

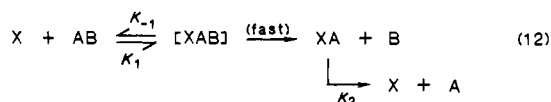
$$K_1 = e^2 \left(\frac{kT}{h} \right) \exp(\Delta S_c^* / R) \exp(-E_a / RT) \quad (11)$$

$$E_a = 7.40 \text{ kcal/mol}; \Delta S_c^* = 17.6 \text{ eu}$$

This entropy of activation is consistent with the assumed value $\Delta S^\circ_{\phi\Omega} \approx 22 \text{ eu}$.

Conclusion

The T-jump technique for measuring relaxation times in the μs range allows one to investigate molecular conversions over low barriers and provides a means for exploring limits of applicability of classical kinetic formulations. The mechanism that accounts for the dissociation of formic acid dimer in the gas phase may have general applicability, since the process has a lower activation



energy than the bond dissociation energy (D_{AB}) whenever $K_2 > K_{-1}$. At present there are too few examples to permit the development of empirical rules for predicting the relative magnitudes of these basic rate parameters. Clearly it is essential that there be significant coupling between the newly formed X-A bond and the dissociating A-B bond.

Acknowledgment. The investigation was supported by a grant from the AFOSR [F49620-84-C-0031].

Registry No. Formic acid, 64-18-6.

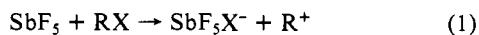
Molecular-Beam Study of Chemiionization Reactions of SbF_5

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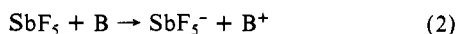
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511-8118. Received March 23, 1987

Abstract: We have studied the energy dependence of the reactive cross sections for three sets of isomeric reactions, all involving the halide or electron transfer to antimony pentafluoride from organic halides. We find that the cross sections for iodide abstraction of the four butyl iodides have virtually the same energy dependence. This strongly suggests that some rearrangement takes place during the reactive collision so that the product in all cases is the stable *tert*-butyl cation. Similar studies on five-carbon acyl chlorides, however, show very different behavior when the resulting acyl cation decomposes by eliminating CO. Finally, results on the competition between halide abstraction and electron transfer from isomers of butenoyl chloride seem to indicate that the two processes do not pass through a common intermediate.

During the past few years we have used crossed molecular beams to study the dynamics of gas-phase chemiionization reactions of SbF_5 in order to understand their basic mechanisms. We have found two different classes of reactions. One is a halide abstraction¹⁻⁴



where X is a halogen and R is an organic or inorganic group. The second is an electron transfer⁵



where B is an organic base. In each case we measured the angular and energy distributions of the product ions. In the case of reaction 1 the product distributions have forward-backward symmetry about the center of mass. This indicates that the reaction proceeds by way of a long-lived complex that sticks together for a rotational period or longer. At the highest available energy, 6.8 eV, the distributions begin to lose this symmetry. This may indicate that at higher energies the lifetime of the complex becomes comparable to the rotational period. Unfortunately, the asymmetry is only just larger than the experimental error, and we cannot go to a higher energy where the lifetime should be still shorter.

In contrast, the product angular and energy distributions for reaction 2 show no such symmetry except for the lowest energy studied. The reaction appears to go by way of a fast, direct mechanism. Our data are explained by a simple model. The two reactants are assumed to collide at large impact parameters, a

grazing collision. The electron jumps from B to SbF_5 . As the products separate, they are attracted to each other by the Coulomb force. The threshold energy should be the vertical ionization potential of B minus the vertical electron affinity of SbF_5 . Because the reaction takes place in a grazing collision, there is very little internal energy transferred except that which is put into the molecules by the vertical electron jump. All translational energy in the reactants above the vertical threshold should go into translational energy of the products. We found this to be true for the reaction of SnCl_4 , where the electron affinity is known, and tetrakis(dimethylamino)ethylene (TDMAE), which has one of the lowest ionization potentials of all organic molecules. The electron affinity of SbF_5 was unknown, but we obtained the same value at three different beam energies. Below the vertical threshold the electron-transfer reaction appears to go by way of a long-lived complex.

We have recently reconfigured the apparatus to study the total reactive cross section as a function of the amount and type of initial energy.⁴ For reaction 1 the cross section rises rapidly above a threshold energy which is typically a few eV and depends on the RX species being studied. Well above the threshold energy, the effect of vibrational energy on the cross section is comparable to or less than that of translational energy. However, near the threshold, the effect of a small amount of vibrational energy may be comparable to that of several times as much translational

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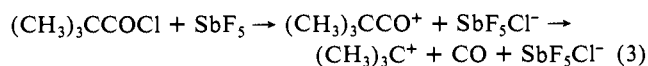
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energy. For reaction 2 our preliminary results show a very complicated dependence on translational and vibrational energies. In both cases, we can form a product ion that can eliminate a neutral fragment to form a more stable ion. For example, pivaloyl chloride reacts to form the tertiary butyl cation



Although the initial halide abstraction is only slightly affected by vibrational energy in the pivaloyl chloride and depends largely on translational energy, the fragmentation depends primarily on the initial vibrational energy. Translational energy has only a small effect on fragmentation.

In the present paper we explore several additional features of these two reactions. Carbocations are well-known to rearrange rapidly. Ion-molecule reactions on isotopically labeled species frequently show extensive rearrangement, even to the point of giving statistically random distributions of all possible isotopic products.⁶ Can such a rearrangement occur during the halide transfer reaction? A possible answer can be obtained by measuring the cross section as a function of energy for several isomeric reactants whose heats of formation are nearly identical but whose product ions have very different energies. Here we use the four butyl iodides. We find that the threshold energies are the same within experimental error for the four isomers. If there were no rearrangement, we would expect that *n*-butyl iodide would have a much higher threshold than *tert*-butyl iodide. However, if rearrangement takes place during the reaction, and the product formed is the most stable product ion, *tert*-butyl cation, then the threshold energies should be comparable.

These same questions can be asked about the fragmentation process. Here we use various isomers of pivaloyl chloride. The results are quite different, however. The different isomers show very different probabilities of decomposition. Evidently, the initial halide abstraction results in a loosely bound complex of SbF_5 and R^+ where rearrangement of the R^+ moiety can occur before the complex dissociates. The acyl cation product will contain vibrational energy and may then fragment, but it is a more tightly bound species and cannot rearrange before the CO is eliminated.

Finally, we explore the interrelation between the halide transfer and the electron transfer. We have found several cases where both reactions occur for the same RX species. Various isomers of butenoyl chloride show varying amounts of electron transfer and chloride transfer. Our current models for both reactions 1 and 2 involve two potential-energy surfaces, one covalent leading to the reactants and one ionic leading to the products. This is certain for the electron transfer and likely for the halide transfer. It is possible that the ionic surface for the halide transfer is the same surface that leads to an electron transfer. The reactants would then approach, and an electron would jump from RX to SbF_5 . The two ions would then collide, a halogen atom would be transferred, and the products would then dissociate. This is analogous to the "harpoon" mechanism observed many years ago in the reactions of alkali metal atoms with halogen molecules.⁷ It is also possible that the two reactions are separate and that there are three surfaces.

Experimental Section

The apparatus has been described previously¹⁻⁵ as has the technique for measuring the reactive cross sections.⁴ Briefly, two seeded supersonic molecular beams intersect in a vacuum chamber. The product ions are extracted by an ion lens, mass selected, and detected. Each beam is prepared by passing a mixture of carrier gas (H_2 , He, or a mixture of 39.8% H_2 and 60.2% He) and a small amount of the reactant through a Pyrex nozzle. A detailed description of how the beams are prepared is given in ref 2. The conditions are such that the final Mach number is small (7-10) so that the vibrational relaxation and dimer formation

are minimized. To a first, crude approximation the vibrational energy distribution is a Boltzmann distribution at the nozzle temperature. The rotational energy is very well relaxed under our conditions and can effectively be neglected. The translational energy distribution is narrow and is calculated with well-known formulas,⁸ including a correction for the nozzle slip factor.⁸ The translational energy increases with nozzle temperature but also depends on the carrier gas. Thus, at a given nozzle temperature, the translational energy will be higher for H_2 than for the mixture, which, in turn, is higher than for He. Thus we have a way of independently varying the translational and vibrational energies of the reactants. The relative translational energy also depends on the intersection angle between the two beams. We can use either 90° or 135° ; the relative energy is higher for the 135° case. The two beams intersect in a grid cage where the product ions are extracted by a 100 V potential. The ions are then mass analyzed by a quadrupole mass filter and detected by an electron multiplier.

The total reactive cross section is given by

$$I = Qn_A n_B v_{rel} \quad (4)$$

where I is the intensity (ions/cm³) of the product, n_A and n_B are the number densities (molecules/cm³) of the beams, and v_{rel} is the relative velocity of A and B. Q is the cross section with units of area. Since we do not know the detailed geometry of the intersection region and cannot get an absolute measure of n , we can only obtain relative cross sections from one set of conditions to another. A filament is mounted directly over the region where the two beams cross. When turned on, it emits electrons that ionize the molecules in the beams. We can therefore measure the relative number density (n) of each beam, and by passing the resulting ions through a retarding-potential-energy analyzer, we can measure their velocity distribution. We find that n is independent of nozzle temperature within our experimental error. The relative cross sections for a given carrier gas are accurate to about 15%. This uncertainty is due largely to changes in beam intensity during a run. The number density in the beam does depend on the type of carrier gas, and the cross sections are normalized to account for this. The uncertainty in this normalization factor causes an additional uncertainty of 15% for the normalization of the cross sections for two different carrier gases. The calculated beam velocity agrees with the measured velocity to 5%. The relative energy is accurate to about 0.4 eV. Some of this is systematic error which is the same from run to run, so that differences in relative energy between runs are also accurate to 0.4 eV.

There are several problems with the SbF_5 beam that affect the experiment. SbF_5 is known to dimerize in the gas phase,⁹ and so the beam contains a small fraction of dimers that can react with RX to produce R^+ . These are effectively eliminated by keeping the nozzle temperature above 270°C , but by fixing the temperature, we cannot examine the effect of vibrational energy in SbF_5 . We cannot easily measure the intensity of the SbF_5 beam because it entails aiming the beam right into the detector, and this greatly shortens the life of the electron multiplier.

Results

Butyl Iodides. The four panels of Figure 1 show the total reactive cross section for each of the four butyl iodide isomers plotted against the relative translational energy. The beam intersection angle is 135° , and three carrier gases are used in the butyl iodide beams: H_2 , the H_2/He mixture, and He. The apparent decrease in cross section at the highest energies for each of the three carrier gases is due to thermal decomposition of the butyl iodide inside the nozzle. The data for the different carrier gases agree to within experimental error, and this indicates that vibrational energy in the iodide does not play a major role in the reaction at high energy, since, at a given translational energy, the nozzle temperature is very much hotter for the heavier carrier gas than for the lighter one. If even a small amount of vibrational energy were specifically required by the reaction, the data would show a sharp rise in the cross section with vibrational temperature given roughly by the Arrhenius equation. This obviously does not occur. Vibrational energy may be interchangeable with translational energy to some extent, or it may play no role in the

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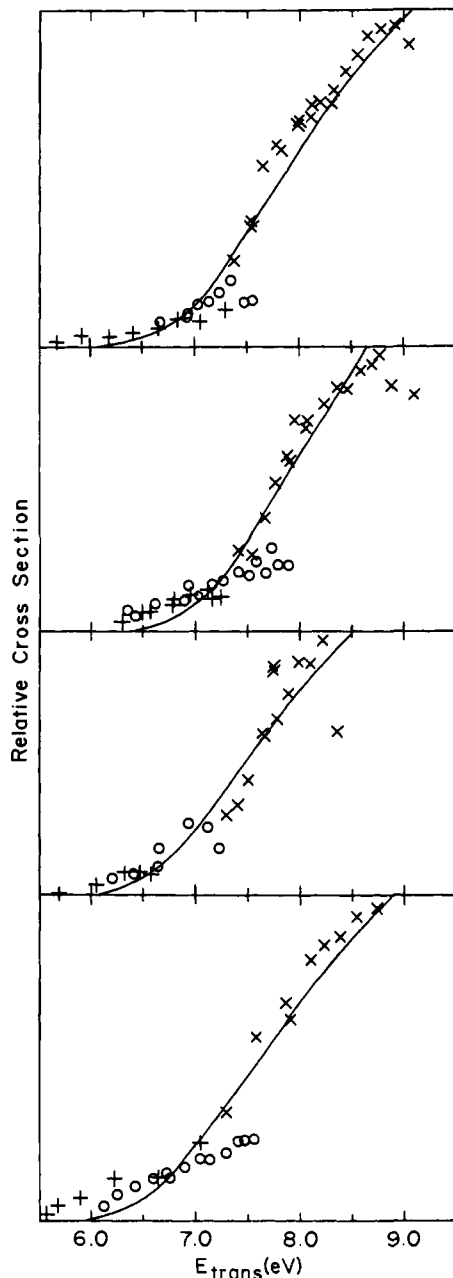


Figure 1. The total reactive cross section for butyl iodide reacting with SbF_5 . The abscissa is the relative translational energy in eV. The four panels are the following, from top to bottom: *n*-butyl iodide, *sec*-butyl iodide, *tert*-butyl iodide, and isobutyl iodide. The carrier gases are as follows: (x) H_2 ; (o) 39.8% H_2 , 60.2% He; (+) He. The beam intersection angle is 135° . The SbF_5 beam was seeded in He carrier gas and held at a fixed temperature of 300°C .

reaction. The data were fit to the simple line-of-centers model convoluted with the distribution in relative energies caused by the spread in beam velocities.⁴ The convoluted cross sections are shown as the solid curves in the four panels. The data for each carrier gas are measured over a range of $30\text{--}400^\circ\text{C}$. The threshold energies which give the best fit of the model to the data in each case are the following: *tert*-butyl iodide, 6.8 eV; *sec*-butyl iodide, 6.8 eV; *n*-butyl iodide, 7.0 eV; and isobutyl iodide, 6.5 eV. They all agree to within the experimental error of 0.4 eV, except for the isobutyl, *n*-butyl difference which is only just outside this error.

As indicated above, these data strongly suggest that some rearrangement must take place during the reaction. If no rearrangement were to take place, we would expect that the threshold for *n*-butyl iodide would be 1.75 eV higher than the threshold for *tert*-butyl iodide because of the much lower energy of the *tert*-butyl cation.

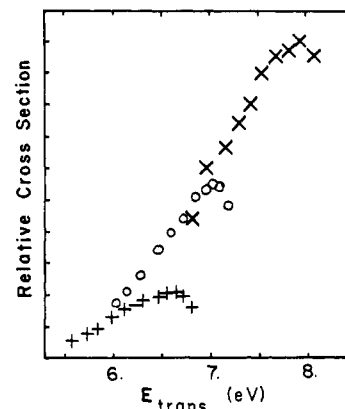


Figure 2. The cross section for total ion formation for the reaction of pivaloyl chloride with SbF_5 versus the relative translational energy. Both the parent and fragment ions are included.

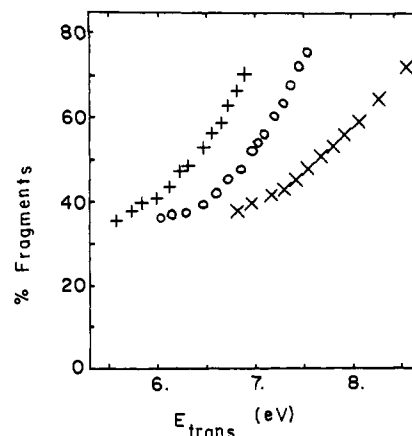


Figure 3. The percentage of fragment to total ions for the reaction of pivaloyl chloride versus relative translational energy.

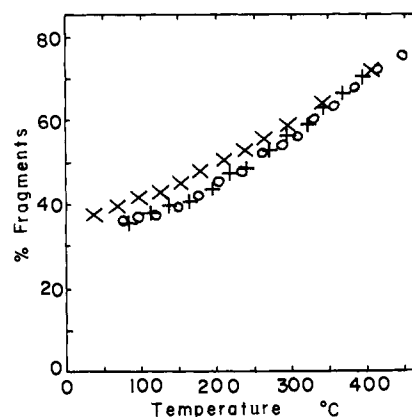


Figure 4. The percentage of fragment ions for the reaction of pivaloyl chloride as a function of nozzle temperature for the pivaloyl chloride beam.

Pivaloyl Chloride. Figure 2 shows the reactive cross section for total ion formation for the reaction of pivaloyl chloride and SbF_5 versus translational energy taken from ref 4. The data for the various carrier gases agree with each other, and this indicates that vibrational energy plays only a minor role in the initial halide abstraction. Figure 3 shows the percentage of all the ions that appear as the daughter ion $[(\text{CH}_3)_3\text{C}^+]$ plotted as a function of translational energy. It is quite apparent that the curves for the three carrier gases do not agree with each other. Thus vibrational energy is important in the fragmentation process. Figure 4 shows the same data plotted against the nozzle temperature. This should approximate the vibrational temperature of the halide beam if we assume little or no vibrational cooling during the nozzle expansion. Now, the data for the three carrier gases are in good

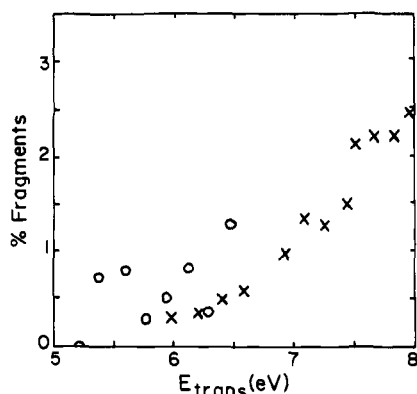


Figure 5. The fragment percentage for the reaction of *n*-valeryl chloride with SbF_5 versus relative translational energy.

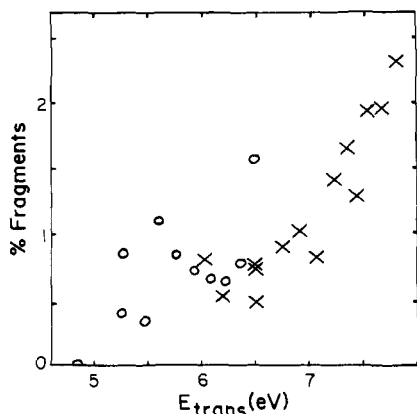


Figure 6. The fragment percentage for the reaction of isovaleryl chloride with SbF_5 versus relative translational energy.

agreement. At a given nozzle temperature, the translational energy for the H_2 carrier gas is very much higher than that for the He carrier gas. The two agree, however, and this indicates that translational energy plays only a minor role in the fragmentation of the pivaloyl cation. Evidently, translational energy determines the outcome of the initial halide abstraction. Initial translational energy in the reactants goes almost completely into translational energy of the products. If only a small amount ended up as vibrational energy in the pivaloyl cation, the fragmentation would show a dependence on translational energy; it does not. Vibrational energy in the pivaloyl chloride goes into vibrational energy in the pivaloyl cation, where it is available for the subsequent decomposition reaction. It should be noted that the data on the percentage of fragmentation are much more accurate than the relative cross sections since, as ratios, they are independent of the number density of either of the beams.

These results contrast markedly with the case of *n*-valeryl chloride

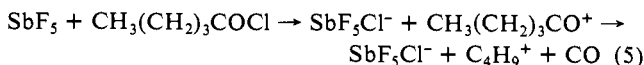
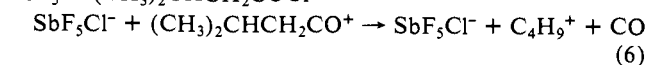


Figure 5 shows the fragmentation percentage versus translational energy. First, the amount of fragmentation is only a few percent as compared to 30–70% for pivaloyl chloride. The experimental error is sufficiently high that it is impossible to predict what mixture of translational and vibrational energy promotes the reaction. The cross section for total ion formation, however, looks similar to that for pivaloyl chloride.

The data for isovaleryl chloride are similar to those for *n*-valeryl chloride



chloride. Figure 6 shows the fragmentation percentage for isovaleryl chloride. As in the *n*-valeryl case the fragmentation percentage is very low.

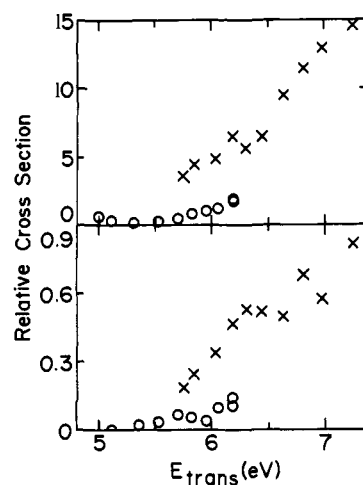


Figure 7. The cross sections for the reaction of crotonyl chloride with SbF_5 versus relative translational energy. The top panel shows the cross section for halide abstraction, and the bottom panel shows the cross section for electron transfer.

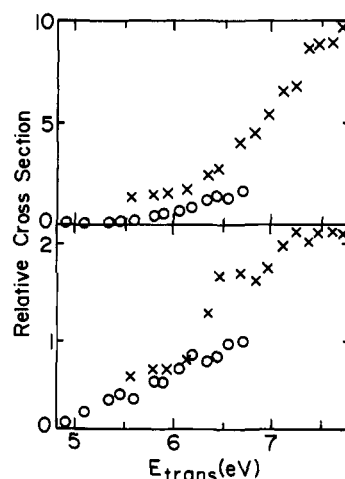


Figure 8. The cross sections for the reaction of methacryloyl chloride with SbF_5 .

As in the case of the butyl iodides, the heats of formation of the various isomers of pivaloyl chloride are similar. This is probably also true of the heats of formation of the various acyl cations that form the primary product for the halide abstraction, since the charge is located on the $C=O$ group. This is why the data for the total ion formation show similar threshold energies of 5.5–5.7 eV for the three cases and why the cross sections for all three cases depend largely on translational energy. The big difference is in the heats of formation of the various alkyl carbocations formed after the elimination of CO. Here pivaloyl chloride gives the very stable *tert*-butyl cation while *n*-valeryl chloride forms the *n*-butyl cation unless some rearrangement occurs. If rearrangement were to occur in the acyl cation, the fragmentation data for the three cases would be similar. They are not, and this indicates that there is little rearrangement before the CO is eliminated.

Electron Transfer. SbF_5 reacts with unsaturated acids to give both halide transfer and electron transfer. We have studied reactions with the isomers of butenoyl chloride: crotonyl chloride [$CH_3CH=CHCOCl$], methacryloyl chloride [$CH_2=C(CH_3)COCl$], vinylacetyl chloride [$CH_2=CHCH_2COCl$], and cyclopropanecarbonyl chloride. Figure 7 shows the cross sections for crotonyl chloride. The top half of the figure is the reactive cross section for chloride abstraction and the bottom half for electron transfer. The scales on the ordinates give the relative magnitudes of the two cross sections. Electron transfer represents about 10% of the ionic products. Both processes have thresholds around 5.6 eV. Figure 8 shows the analogous data for methacryloyl chloride.

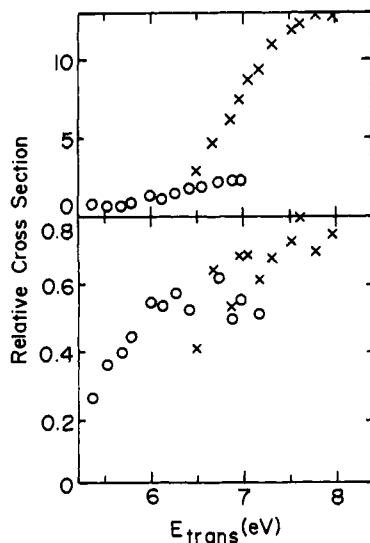


Figure 9. The cross sections for the reaction of vinylacetyl chloride with SbF_5 .

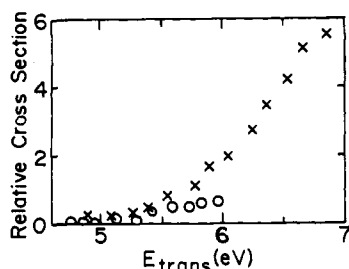


Figure 10. The cross section for chloride abstraction from *trans*-cyclopropanecarbonyl chloride by SbF_5 .

Here the fraction of electron transfer is much higher, around 25%. The threshold for chloride abstraction is slightly higher, 6.0 eV, and the threshold for electron transfer somewhat lower, 5.2 eV; the differences are just outside the experimental error. The data for vinylacetyl chloride are shown in Figure 9. Here, the percentage of electron transfer is quite small, only 8%. The threshold for chloride abstraction is a little higher still, 6.2 eV, but the threshold for electron transfer is about the same as that for crotonyl chloride. Very little fragmentation of the product ions was observed. There are no data on the thermochemistry of the product ions, so the trends must be analyzed in terms of crude bonding theory. When a chloride is abstracted from crotonyl chloride or from methacryloyl chloride, the product ion has the structure of a resonance-stabilized allylic cation. In the case of crotonyl chloride this is a methallyl cation that has secondary character. In the case of methacryloyl chloride the cation has primary character. This suggests that the energy of the carbocation produced from crotonyl chloride might be lower than that produced from the methacryloyl chloride. Vinylacetyl chloride, on the other hand, cannot form an allylic ion, and so its energy would be still higher. Since we have not seen electron transfer from saturated acid chlorides, it is likely that the electron transferred to SbF_5 comes from the double bond. Methacryloyl chloride allows the positive charge to be put in the tertiary position, and so we might expect more electron transfer and a lower threshold in this case. Most of the above explanations are admittedly largely conjecture, but in the absence of hard thermochemical data or a good quantum calculation, it is the best that can be done.

The data for the halide abstraction in cyclopropanecarbonyl chloride are given in Figure 10. The threshold is 5.5 eV which is lower than that for crotonyl chloride. No electron transfer was seen.

Discussion

Both the halide abstraction and electron-transfer reactions of antimony pentafluoride have considerably more complicated re-

Table I. Thermodynamic Data for the Butyl Iodides

isomer	$\Delta H_f(\text{BuI})^a$, eV	$\Delta H_f(\text{Bu}^+)^b$, eV	ΔH_r^c , eV
normal	-0.9	8.7	9.6
sec	-1.0	7.9	8.9
tert	-0.75	7.1	7.85
iso	-1.0	8.6	9.6

^a Heat of formation of BuI from the elements,¹⁰ except for isobutyl iodide which was estimated. ^b Heat of formation of Bu^+ from the elements.¹¹ ^c ΔH for the reaction $\text{BuI} \rightarrow \text{Bu}^+ + \text{I}^-$.

action dynamics than the usual systems encountered in the field of Chemical Dynamics. In previous papers we have used some of the standard methods of molecular beams to determine what happens during the reactive collision. Now we use some of the techniques more typical of Physical-organic Chemistry and compare the results of different isomers. In the case of the four butyl iodides we find that the thresholds for the different isomers are identical to within experimental error. Table I shows the relevant thermochemical data. The heats of formation for the butyl iodides are almost identical. However, the heats of formation of the product ions are very different. The values of ΔH for the process $\text{RX} \rightarrow \text{R}^+ + \text{X}^-$ differ by up to 1.75 eV, well outside the experimental error limits. We conclude from this that it is very likely that all four cases give the *tert*-butyl cation as the product. This confirms our view that the reaction goes through a loosely bound complex consisting of a pair of ions held together by the coulomb attraction. In such a complex it is quite likely that the R^+ ion can rearrange to the most stable isomer.

Our conclusions depend on the assumption that the threshold energy is closely related to the endothermicity of the halide extraction reaction. The reaction has been studied extensively in solution. Arnett and Petro¹² measured ΔH of several different cases and solvents and found that the reaction is exothermic by 6.5–30 kcal/mol depending on the solvent and on the reactants. In solution the reactants are neutral and are only weakly solvated. The products, however, are ionic and strongly solvated. In the gas phase there is no solvation, and the reaction appears to be endothermic by a few eV. It might be argued that the threshold energy is due to some barrier in the surface and that ΔH can be appreciably lower. This is unlikely since the reactions in solution proceed rapidly at low temperature. This means that the activation energy must be low. Since any barrier in the reactant region of the potential-energy surface involves only a partial separation of charges, it is not likely that there will be a large barrier in the entrance region of the surface. The exit (product) side of the potential-energy surface is dominated by the very strong coulomb attraction between the products. While some final interaction might modify the coulomb interaction, it is unlikely to be large enough to create a barrier. The coulomb potential is sufficiently strong and long-ranged that there is no centrifugal barrier on the product side. We are thus left with the conclusion that the threshold energy must be fairly close to ΔH for the reaction.

This picture contrasts with subsequent CO elimination reaction. Here we see very different behavior for pivaloyl chloride, which can give the very stable *tert*-butyl cation, and *n*-valeryl chloride and isovaleryl chloride, which cannot rearrange to give the *tert*-butyl ion. Here, there appears to be little or no rearrangement, and this is entirely consistent with a picture where the acyl cation emerges from the halide abstraction reaction with vibrational excitation and then eliminates CO. The vibrationally excited acyl ion has no easily accessible pathway for rearrangement. Rearrangement would then have to be a concerted process with the rearrangement and elimination taking place almost simultaneously. This would be unlikely. Of course, if the fragment ion rearranges after the CO is eliminated, this will have no effect on our measurements.

Unsaturated acid chlorides react with SbF_5 to give both the halide-transfer reaction and the electron-transfer reaction. The various butenoyl chlorides give different thresholds for the electron transfer and for the halide transfer. The results are entirely

consistent with a picture that the two reactions are separate. The electron for the electron-transfer reaction quite likely comes from a π orbital in the double bond. This does not involve the chlorine atom. So we picture the reactions as occurring on three potential-energy surfaces. The reactants approach along a covalent surface. They may then encounter one of two surface crossings, both ionic in nature. One of these has the structure $RX^+ + SbF_5^-$ and leads to electron transfer, and the other has the structure $R^+ + SbF_5Cl^-$ and leads to halide transfer. Quite likely, the choice of reaction path—which surface crossing is encountered—is governed by the orientations of the reactant molecules as they collide. When the reaction involves a saturated halide, the ionization potential of the halide is high, and the surface leading to

electron transfer may then be inaccessible. However, halide transfer can still take place.

Acknowledgment. Research support from the National Science Foundation under Grant CHE-8201164 is gratefully acknowledged. We also thank Yound-duk Huh for helping in some of the later experiments.

Registry No. SbF_5 , 7783-70-2; $H_3C(CH_2)_3I$, 542-69-8; $H_3CCH_2CH(CH_3)I$, 513-48-4; $(H_3C)_3Cl$, 558-17-8; $(H_3C)_2CH=CH_2I$, 513-38-2; $(H_3C)_3CCOCl$, 3282-30-2; $H_3C(CH_2)_3COCl$, 638-29-9; $(H_3C)_2CHC_2H_5COCl$, 108-12-3; $H_3CCH=CHCOCl$, 10487-71-5; $H_2C=C(CH_3)COCl$, 920-46-7; $H_2C=CHCH_2COCl$, 1470-91-3; cyclopropanecarbonyl chloride, 4023-34-1.

Gas-Phase Reactions of Si^+ and $SiOH^+$ with Molecules Containing Hydroxyl Groups: Possible Ion-Molecule Reaction Pathways toward Silicon Monoxide, Silanoic Acid, and Trihydroxy-, Trimethoxy-, and Triethoxysilane

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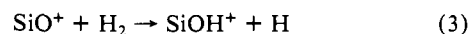
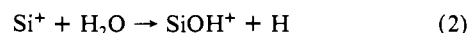
Contribution from the Department of Chemistry and Centre for Research in Experimental Space Science, York University, Downsview, Ontario, Canada M3J 1P3. Received April 1, 1987

Abstract: Reactions of ground-state Si^+ (2P) and $SiOH^+$ ions have been investigated with H_2 , D_2 , CO , H_2O , CH_3OH , C_2H_5OH , $HCOOH$, and CH_3COOH at 296 ± 2 K with the selected-ion flow tube (SIFT) technique. Both ions were found to be unreactive toward H_2 , D_2 , and CO . Ground-state silicon ions were observed to react with the hydroxyl-containing molecules to produce the silene cation $SiOH^+$, which may neutralize by proton transfer or by recombination with electrons to form silicon monoxide. $SiH_3O_2^+$, which may neutralize to produce silanoic acid, was observed to be the predominant product in the reactions of $SiOH^+$ with H_2O , C_2H_5OH , and $HCOOH$, while direct formation of silanoic acid is likely in the reaction observed between $SiOH^+$ and CH_3COOH . A single mechanism involving O-H insertion of the $SiOH^+$ silylene cation provides a plausible explanation for all of the results obtained with this ion. Also, further chemistry was observed to be initiated by $SiH_3O_2^+$. Solvation was the predominant channel seen with water and ethanol while $SiCH_3O_2^+$ and $SiH_5O_3^+$ were the predominant products observed with formic acid. Several reaction sequences were identified in methanol, ethanol, and formic acid which are postulated to lead to the complete saturation of Si^+ forming ions of the type $HSi(OCH_3)_3H^+$, $HSi(OC_2H_5)_3H^+$, and $HSi(OH)_3H^+$ which may neutralize to generate trimethoxysilane, triethoxysilane and trihydroxysilane, respectively.

It is well-known that the gas-phase chemistry of silicon is quite different from that of carbon.^{1,2} For example, the silicon-oxygen double bond is much less commonly known than the carbon-oxygen double bond. Experimental evidence for the existence of silicon analogues of the simple carbon molecules of formaldehyde and formic acid has been achieved only recently with matrix experiments at 17 K in a study of photoinduced reactions of oxygen atoms with silane.³ There is a strong indication that the silicon analogue of formaldehyde is formed in the gas phase as well. The emission recently observed from the product of the reaction of ozone with silane can be ascribed to an energy-rich H_2SiO molecule.⁴ Also the ion/molecule reaction 1 has been observed in the gas phase.^{5,6} The ionic product of this reaction is likely



to be protonated silanone and to yield silanone upon neutralization by proton transfer or recombination with electrons. Protonated silicon monoxide has also been shown to be produced in the gas phase by the ion/molecule reactions 2 and 3.⁷ Reaction 2 is believed to be responsible for the formation of $SiOH^+$ in the



Earth's atmosphere (in which silicon is introduced by meteor ablation).⁷ Also, reaction 3 has been suggested as a critical step in the production of silicon monoxide in interstellar gas clouds by the neutralization of $SiOH^+$.^{8,9}

Here we report results of gas-phase measurements of the chemistry initiated by Si^+ in the vapors of water, methanol, ethanol, formic acid, and acetic acid. The study provides several new pathways for the formation of $SiOH^+$ which itself is found to be reactive. For example, $SiOH^+$ ions were found to dehydrate formic acid and ethanol molecules to form $SiH_3O_2^+$ ions. The deprotonation of the latter ions by proton transfer to a molecule

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