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(ii) H_2O and OH Protons. Considering first the proton in the OH group in OH–FeP, the model compound for hematin, the dipolar interaction is seen from Table VI to be the dominant contributor to the hyperfine field. The direct contribution A_d is also sizable, because as mentioned earlier, the d_{z^2}-like molecular orbital has significant density at the proton site. However, it is cancelled substantially by A_{ex} from the π-like (with respect to the OH bond) spin density on the oxygen atom. The net hyperfine field on the OH proton of hematin is the largest of all the protons in all the systems we have analyzed. From our experience regarding the relationship of results for fluoromyoglobin and fluorohemin, we expect from analogy with hematin that the proton hyperfine constant in hydroxymyoglobin would also be sizable.

As regards the water protons, in both H_2O–$Mn^{II}P$ and Met–Mb, the net hyperfine constants (Tables VI and VII) are sizable, relatively large compared to the meso protons, but considerably smaller than for the OH proton in hematin. For both the H_2O-containing systems, the dipolar contribution is seen to be the leading one, but A_d and A_{ex} also make important contribution to the total hyperfine constant, A_H. The experimental value of A_H is available only for Met–Mb and is seen to lie between the theoretical values for the two choices of A_{ex}, again indicating that the actual values of A_{ex} would lie between the two choices. It is also gratifying that experimental[11] data in Met–Mb (Table VII) verify the theoretical result of the net hyperfine constant for water proton being an order of magnitude larger than for the meso proton.

(iii) Imidazole Protons. With respect to the relative sizes of the dipolar contribution B_{zz} and the isotropic contribution $A_d + A_{ex}$, the imidazole protons are seen from Table VII to fall into two categories. For the H_a and H_b protons, while the dipolar contribution is the major one, the isotropic effects also makes a significant net contribution. On the other hand, for H_δ, both A_d and A_{ex} are small, making B_{zz} the dominant contributor. Of the three types of proximal imidazole protons, experimental data are available only for H_δ in both F–Mb and Met–Mb. As mentioned earlier, our model compound for Met–Mb does not have an H_δ in this compound. For F–Mb, however, the experimental value is seen to be in good agreement with theory. It is also satisfying that the theoretical and experimental results[11] both have the trend that the H_δ hyperfine constant in F–Mb and Met–Mb is substantially smaller than that for the water protons in Met–Mb.

IV. Conclusion

One of the main features of our results is that the dipolar effect makes a major contribution to the hyperfine fields at the protons in high-spin heme and hemoglobin systems. Further, our analysis shows that it is important in this respect to consider the actual unpaired spin population distribution over the entire molecule in question, instead of making the commonly used approximation[10,13,22] of taking all the unpaired spin population as localized on the central metal atom. Also the direct and exchange contact contributions, while usually smaller than the dipolar in magnitude, have to be considered carefully because they have an important influence on the net hyperfine constant, either because in some instances they combine to make significant contributions or in others because they nearly cancel each other. For a number of the protons that we have considered and where experimental data are available, the experimental trend of variation among different protons is well reproduced by them, and also satisfactory agreement between theory and experiment is found for the actual magnitude of the hyperfine constants for individual protons. It would be helpful to have further experimental results to check the calculated hyperfine constants for a number of the protons where data are not currently available. However, from the satisfactory agreement between theoretical and experimental hyperfine constants for the variety of protons where data are already available, one can conclude that the unpaired spin populations that have been obtained in the present work give a reasonably accurate description of the true state of affairs in the peripheral regions of heme and hemoglobin systems, complementing similar conclusions found[5,6] for the more central regions of these systems from the analysis of ${}^{57}Fe$ and ${}^{14}N$ hyperfine fields.

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Gas-Phase Chemiionization Reactions of Antimony Pentafluoride

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Abstract: Using crossed molecular beams, we have studied the reactions of SbF_5 and its polymers with organic halides (RX). Monomer SbF_5 reacts with some RX species to produce $R^+ + SbF_5X^-$. Dimer reacts with a wider variety of RX species to produce $R^+ + SbF_6^- + SbF_4X$. Unless R^+ is particularly subject to cleavage, only the parent R^+ is observed; this indicates that the product is formed with only a small amount of internal energy.

It has recently become possible to study, in the gas phase, well-known solution reactions and thereby learn about the effects of solvent.[1] Studies of ion–molecule reactions with use of ICR show that differences in solvation energy between the reactants, the transition state, and the products can make large differences in the rate and thermochemistry of reactions in the gas phase and in solution. We report here the results of a gas-phase study of a chemiionization reaction which is well-known in solution,[2]

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

Reaction 1 is commonly used to prepare stable solutions of carbonium ions for structural analysis by NMR or for further reaction. The reaction may be viewed as a halide abstraction by the extremely strong Lewis acid SbF_5. It occurs rapidly and irreversibly in solution for tertiary and secondary halides. The

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Table I. Literature Values of the Heats of Reaction in the Gas Phase

	ΔH^{298}, kcal/mol, for $RX \rightarrow R^+ + X^-$ with X =			
R	F^a	Cl^a	Br^a	I^a
$PhCH_2X^b$	$174^{b,c}$	$148^{b,d}$	$135^{b,d}$	$139^{b,d}$
	$172^{b,c}$	$146^{b,d}$	$133^{b,d}$	$137^{b,d}$
PhCOX	$174^{c,e}$	$154^{e,f}$	$143^{e,f}$	$138^{e,f}$
$t\text{-}C_4H_9X$	$173^{c,g}$	$148^{d,g}$	$139^{d,g}$	$133^{d,g}$
$i\text{-}C_3H_7X$	$192^{d,g}$	$163^{d,g}$	$155^{d,g}$	$150^{d,g}$
CH_3COX	$216^{h,i}$	$176^{d,i}$	$166^{d,i}$	$159^{d,i}$

[a] The heats of formation of X^- are: −64.7 (F), −58.8 (Cl), −55.9 (Br), −47.0 (I) kcal/mol. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schum, *NBS Tech. Note (U.S.)*, 270-3 (1968). [b] The top line refers to the benzyl cation as the product and the bottom to the tropylium ion. ΔH_f^{298} of the benzyl cation is taken from F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 100, 3290 (1978), and that of the tropylium ion from B. A. Thrush and J. J. Zwolenik, *Discuss. Faraday Soc.*, 35, 196 (1963). [c] ΔH_f^{298} of $PhCH_2F$, PhCOF, and $t\text{-}C_4H_9F$ are taken from J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949); J. L. Franklin, *J. Chem. Phys.*, 21, 2029 (1953). [d] ΔH_f^{298} of $PhCH_2X$, $t\text{-}C_4H_9X$, $i\text{-}C_3H_7X$, CH_3COX (X = Cl, Br, I), and $i\text{-}C_3H_7F$ are given by J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970. [e] ΔH_f^{298} of $PhCO^+$ is from J. R. Majer and C. R. Patrick, *Trans. Faraday Soc.*, 59, 1274 (1963). [f] ΔH_f^{298} for PhCOX (X = Cl, Br, I) is taken from A. S. Carson, H. O. Pritchard, and H. A. Skinner, *J. Chem. Soc.*, 656 (1950). [g] ΔH_f^{298} for $t\text{-}C_4H_9^+$ and $i\text{-}C_3H_7^+$ is given by F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 101, 4067 (1979). [h] ΔH_f^{298} for CH_3COF is from D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Shum, *NBS Tech. Note (U.S.)*, 270-3 (1968). [i] ΔH_f^{298} for CH_3CO^+ is from R. I. Reed and J. C. D. Brand, *Trans. Faraday Soc.*, 54, 478 (1958); A. S. Carson and H. A. Skinner, *J. Chem. Soc.*, 936 (1949).

solvation energy of the neutral reactants is much less than the solvation energy of the ionic products so that the thermochemistry and rate should be quite different in the gas phase.

Only a few chemiionization reactions have been studied in detail in the gas phase,[3] and many of these involve electron jumps rather than chemical reactions with nuclear rearrangement. A reaction like (1) offers a great advantage over other reactions in a molecular-beam study because the reactants are both stable, neutral molecules and can be formed into beams of high intensity. The products, however, are already ionized and can be mass analyzed and detected with near unit efficiency. SbF_5 is well-known to polymerize in the gas phase[4] so that, by studying the reactions of the monomer and of the various polymers, we can, in effect, look at the effects of solvation on the reaction.

We previously reported the discovery of (1) in the gas phase and determined a variety of RX species which react.[5] However, we were not able to mass analyze the products and were not able to separate the reactions of the monomers and polymers. We have now done this and give the results here.

Experimental Section

The crossed-beam machine has been described previously[5,6] but has been modified extensively for this experiment. Briefly, two seeded supersonic nozzle beams of the reactants intersect at 90° in a vacuum chamber. The ion products are collected, mass analyzed, and detected. The beam of SbF_5 is made by bubbling the inert carrier gas (He or H_2) through liquid SbF_5. The resulting gas mixture is passed through a trap filled with glass beads in order to remove small droplets of SbF_5 which may be carried over from the bubbler. The temperature of the trap is always kept slightly lower than that of the bubbler and thus determines the partial pressure of SbF_5 in the beam. Temperatures of −20 to 20 °C are used to give pressures of 0.1–1 torr of SbF_5 in 300–700 torr of carrier gas. Stainless steel and Teflon tubing are used to connect the vacuum line to the nozzle. The nozzle, 130 μm in diameter, is made of Pyrex glass, melted down and ground back to the desired diameter. A coarse frit is placed behind the opening to remove fine particles which can clog the nozzle and to assure that the gas is fully heated. Both the nozzle and frit are wrapped with heating wire and can be heated up to 200 °C. In our earlier experiments we had frequent problems with clogged nozzles. These were solved by using the frit and by flowing the carrier gas (without SbF_5) through the system for about an hour following each run.

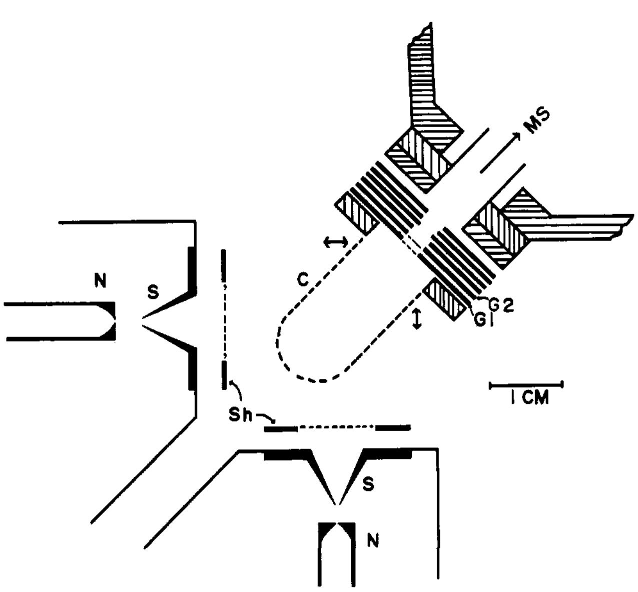

Figure 1. Schematic of the central portion of the apparatus: C, grid cage; G1 and G2, extraction and energy analyzer grids; MS, to mass spectrometer; N, nozzle; S, skimmer; Sh, shield plate. The ionizer filament is above the beams with electrons traveling down through the beam intersection region.

Pure SbF_5 is a colorless and very viscous liquid at room temperatures which freezes at 7 °C but can easily be supercooled to −20 °C. It rapidly absorbs water from the air to form an HF complex, and, when it does, the viscosity decreases markedly. SbF_5 was purchased from Aldrich or Ozark Mahoning and distilled, the first third which contains HF being discarded. The remaining two thirds of the solution was vacuum distilled into the bubbler. Care must be taken to keep the product dry; therefore, the vacuum line contains greaseless Teflon stopcocks.

The RX beam is formed by passing the carrier gas past a rubber septum into the nozzle. Liqud RX is injected through the septum into the carrier gas by using a motor-driven microsyringe. The nozzle is identical with the one used for SbF_5 except that the diameter is 80 μm. The syringe is a 25 μL gas-tight syringe purchased from Analab. Both the syringe and liquid are outgassed under vacuum before the syringe is filled in order to avoid air bubbles in the liquid.

Figure 1 shows the central part of the apparatus. Each beam source is enclosed in a separate chamber pumped by a 6 in. diffusion pump. The two beams intesect in a grid cage. The detector operates in two modes. If a potential is placed on the first grid behind the cage, most of the ions of the desired charge are extraced from the reaction region. If the first grid is at the same potential as the cage, only those ions actually directed at the orifice will be detected. By rotating the detector relative to the beam sources we can take an angular distribution of the product ions. The second grid can then be used as a retarding-potential energy analyzer. In this study we use the first mode to extract most of the ions. In both modes the ion beam is bent by 90°, mass selected by a quadrupole mass filter (Extranuclear Corp. 0.95 cm poles), and detected by a Channeltron electron multiplier. A filament is placed just above the cage so that we can ionize either beam by electron bombardment.

It must be emphasized that the energy distributions in the beams are not thermal. As a result of the nozzle expansion the two beams are rotationally cold, vibrationally thermal, and have a relative kinetic energy of 2.5-11.5eV depending on the type of carrier gas, the nozzle temperatures, and the masses of the reactants. We deliberately use a low Mach number (~4-10) so that the vibrational modes are not substantially

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cooled. We can then increase the vibrational energy by heating the nozzle.

Results and Discussion

In addition to reaction 1 for monomers we have seen the following reactions with polymers of SbF_5:

$$Sb_2F_{10} + RX \rightarrow SbF_6^- + R^+ + SbF_4X \quad (2)$$

$$Sb_2F_{10} + RF \rightarrow Sb_2F_{11}^- + R^+ \quad (3)$$

$$Sb_3F_{15} + RX \rightarrow Sb_2F_{11}^- + R^+ + SbF_4X \quad (4)$$

In the case of benzoyl chloride (C_6H_5COCl) and several other RX species, we observe the following behavior. When the bubbler and trap on the source for SbF_5 are cooled to -20 °C and when the SbF_5 nozzle is heated to 200 °C (monomer conditions), the electron bombardment ionizer shows roughly 95% monomer. The exact amount is uncertain because the relative ionization cross sections and fragmentation patterns are unknown. Under these conditions, we observe $C_6H_5CO^+$ and SbF_5Cl^- with a smaller amount of SbF_6^-. As we raise the trap temperature and/or lower the nozzle temperature, the fraction of dimer in the beam increases, and the ratio of SbF_6^-/SbF_5Cl^- increases. This indicates that SbF_6^- is coming from the reaction of a polymeric species, almost certainly the dimer. As the nozzle temperature is lowered to 50 °C and the bubbler and trap are warmed to +20 °C, we see some $Sb_2F_{11}^-$, evidently formed by the reaction with trimer. These conditions result in the consumption of large quantities of SbF_5 and the resulting contamination of the ion lens system, and so we have not studied the trimer reactions in detail. Under all conditions, $C_6H_5CO^+$ is the only cation observed. In no case could we detect $Sb_2F_{10}Cl^-$, a possible product of the reaction with dimer.

Benzyl fluoride ($C_6H_5CH_2F$) gave large amounts of SbF_6^- under monomer conditions, as expected, but, as the fraction of dimers increased, a large amount of $Sb_2F_{11}^-$ was observed—more than an order of magnitude higher than in the case of benzoyl chloride. Apparently, in this case the dimer can react by (3) to form $Sb_2F_{11}^-$. Because we cannot detect the neutral product, we cannot determine the fraction of dimers which react by (2) and (3).

In solution studies the ion $Sb_2F_{11}^-$ is very stable. The NMR shows two sharp peaks, one with ten equivalent fluorines and the other a single fluorine, probably bridging the two Sb atoms.[7] On the NMR time scale (~0.1 s) they do not exchange. Our results are consistent with this picture for $Sb_2F_{11}^-$ but indicate that $Sb_2F_{10}Cl^-$ is either very much less stable or unstable. This does not appear to be due to the larger size of the chlorine, since we have seen SbF_5Br^- from benzoyl bromide. Possibly the d orbitals on the chlorine stabilize SbF_4Cl and allow $Sb_2F_{10}Cl^-$ to dissociate either during or subsequent to the reaction. If $Sb_2F_{10}Cl^-$ were only slightly bound, then statistical considerations would favor a three-body breakup as indicated in (2).

We considered that SbF_6^- might be formed by a complex of SbF_5 and HF,

$$HSbF_6 + RCl \rightarrow SbF_6^- + R^+ + HCl \quad (5)$$

As mentioned above, SbF_5 reacts with water in the air to form HF which then probably complexes with SbF_5. We deliberately added water to the SbF_5 in the middle of a run and saw no increase in SbF_6^-. Since the HF is the more volatile component, (5) would predict that the SbF_6^- signal should decrease during a long run; it does not.

For other substances such as benzyl chloride ($C_6H_5CH_2Cl$), no reaction is seenwith monomer. Under monomer conditions, only small amounts of $C_7H_7^+$ and SbF_6^- are seen. No SbF_5Cl^- is observed. As the fraction of dimer increases, the intensity of SbF_6^- and $C_7H_7^+$ increases. This result indicates that the dimer is more reactive than the monomer. Under typical dimer conditions (low nozzle temperature) the translational and vibrational energy available for the dimer reaction is comparable to that available for reaction with the monomer at higher nozzle temperatures; yet the dimer reacts, and the monomer does not. This could be due either to a larger heat of reaction for the monomer or to a larger activation barrier.

We have seen reaction of monomer SbF_5 (eq 1) with benzoyl chloride (C_6H_5COCl) and bromide, pivaloyl chloride [$(CH_3)_3CCOCl$], benzal chloride ($C_6H_5CHCl_2$), and benzyl fluoride ($C_6H_5CH_2F$). Benzoyl and pivaloyl fluorides react only with dimers and higher polymers. Many other halides react with dimers including many of the substances reported previously.[5] These include benzyl chloride and bromide, *tert*-butyl bromide and iodide, and isopropyl iodide. Isopropyl chloride and bromide and *tert*-butyl chloride do not react with monomer or dimer. By injecting known mixtures into the RX beams, we have measured relative reactivities. Under a variety of beam conditions, benzyl chloride is slightly more reactive than isopropyl iodide, and benzyl bromide is 2.5–10 times as reactive. For alkyl halides, there seems to be a trend F > I > Br > Cl. In the latter three cases, this may be due to bond strengths, polarizibility, or the increased mass of the heavier halides, which gives rise to a higher kinetic energy in the nozzle beam. In the case of fluorides, it is likely due to an increased strength of the Sb–F bond.

Unfortunately, the overall thermochemistry of eq 1–4 is unknown in the gas phase. Arnett and Petro have measured the heats of reaction of several halides with SbF_5 in solution.[8] The reactions with *tert*-butyl fluoride and chloride are both exothermic by 12–30 kcal/mol depending on the solvent, while the reactions with isopropyl fluoride and chloride are exothermic by 4–20 kcal/mol. As discussed above, the heats of reaction in the gas phase will be very different due to the large solvation energy of the product ions. We can break the overall heat of reaction into two parts:

$$RX \rightarrow R^+ + X^- \quad (6)$$

$$SbF_5 + X^- \rightarrow SbF_5X^- \quad (7)$$

or

$$Sb_2F_{10} + X^- \rightarrow SbF_6^- + SbF_4X \quad (8)$$

There are no data on eq 7 and 8 and on the other anionic half-reactions, but considerable data exist on eq 6. Table I gives the best literature values of the heats of reaction for eq 6. We cannot tell whether the reaction with benzyl halides gives the benzyl or the tropylium cation so both values are given. The uncertainty is about 5–10 kcal/mol in most cases. Reactions 7 and 8 are expected to be strongly exothermic but not by as much as 130 kcal/mol so that the overall reaction is probably endothermic in the gas phase. There is an overall trend in ΔH: F > Cl > Br > I. Fluoride reactions are very much more endothermic than chloride reactions due to the greater strength of the C–F bond. However, the reaction of F^- in eq 7 and 8 is likely to be more exothermic than that of Cl^-, and this may more than make up the difference. Finally, it must be stressed that reactivity is determined by more than just thermochemistry. Our preliminary data[5] indicate a possible activation energy. It is also possible that there are neutral products that we cannot detect.

With the exception of pivaloyl halides [$(CH_3)_3CCOX$] only the parent R^+ was observed. The pivaloyl cation can eliminate CO to form the highly stable *tert*-butyl cation. We see 50–85% of the parent pivaloyl cation depending on beam conditions; the remainder is *tert*-butyl cation. In contrast, the electron-bombardment ionization at 70 eV gives only 1.5% of the parent or pivaloyl cation, 25% *tert*-butyl, and 73.5% smaller fragments. Electron-bombardment ionization is a sudden process which introduces large amounts of internal energy into the products. In contrast, the chemiionization with $(SbF_5)_n$ is a gentle, nearly adiabatic process, which apparently results in products with little excess energy.

We have recently measured the distributions in scattering angle and translational energy of both product ions. Our preliminary data on the reaction of monomer SbF_5 with benzoyl chloride show that the CM product contours for both ions have the required

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symmetry about the relative velocity vector and that both are centered around the center of mass. These data indicate that the reaction proceeds by way of a long-lived complex, as would be expected in view of the strong coulombic attraction between the products.

In summary, SbF_5 and its polymers have a complicated and varied chemistry which may be useful in the gas phase, as it is in solution, for the preparation of carbonium ions for spectroscopic and kinetic studies. It also offers the chemical dynamicist the opportunity to study a class of reactions quite different from those ordinarily encountered.

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Gas-Phase Elimination Reactions of Ethers Induced by Amide and Hydroxide Ions

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Abstract: The flowing afterglow technique has been employed to study the gas-phase reactions of a series of dialkyl ethers with amide and hydroxide ions. Ethers with β-hydrogens react rapidly by elimination rather than substitution mechanisms, and they demonstrate considerable specificity in the direction of elimination. With amide ion elimination proceeds primarily by removal of the most acidic hydrogen with little or no evidence of alkoxide stability playing a role. With hydroxide ion as the base the stability of the leaving groups appears to be of some importance, and cluster ions between water and the alkoxide ions are the major products. Evidence is presented for a long-lived complex of reaction products which can react further before separating.

When bimolecular elimination (E2) reactions are carried out in solution, reaction rates, product distributions, and even reaction stereochemistry can be profoundly influenced by substituent and leaving-group effects in the substrate or by variations in the attacking base. It has become increasingly feasible to observe such fundamental organic processes in the gas phase and hence in the complete absence of solvent, and it is, of course, important to determine if relationships so well documented in solution will also be found under these new conditions. Two versatile techniques are most commonly used for such studies of gas-phase ion-molecule reactions. Beauchamp and his co-workers[1] used ion cyclotron resonance (ICR) spectroscopy[2] to examine elimination reactions of fluorinated ethanes and ethylenes induced by methoxide ion and other bases. These studies delineated the general features of gas-phase E2 reactions and examined effects of the highly polar fluorine substituents. In this paper, we report studies of E2 reactions[3] using the flowing afterglow (FA) technique[4] in which we have examined effects of alkyl substitution and, to some extent, base strength and leaving-group effects.

Although studies of ionic organic reaction mechanisms in the gas phase are generally more direct and less complicated than similar studies in solution, there are several limitations. In the gas phase, one is usually limited to the detection of the *ionic* products of the reactions.[5] In a typical E2 reaction, the alkene which is formed is not detected and only the (charged) leaving group is seen. Indeed, it is not even known in such a fundamental reaction as that between ethyl bromide and hydroxide ion whether the product is that expected from an S_N2 (ethyl alcohol) or from an E2 (ethylene) reaction (eq 1). All that has been measured is the loss of the OH^- signal and the appearance of Br^-.

$$OH^- + CH_3CH_2Br \xrightarrow{S_N2} Br^- + CH_3CH_2OH \tag{1a}$$

$$OH^- + CH_3CH_2Br \xrightarrow{E2} Br^- + H_2O + CH_2{=}CH_2 \tag{1b}$$

Gas-phase ion-molecule rate constants, which can generally be measured rather easily, are of less use for mechanistic studies than might be anticipated. In the gas phase, ions and neutrals are attracted to one another by ion-induced-dipole and ion-permanent-dipole forces of up to about 20 kcal mol^{-1} at typical reaction distances. Thus many reactions which might be slow in solution occur rapidly and without apparent activation energy in the gas phase. For example, methyl and neopentyl chloride react with fluoride ion in the gas phase at nearly the same exceedingly fast overall rate, even though there is a steric barrier to displacement at a neopentyl carbon.

To circumvent both of these problems, we chose to investigate reactions of alkyl ethers with strong bases in the gas phase. In such a reaction the nature of the ionic product (the alkoxide ion) would allow us to deduce the effect of substituents on the direction of elimination (eq 2). By varying the alkyl groups in dialkyl

$$B^- + CH_3CH_2OCH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2O^- + BH + CH_2{=}CH_2 \tag{2a}$$

$$B^- + CH_3CH_2OCH_2CH_2CH_3 \rightarrow CH_3CH_2O^- + BH + CH_3CH{=}CH_2 \tag{2b}$$

ethers, we hoped to determine how alkyl substitution would affect the relative production of the two alkoxide ions. We have measured a few absolute rate constants for typical eliminations of ethers, but in general we need only measure relative rates, i.e., competition between two internal reaction channels within a single ion-dipole complex.

Experimental Section

These studies were performed with a flowing afterglow system which has been described previously.[6] Briefly the apparatus consists of a

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