distribution in a seeded nozzle beam is quite narrow and can be varied over a wide range.[2] Furthermore, we can separately control the vibrational and translational distributions in a nozzle beam and thereby determine which type of energy is effective in promoting the reaction. This separation cannot be done in a gas at thermal equilibrium.

We have previously carried out this type of experiment on two other types of reaction: the abstraction of a halide ion by SbF_5[3]

$$SbF_5 + RX \rightarrow SbF_5X^- + R^+ \qquad (2)$$

and the transfer of an electron to a neutral electrophile[4]

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

In the case of reaction 2 the reactive cross sections rise rapidly as a function of relative translational energy above the threshold. The cross sections do not appear to depend on the vibrational energy in RX. In the case of reaction 3 we observed similar behavior at low energies but found that, at high energies, the cross section decreases rapidly as the translational energy increases but rises as the vibrational energy increases. This behavior is consistent with a model where the reaction takes place on two potential-energy surfaces, one covalent corresponding to the reactants, and one ionic corresponding to the products. At high energies the electron does not have the time to jump between the reactants, and the cross section decreases as the translational energy increases. The positions and coupling matrix elements depend on vibrational coordinates, and so the cross section depends on the vibrational energy. Reaction 1 offers several advantages over the others. Here we can make use of the extensive tabulations of absolute, gas-phase acidities and basicities measured by ICR (ion cyclotron resonance) and other techniques[5] to choose reactions and to calculate the thermodynamic thresholds. In the case of reaction 2 there are no gas-phase data, and in the case of reaction 3 the data are neither extensive nor accurate. Furthermore, we often have a greater range of beam conditions available for reaction 1 than in the other cases.

Experimental Section

The experimental procedure has been described in detail in several previous publications.[3,4,6] Briefly, two seeded, supersonic beams are crossed at 90° or at 135° in a large vacuum chamber. The chemiionization reaction takes place in the center of the chamber inside a cage made of nickel grid. The ions are extracted by an electric field, mass selected by a quadrupole mass filter, and then detected by a Channeltron electron multiplier. By reversing the electric fields we can detect both positive and negative ion products. A filament is mounted just above the beam intersection region. When heated, it gives off a beam of electrons that ionize the beams. We can thus measure the relative intensities of the two beams under a variety of beam conditions.

The nozzle beams are prepared by bubbling the carrier gas (He, H_2, or a mixture of 60% He and 40% H_2) through the liquid reactant. The amount of the reactant is determined by the vapor pressure. The gas is then filtered to remove droplets and passed into the Pyrex nozzle. The nozzle is 40-80 μm in diameter. The nozzle assembly can be heated up to 400 °C. The beam is then collimated by a skimmer 1-2 mm in diameter. The vibrational energy of each beam is controlled by varying the nozzle temperature. The relative translational energy is varied by changing the two nozzle temperatures, by changing the carrier gases, and by changing the beam intersection angle. The reactive cross section is then given by

$$Q_{react} = I_{prod}/(n_A n_B v_{rel}) \qquad (4)$$

where I_{prod} is the product intensity, n_A and n_B are the number densities

---

(1) Herschbach, D. R. *Adv. Chem. Phys.* **1966**, *10*, 319. Herschbach, D. R. *J. Chem. Soc., Faraday Discuss.* **1973**, *55*, 233.

(2) Anderson, J. B. *Molecular Beams and Low Density Gas Dynamics*; Wegener, P. P., Ed.; Marcel Dekker: New York, 1974.

(3) Lee, L.; Russell, J. A.; Su, R. T. M.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **1981**, *103*, 5031. Russell, J. A.; Hershberger, J. F.; McAndrew, J. J.; Cross, R. J.; Saunders, M. *J. Phys. Chem.* **1984**, *88*, 4494. Hershberger, J. F.; McAndrew, J. J.; Cross, R. J.; Saunders, M. *J. Chem. Phys.* **1987**, *86*, 4916. Arena, M. V.; Hershberger, J. F.; McAndrew, J. J.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 6658.

(4) Russell, J. A.; Hershberger, J. F.; McAndrew, J. J.; Cross, R. J.; Saunders, M. *J. Chem. Phys.* **1985**, *82*, 2240. Hershberger, J. F.; Huh, Y. D.; J. F.; McAndrew, J. J.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **1988**, *110*, 1104.

(5) Aue, D. H.; Bowers, M. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 1. Bartmess, J. E.; McIver, R. T. *Ibid.*, Vol. 2, p 87. Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1985**, *13*, 695. Hartman, K. N.; Lias, S. G.; Ausloos, P.; Rosenstock, H. M.; Schroyer, S. S.; Schmidt, C.; Martinsen, D.; Miline, G. W. A. In *A Compendium of Gas Phase Basicity and Proton Affinity Measurement*; National Bureau of Standards: Washington, DC, 1979, NBSIR 79-1777. Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85. Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187.

(6) Hershberger, J. F.; McAndrew, J. J.; Russell, J. A.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **1984**, *106*, 7995.

0002-7863/90/1512-3774$02.50/0

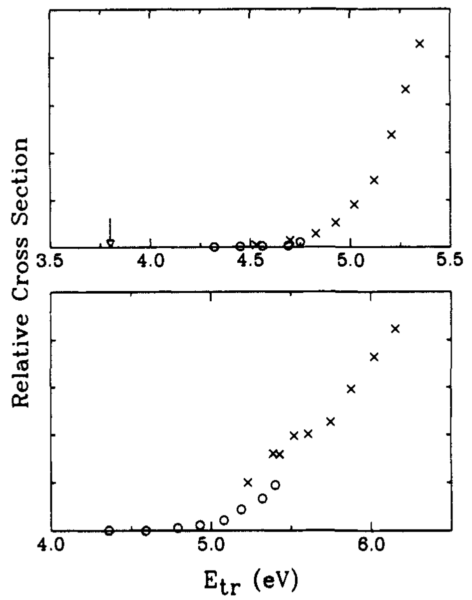

Figure 1. The relative cross section (in arbitrary units) for the reaction of tri-*n*-butylamine with CF_3COOH vs the relative translational energy. The top panel shows the data for a 90° beam intersection angle and the bottom panel the data for a 135° intersection angle. Two carrier gases are used: a mixture of 60% He and 40% H_2 (O) and H_2 (×). The relative translational energy is varied by changing the temperature of the nozzle for the amine beam. The beam for CF_3COOH is seeded in H_2 at 296 °C for the 90° case and is seeded in He at 289 °C for the 135° case.

of the two beams, and v_{rel} is the relative velocity. We cannot determine the absolute *n*'s, but we can get the relative values and can therefore get the relative Q as a function of the beam conditions.

Results

Figure 1 shows the relative cross section as a function of relative translational energy for the reaction of trifluoroacetic acid with tri-*n*-butylamine

$$CF_3COOH + NBu_3 \rightarrow CF_3COO^- + HNBu_3^+ \qquad (5)$$

The top panel shows the results for a beam intersection angle of 90° and the bottom panel the results for 135°. As the beam intersection angle increases, more of the beam energy goes into the relative kinetic energy that is available for the reaction and less goes into the energy of the center of mass that is not available for reaction. The energy is varied by changing the temperature of the NBu_3 nozzle. Two carrier gases are used: a mixture of 60% He and 40% H_2 (O) and H_2 (×). Roughly, the nozzle expansion accelerates the reactant seed gas up to the velocity of the carrier gas. There are corrections to this, which we use in calculating the energies.[2] Therefore, to get a given relative translational energy using He we need a much higher nozzle temperature than to get the same energy using H_2. As the nozzle temperature is increased, both the vibrational temperature and the translational energy of the seed gas increase. We assume that rotational cooling is quite efficient in the nozzle expansion so that the rotational energy is quite low. There is probably some vibrational cooling as well, but we deliberately use low Mach numbers (5–10) in the nozzle expansion to limit to amount of vibrational cooling. It is obvious from the figure that the data for the two carrier gases overlap, and therefore vibrational energy in the reactants plays little or no role in the reaction.

There are two extreme, limiting models for the role of vibrational energy. In one case, a certain amount of vibrational energy is absolutely required for the reaction—it cannot be replaced by translational energy. In this case, a simple model calculation[7] shows that the cross section should be proportional to an Arrhenius-type factor with the required vibrational energy as the activation energy and the nozzle temperature as the temperature.

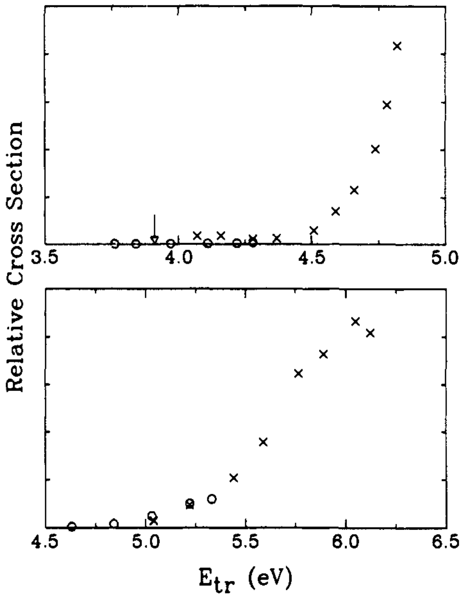

Figure 2. The cross section for the reaction of tri-*n*-propylamine with CF_3COOH. See Figure 1 for details.

This type of behavior predicts a very large, exponential rise in the cross section with nozzle temperature and therefore a large dependence on the type of carrier gas. This is clearly not consistent with our data. At the other extreme, we can assume that vibrational and translational energies are freely interchangeable. In this case we expect a much smaller effect—one that we cannot readily distinguish in the data. Although we have many vibrational modes in the reactants (18 in CF_3COOH and 114 in NBu_3) and therefore can put up to 1 eV into vibration, the critical bonds and modes contain only thermal energies.

The arrow gives the thermodynamic threshold for the reaction as obtained from accurate ICR data on absolute, gas-phase acidities and basicities.[5] The dynamic threshold appears to be higher than that by 0.9 eV. There are three possible reasons for this. A classical trajectory exactly at the threshold may involve vibrational energy in one or more modes, and we have only a negligible part of the beam with the required amount of vibrational energy in these modes. There may be some dynamic reason why the system cannot react at the threshold such as an activation barrier or some other peculiarity of the surface. Finally, the threshold law may be decidedly nonlinear. Since our extrapolation to obtain the threshold is basically linear, we may obtain the wrong value. For example, if the cross section rises exponentially above the threshold, our cross sections might be fully compatible with the thermodynamic threshold although the extrapolated threshold will not be.

The second explanation is probably not true. Although the overall reaction is strongly endoergic, the potential-energy surface (PES) goes through a deep well corresponding to an ion pair bound together by the Coulomb attraction. The reaction is probably exoergic to the bottom of the well. It is certainly strongly exoergic in solution where the ion products are solvated. According to Hammond's postulate any barrier should be in the entrance valley of the PES and thus requires translational not vibrational energy to get over it. Furthermore, our previous studies[6] on the angular and energy distributions of the products from the reaction of HI with NBu_3 showed that the reaction proceeds just above threshold by way of a modified stripping process. The acid and base suffer a grazing collision during which the proton is transferred, and the products recede, slowed by the Coulomb attraction. In this case it is unlikely that there is any fancy structure in the PES affecting the reaction. A combination of the first and third effects is most likely.

Figure 2 shows the cross section for the reaction of CF_3COOH with tri-*n*-propylamine. It is very similar the case of butylamine as it should be. Figure 3 shows the cross section for the reaction of CF_3COOH with tetrakis(dimethylamino)ethylene (TDMAE)

---

(7) Cross, R. J. *Chem. Phys. Letts.* **1979**, *62*, 469.

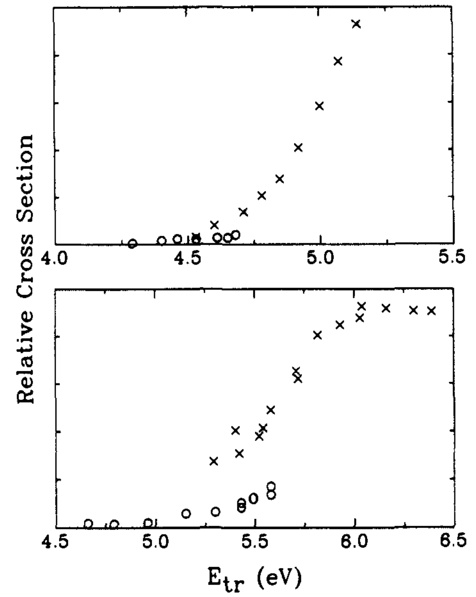

Figure 3. The cross section for the reaction of tetrakis(dimethylamino)ethylene (TDMAE) with CF_3COOH. Two cation products are formed, and the data show the sum of the two intensities.

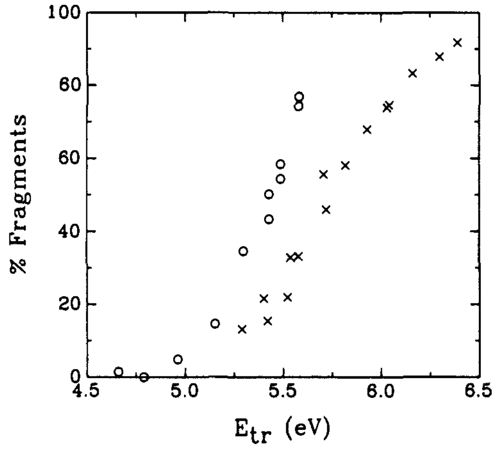

Figure 4. The fraction of the products of the reaction of TDMAE with CF_2COOH that form fragment ions as a function of relative translational energy at the 135° beam intersection angle.

$[(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2$. The absolute basicity of TDMAE is unknown, but the data suggest that it is a stronger base than NBu_3 or NPr_3. In the case of TDMAE we see an additional effect in the reaction. The protonated TDMAE product decomposes by the elimination of dimethylamine. We see both the parent and daughter ions. The data in Figure 3 show the sum of the two intensities. As before, the cross section depends strongly on translational energy, and vibrational energy makes little or no contribution. In Figure 4 we plot the fraction of the cations that are the fragment vs. the translational energy. As before, the translational energy is varied by changing the temperature of the TDMAE nozzle. Now we see a large effect of vibrational energy. Fragmentation is much more likely for the mixture than for H_2. Remember that, at a given relative translational energy, He carrier gas has the higher vibrational temperature. The vibrational energy in the beam can be obtained very roughly by using an approximate vibrational heat capacity[8] and integrating this over temperature. In Figure 5 the same data are replotted as a function of $E_{tr} + {}^1/_2E_{vib}$. We see that the amount of fragmentation is determined by both relative translational and vibrational energies. A plot of the fragmentation fraction vs $E_{tr} + E_{vib}$ shows a dependence on the type of carrier gas, but now the points for H_2 lie above those

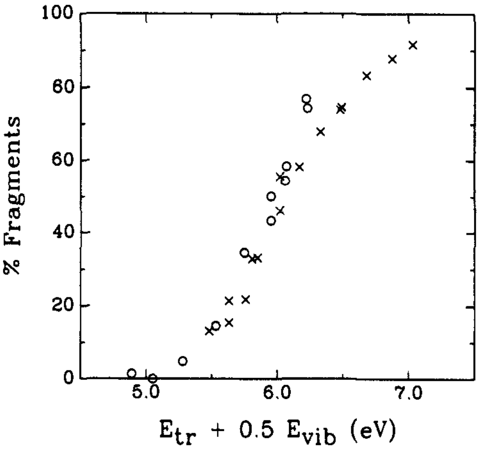

Figure 5. The data from Figure 4 are plotted as a function of $E_{trans} + {}^1/_2E_{vib}$ to show the effect of vibrational energy on the fragmentation process.

for the mixture. The data show that translational energy is very roughly twice as effective as vibrational energy in promoting fragmentation.

The data can be explained quite simply. The initial proton transfer occurs rapidly, in a few picoseconds. The reaction is governed by relative translational energy. Vibrational energy in the TDMAE is distributed randomly among its 108 vibrational modes and is largely or completely unavailable to participate in the reaction. If the reaction occurred by way of a long-lived complex lasting many tens of picoseconds, we would expect equilibration between translation and vibration, and this does not appear to be the case. After the proton transfer almost all the initial vibrational energy and some of the initial translational energy are deposited in the protonated TDMAE product ion. Some time later (nanoseconds or microseconds) this ion decomposes, if possible, by a straightforward unimolecular decay by breaking its weakest bond. Clearly, adding vibrational energy to the TDMAE will enhance the fragmentation, since this energy remains in the cation.

These data are consistent with our earlier results on halide abstraction by SbF_5. In the reaction with pivaloyl chloride[3]

$$SbF_5 + (CH_3)_3CCOCl \rightarrow SbF_5Cl^- + (CH_3)_3COO^+ \rightarrow SbF_5Cl^- + (CH_3)_3C^+ + CO \quad (6)$$

we found that the cross section for total ion formation depends only on translational energy, but that the fraction of fragment ions depends exclusively on vibrational energy. In the case of phenylacetyl chloride[3]

$$SbF_5 + C_6H_5CH_2COCl \rightarrow SbF_5Cl^- + C_6H_5CH_2CO^+ \rightarrow SbF_5Cl^- + C_6H_5CH_2^+ + CO \quad (7)$$

we found that the fraction of product ions depends on both translational and vibrational energy. The overall mechanism appears to be the same in all three cases. They differ only in how much of the initial translational energy is deposited in the cation product. If the reaction cross section is large, the reaction will take place at large impact parameters, and little translational energy will be put into the products. If the cross section is smaller, the collision takes place at smaller impact parameters—a harder collision, and more energy goes into vibration of the products.

In all of the above experiments the CF_3COOH was seeded in H_2 or He and kept above 270 °C. Figure 6 shows the cross section as a function of relative translational energy, where the translational energy is varied by changing the temperature of the CF_3COOH nozzle rather than the nozzle for the base. The behavior is very different. The cross section appears to drop rapidly as the energy increases and then rises again at higher energies. Furthermore, the cross section depends strongly on the type of carrier gas. This strange behavior is simply explained by the fact that CF_3COOH, like all carboxylic acids, forms a dimer in the gas phase. Each proton forms a hydrogen bond with the carbonyl

---

[8] Bennewitz, K.; Rossner, W. *Z. Phys. Chem.* **1938**, *B39*, 126. Dobratz, C. J. *Ind. Eng. Chem.* **1941**, *33*, 759.

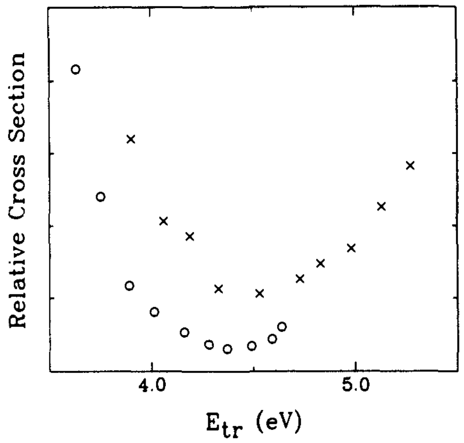

Figure 6. The relative cross section for the reaction of TDMAE and CF_3COOH vs relative translational energy. The translational energy is varied by changing the nozzle temperature of the CF_3COOH.

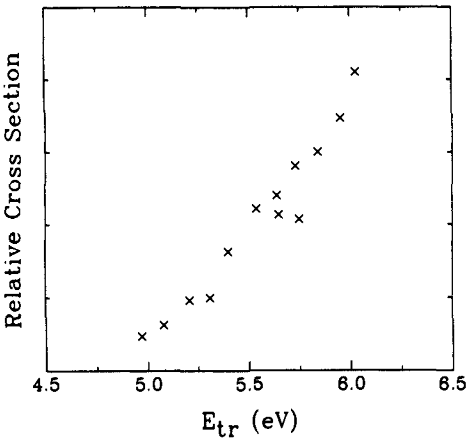

Figure 7. The cross section for the reaction of TDMAE and $(CF_3COOH)_2$ vs relative translational energy (calculated for the dimer). The CF_3COOH nozzle is kept at 20 °C to ensure that the beam composition is mostly dimers.

oxygen on the other molecule to form a dimer with an eight-membered ring. The equilibrium constant has been measured as a function of temperature.[9] Energy favors the dimer, but entropy favors the monomer. Under our beam conditions the beam is mostly dimers at 20 °C and almost all monomers by 300 °C. Both species react with roughly equal cross sections and roughly equal threshold energies. However, the dimer has twice the mass of the monomer so that, under the same beam conditions, the dimer has roughly twice the kinetic energy of the monomer. Therefore, at monomer energies below the threshold, we can see the reaction of the dimer. The apparent cross section decreases at low energies because the amount of dimer decreases as the nozzle temperature is raised. The cross section rises again at high energies because there is almost no dimer left, and the reaction cross section for the monomer rises with energy. The cross section depends strongly on the type of carrier gas because the dimer fraction depends on nozzle temperature not on the translational energy. To get a given translational energy we need a higher nozzle temperature for the mixture than for H_2. This gives less dimer and therefore a lower signal intensity.

We can see both the cation product and the anion products of the reaction. The monomer clearly gives only $CF_3CO_2^-$. At low energies the dimer gives $(CF_3COOHOOCCF_3)^-$ as expected. However, the intensity of this peak drops more rapidly that we would expect if this were the only product of the dimer reaction. Our data indicate that, as the energy rises, the dimer product dissociates to give $CF_3CO_2^-$ and CF_3COOH. Unfortunately, we cannot distinguish $CF_3CO_2^-$ from the dimer reaction from the same product obtained directly from the monomer reaction.

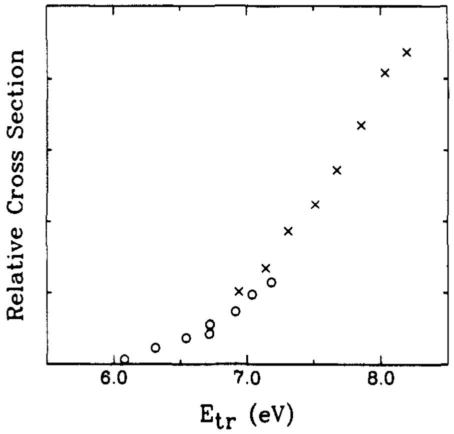

Figure 8. The cross section for TDMAE and trifluoropentanedione (TFPD) vs relative translational energy. The data show the sum of the intensities of the two cation products. The energy is varied by changing the temperature of the TDMAE beam while keeping the nozzle for TFPD at 308 °C.

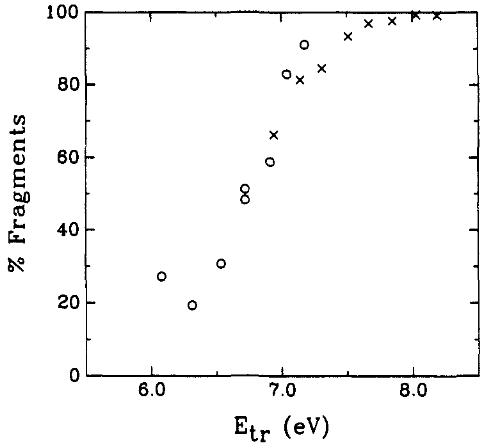

Figure 9. The fraction of the product ions that form fragments in the reaction of TDMAE and TFPD.

Figure 7 shows the cross section for the dimer reaction as a function of the relative translational energy. The CF_3COOH is kept at 20 °C to ensure that it is mostly dimer. There is still a small amount of dimer present at 20 °C, but its kinetic energy is well below the threshold for reaction, so it does not interfere with the dimer reaction. The threshold energies of the monomer and dimer reactions are similar as are the magnitudes of the cross sections. The difference in the thermodynamic thresholds is the difference in binding energies of the neutral and ionized CF_3COOH to the neutral molecule, and this is apparently less than the uncertainty of our energy (±0.4 eV). We might expect that the dimer would have the larger cross section since it has two protons, but both are tied up in hydrogen bonds, and this might decrease their availability somewhat.

We then used the acid trifluoropentanedione ($[CF_3COCH_2COCH_3]$, TFPD) with the idea that it does not dimerize as readily as carboxylic acids due to the intramolecular hydrogen bonding. The molecule is acidic because removal of one of the two central hydrogens creates an anion with the charge distributed on both carbonyl oxygens; however, the acidity is less than that of CF_3COOH. Figure 8 shows the cross section of TFPD and TDMAE. The translational energy is varied by changing the nozzle temperature of the TDMAE. Again, the cation product fragments. The data in Figure 8 show the sum of the intensities of both products. The data are very similar to those of the previous cases. The cross section is determined predominantly or exclusively by relative translational energy. Figure 9 shows the fraction of the fragment product vs relative translational energy. The data for the three carrier gases nearly overlap, which means that vibrational energy in the TDMAE has

---

[9] Taylor, M. D.; Templeman, M. B. J. Am. Chem. Soc. 1956, 78, 2950.

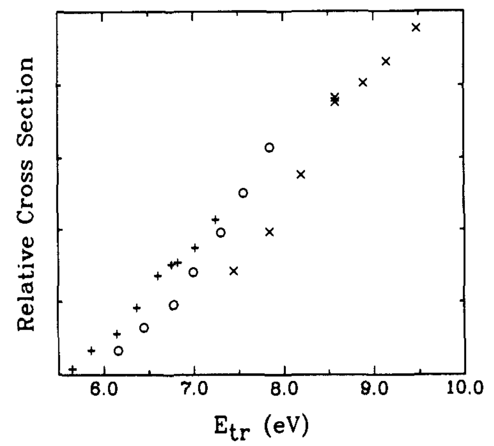

Figure 10. The cross section for the reaction of TDMAE and TFPD vs relative translational energy. The energy is varied by changing the temperature of the TFPD nozzle. The points designated + use He as a carrier gas.

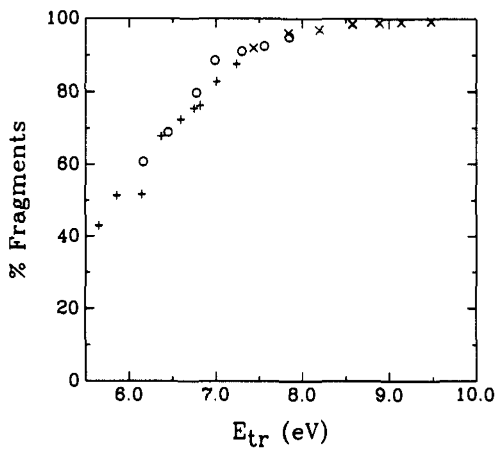

Figure 11. The percentage of fragment ions for the reaction of TFPD and TDMAE vs relative translational energy. The energy is varied by changing the nozzle temperature of the TFPD.

little effect on the fragmentation. Unlike the case of CF_3COOH, the fragmentation is determined largely by translational energy. A likely explanation is that the reaction with TFPD takes place at smaller impact parameters than the reaction with CF_3COOH because it is more endothermic, and therefore a harder collision is needed. If this is true, then one would expect that more of the translational energy in the reactants would be deposited into vibrational energy of the products.

Figure 10 shows the cross section for total ion formation as a function of translational energy, but now the translational energy is varied by changing the nozzle temperature for TFPD. We see a clear difference in cross section for the different carrier gases. This would appear to indicate that the cross section is strongly enhanced by vibrational energy in the acid. This may well be the case. However, there is also another explanation. TFPD exists as three isomers: a keto form [$CF_3COCH_2COCH_3$] and two enol forms [$CF_3COH{=}CHCOCH_3$] and [$CF_3COCH{=}COHCH_3$]. Usually, the enol form of a ketone is present only in very small amounts, although it is known to be involved in many reactions. Here, however, the enol is stabilized by hydrogen bonding to the other carbonyl and, in one case, to the fluorines. The equilibrium constant has been measured:[10] the enol forms are favored at low temperatures and the keto form at high temperatures. Our results can then be interpreted by assuming that the keto form is more reactive than the enol forms, and thus the apparent cross section rises with the temperature of the TFPD. The difference in reactivity is a dynamic phenomenon not an energetic one. All three isomers give the same anion. Since there is only a small difference in energy between the isomers, ΔH for the different reactions must be very close. In the keto form there are two acidic hydrogens. In the enol forms there is only one: the OH hydrogen which, however, is part of a hydrogen bond and may be more difficult to remove in a fast collision. Finally, Figure 11 shows the fraction of the cation fragments as a function of the translational energy, where the translational energy is varied by changing the temperature of the TFPD. Vibrational energy in the acid appears to have no effect on the fragmentation of the cation product. This result is not unexpected if our model of a fast proton transfer is correct.

Discussion

We have used crossed seeded nozzle beams to study the cross section versus energy of several reactions involving neutral acids and neutral bases to form the ions of a salt. All our data are consistent with a simple model that the proton transfer is a rapid process that takes place in a grazing collision. The two product ions are then slowed down by their mutual Coulomb attraction. The cross sections all rise rapidly above a threshold as functions of the relative translational energy. They appear to be insensitive to vibrational energy in the base and are likely to be insensitive to vibrational energy in the acid, although our data are not as clear on this point. Although we can put up to 1 eV into vibrational energy, it is distributed among a large number of normal modes so that very little is likely to be found in the critical mode or modes that might contribute to reaction. A complete test of the effect of vibrational energy would require specific excitation of one or two modes. This type of experiment would be quite difficult for our systems. With the large number of degrees of freedom, any appreciable amount of excitation in one mode would be rapidly dissipated throughout the molecule by intramolecular vibrational relaxation (IVR), which is known to occur on a picosecond time scale. In all cases the measured reaction threshold appears higher by ~0.9 eV than the thermodynamic threshold obtained by independent studies (usually ICR). This difference may indicate that vibrational energy is important near threshold. It may also be the result of an incorrect extrapolation of our data to find the threshold. If, for example, the true cross section rises exponentially above threshold, a linear extrapolation will give a value that is too high.

In the case of TDMAE the cation product can fragment by the elimination of dimethylamine. The amount of fragmentation depends on the vibrational energy in the TDMAE and also on the translational energy. The fragmentation occurs on a much longer time scale than the proton transfer and seems to be a case of unimolecular decay. If there is sufficient vibrational energy in the product, it will break the weakest bond. This result shows that our beams do, indeed, have vibrational energy, and that much of this vibrational energy is left in the cation product after the proton is abstracted.

In the case of CF_3COOH we can see reaction of both the monomer and the dimer. The threshold energies and the energy dependence of the cross sections are very similar. In the case of trifluoropentanedione the reaction cross section rises rapidly with the nozzle temperature. This may show a very sensitive dependence on vibrational energy, or it may be due to the equilibrium between keto and enol forms of the acid. Thermodynamics favors the enol form at low temperatures, but the equilibrium shifts toward the keto form as the temperature is raised. With only one acidic proton which is tied up in a hydrogen bond, the enol form is likely to be less reactive than the keto form.

Acknowledgment. We are grateful to the National Science Foundation for research support under Grant CHE-8901577. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to Mr. Yu-fong Yen for help in the later phases of this work.

---

(10) Burdett, J. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 2105.