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Chemical Reactions of Anions in the Gas Phase

Charles H. DePuy, Joseph J. Grabowski, Veronica M. Bierbaum

Summary. Anions of many types, both organic and inorganic, familiar and exotic, can be generated in the gas phase by rational chemical synthesis in a flowing afterglow apparatus. Once formed, the rates, products, and mechanisms of their reactions with neutral species of all kinds can be studied, not only at room temperature but at higher energies in a drift field. These completely unsolvated ions undergo a large number of reactions that are analogous to those they undergo in solution, as well as some that are less familiar. New types of ions, for which there are no counterparts in solution, can be produced and their chemical reactions explored.

The study of bimolecular reactions between ions and neutral molecules in the gas phase presents special experimental difficulties. The usual conditions for the generation of gaseous ions (low pressure and short residence time of the ions in the instrument) are the opposite of those necessary for the occurrence of reactions. The problems are compounded for the study of anions, since they themselves must often be prepared indirectly in one or more bimolecular steps. Thus, the study of the chemistry of gas phase anions has lagged behind comparable studies of cations, despite the fact that most synthetically useful organic reactions involve anions rather than cations.

Although high-pressure mass spectrometry, tandem mass spectrometry, and ion beam experiments have made important contributions to the field, the most widely used experimental technique, especially for organic reactions, has been that of ion cyclotron resonance (ICR) spectroscopy, in which ions are allowed to react by trapping them at low pressures for relatively long periods of time (*1*). The recent development of Fourier transform ICR should make this technique even more versatile.

For our work, we have used the lesser known, but equally powerful, flowing afterglow technique developed by Ferguson *et al.* (*2*). Bohme and Young (*3*) were the first to make extensive use of this method for the investigation of organic reactions of anions and, more recently, McDonald and Chowdhury (*4*) have made important contributions. Here, too, a recent experimental development, namely, the selected ion flow tube (SIFT) technique of Adams and Smith (*5*), has greatly increased the versatility of the method. In the flowing afterglow, bimolecular reactions are made possible by working at both moderately high pressures and relatively long ion residence times, and anions can readily be generated and studied. In this article, we use examples mainly from our own work to illustrate the similarities and differences between reactions of ions in solution and those in the gas phase.

Why Study Ion-Molecule Reactions?

The original impetus for the development of the flowing afterglow technique was the study of the chemistry of the ionosphere (*6*), that part of our atmosphere between 50 and 400 kilometers. At these altitudes, solar radiation photoionizes the atmospheric gases, and the chemistry is dominated by ion-molecule reactions. As radio astronomers became aware that interstellar space swarms with complex organic molecules (*7*), it was postulated that many, if not all, such molecules are formed by reactions of ions. Gas phase ion-molecule chemistry has also been used to account for the complex chemistry of the atmospheres of the planets (*8*). Ion reactions are important in flames, discharges, and lasers, and they may play a key role in plasma etching of silicon semiconductors as well as in other industrial processes. Fundamental thermochemical data are also potentially available from studies of gas phase ion-molecule chemistry (*9*). Finally, experimental data on the kinetics of ion-molecule reactions have been of critical importance in the evaluation of theories of reaction dynamics and have stimulated the further development and refinement of these theories (*10*).

Our interest in this area arose from a long involvement with research on the mechanisms of ionic organic reactions in solution. A recurrent question in this field has been that of the role of solvation. When we think we are studying the reactions of an ion in solution, are we really studying the solvent instead? As we desolvate hydroxide ion, we know it becomes more reactive, but do its chemical reactions really change or does it simply undergo the same reactions more rapidly? The ultimate answers should be available from studies of totally unsolvated and partially solvated ions in the gas phase.

Nature of Ion-Molecule Reactions

Before we describe the flowing afterglow apparatus and some of our results, it would be well to consider the energetics of ion-molecule reactions in the gas phase, since they differ profoundly from neutral-neutral reactions or ion-neutral reactions in solution. In a chemical reaction involving neutral species, the reac-

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Charles DePuy is a professor of chemistry, Joseph Grabowski is a graduate student research assistant, and Veronica Bierbaum is a senior research associate in the Department of Chemistry, University of Colorado, Boulder, Colorado 80309.

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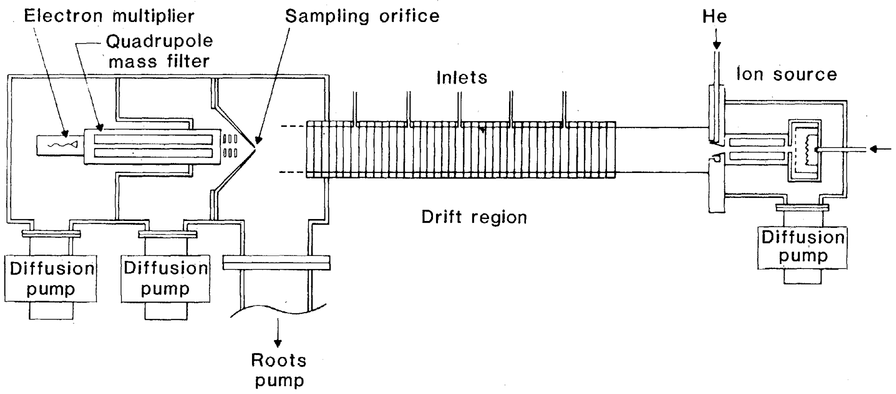


Fig. 1. In the SIFT modification of the flowing afterglow apparatus, ions of a single mass-to-charge ratio are injected and allowed to react with neutrals. If desired, they can be given kinetic energy by a drift field.

tants encounter one another only by diffusion, and when they collide, they possess only thermal energy. Since most reactions have an activation barrier, neutral-neutral reactions at room temperature are ordinarily slow and become even slower at lower temperatures (for example, the very low temperatures of interstellar space). In solution, ions are greatly stabilized by solvation, and energy must usually be supplied in order to surmount an activation barrier.

By contrast, ions in the gas phase attract neutrals by ion-dipole and ion-induced dipole forces, so that by the time they reach typical reaction distances they have as much as 20 kilocalories of relative kinetic energy per mole, more than enough to overcome many activation barriers. This same amount of energy is required to separate the products once formed, so that only reactions that are overall thermoneutral or exothermic are observed. However, this ion-dipole energy can be "borrowed" within the reaction complex to overcome activation barriers or to fuel reversible endothermic reactions. As a consequence, many ion-molecule reactions occur at nearly every collision, even at very low temperatures.

The Flowing Afterglow Technique

A flowing afterglow apparatus used in our laboratory is shown schematically in Fig. 1. It consists of a stainless steel flow tube (100 by 8 centimeters) in which ion-molecule reactions are carried out, a quadrupole mass filter and electron multiplier for analysis and detection of the ions, and gas handling and pumping equipment. A buffer gas, usually helium, is continuously pumped through the flow tube by a large capacity pump, establishing pressures near 0.5 torr and flow velocities of 10^4 cm per second. Ions are generated by electron impact on trace amounts of added gases, either directly in the flow tube (conventional flowing afterglow) or in an external ion source. In the latter configuration, ions are extracted and separated by a quadrupole mass filter, and ionic species of a single mass-to-charge ratio are injected into the flow tube, thus converting the flowing afterglow into a SIFT (*5*). In either case, the ions are allowed to flow at least 30 cm down the tube before addition of the neutral reagent. During this time, the ions undergo many thousands of collisions with helium, thus ensuring that they are in thermal equilibrium with the buffer gas. The ion population is continuously sampled through an orifice at the end of the flow tube, analyzed, and detected. In measuring kinetics, the reaction distance, and therefore the reaction time, may be varied by changing the point of reactant addition, or the neutral concentration may be varied.

Our flow tube consists of a series of thin cylindrical sections that are electrically connected and grounded for thermal energy ion-molecule experiments. However, the flow tube can easily be converted to a drift tube (*11*) by inserting precision resistors between adjacent rings and applying a voltage across the complete assembly. Ions are accelerated to a steady-state drift velocity by the resultant electric field, and ion-molecule reactions and mechanisms can be studied as a function of ion kinetic energy.

Table 1. Gas phase acidities. The gas phase acidity is the energy required to remove a proton from RH; that is, it is ΔH for the reaction RH → R^- + H^+. Values are taken from (*18*).

RH	Acidity (kcal/mole)
CH_4	416
NH_3	404
H_2	401
C_6H_6	398
H_2O	391
$CH_2{=}CHCH_3$	390
CH_3OH	379
$C_6H_5CH_3$	379
HF	371
CH_3COCH_3	369

The flowing afterglow technique with SIFT-drift capabilities has a number of valuable features for the study of ion-molecule reactions. Two of the most important are chemical versatility and control of reaction energy. Reactant ions can be generated by various techniques, the most important of which is chemical synthesis within the flow tube. With the SIFT, almost any positive or negative ion, including highly reactive or isotopically labeled ones, can be injected into the flow tube and studied in the absence of neutral precursors and ions of other masses. The choice of neutral reagents is similarly wide. Stable neutrals can be added easily. Unstable neutrals can be generated by pyrolytic, photochemical, or other techniques at their inlet to the flow tube. Atoms, radicals, and even vibrationally excited molecules have been studied with the flowing afterglow technique (*12*). Ordinarily, the relatively high helium pressure ensures that the reactant ions are at thermal energy. However, with the flow-drift technique, ion-molecule reactions can be studied at energies between 0 and 10 electron volts. Temperature-variable flowing afterglows have been constructed in which reactions can be examined between 80 and 900 K (*13*).

Ion Synthesis

As organic chemists, we are particularly interested in the study of anions (*14*), since the vast majority of synthetically useful ionic organic reactions proceed through anionic rather than cationic intermediates. However, the usual methods of ionization lead to the ejection of an electron and the formation of cations. Only a relatively few molecules give rise efficiently to anions in the gas phase. These anions may then be used for the synthesis of others through ion-molecule reactions.

We usually begin our experiments with amide (H_2N^-), hydroxide (HO^-), or fluoride (F^-) ions, since these can be made readily. Amide and fluoride are produced by electron impact on NH_3 and NF_3, respectively. Hydroxide ion is produced by electron impact on water or, preferably, on a mixture of N_2O and CH_4 (Eq. 1).

$$N_2O \xrightarrow{e^-} N_2 + O^- \xrightarrow{CH_4} HO^- + CH_3 \qquad (1)$$

In the gas phase, these ions are extremely reactive and highly basic. For example, amide ion reacts at every collision with many gases to form new ions (Eqs. 2 to 5) (*15, 16*).

$$H_2N^- + N_2O \rightarrow N_3^- + H_2O \tag{2}$$

$$H_2N^- + CO_2 \rightarrow OCN^- + H_2O \tag{3}$$

$$H_2N^- + SO_2 \rightarrow OSN^- + H_2O \tag{4}$$

$$H_2N^- + SCO \rightarrow H_2NS^- + CO \tag{5}$$

Here, the flow nature of the flowing afterglow is especially useful. By adding the reactant gas near the beginning of the flow tube, H_2N^- can be completely converted into, for example, OCN^- whose reactions can then be examined by adding another neutral reagent farther downstream. Even multistep ion syntheses are possible; for example, phosphorous analogs of nitrogen-containing ions can be prepared as shown in Eq. 6 (*17*).

$$H_2N^- \xrightarrow{PH_3} H_2P^- + NH_3 \xrightarrow{CS_2} SCP^- + H_2S \tag{6}$$

This is especially important for production of ions like SCP^- for which there are no solution counterparts and hence no simple precursors.

Because amide and hydroxide ions are such strong bases in the gas phase, they can be used to prepare carbanions directly by proton abstraction. The gas phase acidities of a number of common compounds are listed in Table 1 (*18*). Since water is less acidic than most organic molecules, hydroxide ion will abstract a proton from propylene, toluene, and molecules containing carbonyls or other electron-attracting groups. Amide ion is an even stronger base and will abstract a proton from benzene, butadiene, and many other compounds containing aryl and vinyl protons (Fig. 2). Only alkyl anions and the vinyl anion itself cannot be formed by simple proton abstraction reactions with H_2N^- or HO^-.

One drawback of producing ions directly in the flow tube is that their neutral precursor is then present in large excess. For example, electron impact on N_2O produces O^-, but this ion is destroyed by rapid reaction with N_2O. Electron impact on O_2 also forms O^-, and although O^- is not destroyed by O_2, many other ions are (*19*). In the low-pressure ion source of the SIFT, O^- can be separated from its neutral precursor and from other ions produced in the ionization process and injected into the flow tube. Indeed, direct electron impact on partially enriched water gives a mixture of $^{16}O^-$, $H^{16}O^-$, $^{18}O^-$, and $H^{18}O^-$; ions corresponding to any one of these species can be separated and injected. Thus the SIFT is especially suited for tracer studies with isotopically labeled ions.

The contrast between the reactions of amide and hydroxide ions with carbon dioxide is instructive. Amide forms cyanate at every collision by addition and elimination of water (Eq. 3). Hydroxide ion, under the same conditions, appears to react much more slowly, even though addition to form the bicarbonate ion is highly exothermic. In the gas phase, simple addition reactions between small ions and molecules are inefficient because the adducts have no way to get rid of the excess energy acquired from the bond formation; thus the bicarbonate ion dissociates back to hydroxide ion and carbon dioxide (Fig. 3) (*20*). Formation of the bicarbonate ion gradually increases as the helium pressure is raised, since energy is removed from the adduct by collision with the buffer gas. However, if $H^{18}O^-$ is injected and allowed to react with CO_2, a fast "invisible" reaction is exposed. The $H^{18}O^-$ ion is rapidly converted to $H^{16}O^-$ via a proton transfer within the adduct (Fig. 3), a process that is, of course, not observable in the reaction between unlabeled hydroxide and carbon dioxide. Proton transfer among the oxygens of bicarbonate ion must be fast compared to decomposition since the oxygen atoms become equivalent or nearly so in the course of a single collision. Similar exchanges occur between $H^{18}O^-$ and SO_2 (fast) and N_2O (slow) (*21*).

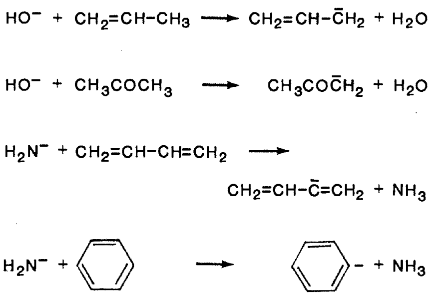


Fig. 2. Many types of carbanions can be produced in the gas phase by proton abstraction with hydroxide or amide ion. In solution, HO^- and H_2N^- are much less basic because of solvation.

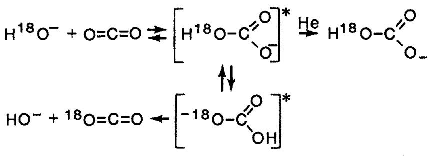


Fig. 3. Formation of the bicarbonate ion by addition of hydroxide to carbon dioxide cannot be observed unless the energy released in the addition is removed by collision with helium. However, tracer studies show that addition and intramolecular proton transfer occur at nearly every collision.

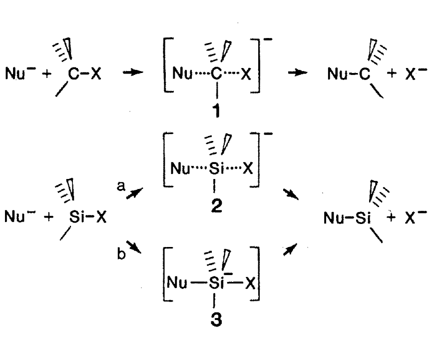


Fig. 4. The mechanism of nucleophilic displacement reactions on carbon and silicon halides can be studied by investigating the effect of the nucleophile on the reaction rate. Displacement on carbon occurs through the symmetrical transition state (**1**), whereas displacement on silicon occurs through a pentacovalent intermediate (**3**).

Displacement Reactions on Carbon and Silicon

One of the most fundamental reactions in organic chemistry is that between an alkyl halide and an anion (Nu^-). From extensive studies in solution, it is known that the anion attacks the carbon–halogen bond from the rear and that a new Nu–C bond forms simultaneously with the breaking of the carbon–halogen bond (Fig. 4). Structure **1**, with a new bond partially formed and an old one partially broken, represents an energy maximum on the reaction pathway, since carbon can accommodate a maximum of four covalent bonds.

Silicon lies just below carbon in the periodic table and forms an extensive series of compounds resembling those of carbon. However, silicon is capable of expanding its valence shell to accept five or even six bonds. Thus a silicon halide could react with an anion in the same way that carbon does (path a in Fig. 4), or there could be an actual pentacovalent intermediate formed (path b), which subsequently decomposes to products. Although the distinction may seem almost trivial, if even simple silicon compounds react easily via a pathway unavailable to carbon, it becomes difficult to draw analogies between reactions of carbon and silicon compounds, despite structural similarities.

To probe this question, we have compared the rates of reaction of methyl iodide and trimethylsilyl chloride with a series of anions of different reactivity, taking advantage of our ability to synthesize anions in the flow tube as described above (*22*). The two halides show dramatically different responses to changes in the reactant anion. For methyl iodide, there is a gradual decline in reactivity as the anion becomes less basic, much the same change as is observed in solution. Trimethylsilyl chloride, in contrast, either reacts with an anion at essentially every collision or does not react at all. This is exactly the behavior expected if a pentacovalent intermediate is formed each time the anion and the silyl chloride come together. The intermediate will then decompose in a direction determined by the thermochemistry of the reaction, either to products, if that is thermodynamically favorable, or back to starting materials, if that is the favorable direction.

Indeed, pentacovalent silicon anions of types that have been postulated but not observed in solution can be prepared and studied in a flowing afterglow (Eq. 7).

$$(CH_3)_4Si + F^- \xrightarrow{He} (CH_3)_4SiF^- \qquad (7)$$

In these experiments, the relatively high pressure in the apparatus is crucial, since the exothermicity of the reaction must be removed from the product ion by collision with helium, or else they will redissociate.

Complex Organic Reactions

Since carbanions of nearly any type can be generated in the gas phase by proton abstraction with amide or hydroxide ions, examining their chemistry is straightforward. Indeed, they undergo a wide variety of chemical reactions, most of which are completely analogous to ones familiar to any organic chemist who carries out reactions in solution. For example, the allyl anion reacts with nitrous oxide by a diazotransfer reaction to form vinyl diazomethane anion (*15*). The allyl anion adds to N_2O, there is an intramolecular proton transfer, and hydroxide ion is lost to form vinyldiazomethane (Fig. 5). However, the ion and neutral products are still in a complex, and before they separate, a proton transfer occurs to form the diazo anion and water. It is important to recognize that this final proton transfer must occur before separation of the ion and the neutral products; once separation has occurred, the vinyldiazomethane, because of its low concentration, would never be reionized. Usually the most stable anion emerges from a reaction complex, although in highly exothermic reactions there may be separation before equilibration is complete.

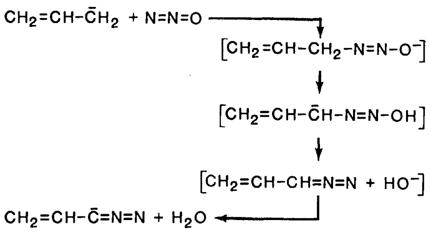


Fig. 5. During a single ion-molecule encounter, complex multistep reactions can occur.

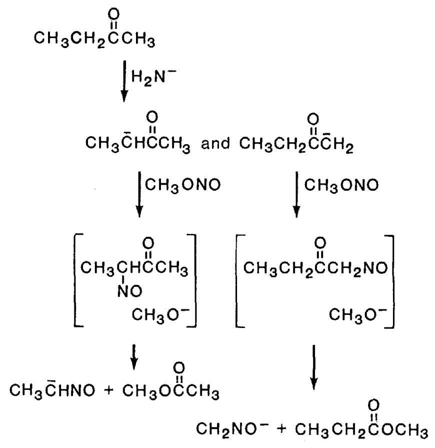


Fig. 6. Proton abstraction often gives a mixture of isomeric anions. Chemical reactions can then be used to elucidate the structures of these ions.

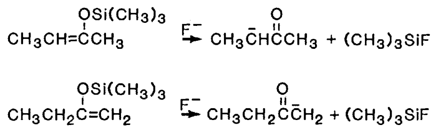


Fig. 7. Trimethylsilyl derivatives are excellent precursors of specific isomeric anions when proton abstraction generates a mixture of ions.

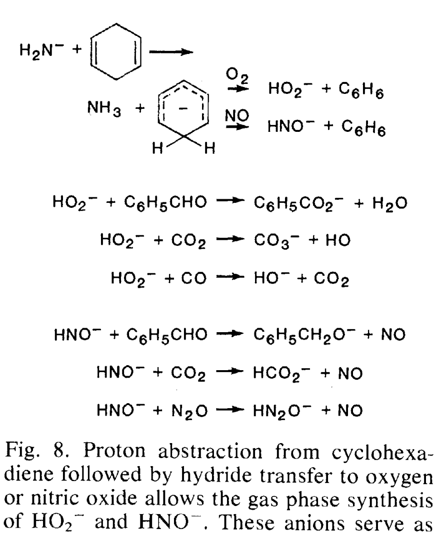


Fig. 8. Proton abstraction from cyclohexadiene followed by hydride transfer to oxygen or nitric oxide allows the gas phase synthesis of HO_2^- and HNO^-. These anions serve as excellent oxidizing and reducing agents, respectively, for a variety of organic and inorganic molecules.

The assignment of ion structure has always been a central issue in mass spectrometry, and a variety of techniques, including collisional activation, have provided important structural data. However, chemical reactions, if they are properly chosen, can be used to determine ion structure in the gas phase just as they are used to determine molecular structure in solution. For example, proton abstraction from methyl ethyl ketone forms a mixture of isomeric enolate anions; since they have the same mass-to-charge ratio, the product ions will appear as a single peak in the mass spectrum. Reaction of this mixture of ions with methyl nitrite forms nitrosomethane and nitrosoethane anions (Fig. 6) (*23*). We picture these products as arising from nitrosation and cleavage within the reaction complex. To show that the reaction is indeed diagnostic of the structure of these ions, we needed a means of generating each, uncontaminated with the other. This can be done by reaction of their trimethylsilyl derivatives with fluoride ions (*24*). For example, the isomeric enolate ions can be formed from the isomeric silyl enol ethers, and each reacts as predicted with methyl nitrite (Fig. 7).

Oxidation and reduction reactions can also be carried out efficiently in the gas phase. The cyclohexadiene anion, formed by reaction of cyclohexadiene with amide, is a potent gas phase hydride donor, since transfer of hydride forms the highly stable benzene molecule. This anion, in turn, can be used to make the oxidant HO_2^- or the reductant HNO^-. The former oxidizes benzaldehyde to benzoate; the latter reduces it to benzylalkoxide ion (Fig. 8) (*25*).

These simple reactions demonstrate the range of standard organic reactions that can be performed in the gas phase. Condensations, Michael additions, fragmentations, and rearrangements all proceed with ease in properly chosen systems. Most types of reaction that occur in solution appear to have gas phase ion-molecule counterparts.

Hydrogen-Deuterium Exchange in the Gas Phase

Hydrogen-deuterium exchange has been widely used in solution for proofs of structure and for mechanistic studies, and we have shown that it can be of equal value in the gas phase (*26*). For example, the anion from 1-hexene can be generated by proton abstraction with amide ion. If D_2O is added downstream, rapid H-D exchange occurs (Fig. 9). The extent of exchange depends on the concentration of D_2O and, with high flows,

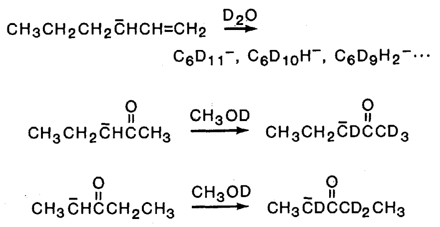


Fig. 9. Hydrogen-deuterium exchange occurs readily in many anions and can be used to study ion structure.

essentially complete exchange of all 11 protons can be observed.

More acidic hydrogens—for example, those next to carbonyl groups—do not exchange with D_2O, but readily exchange with the stronger gas phase acid CH_3OD. Just as for molecules in solution, H-D exchange can be used to count the number of acidic protons in an ion. For example the 2- and 3-pentanone enolate ions exchange four and three hydrogens with CH_3OD, respectively (Fig. 9).

For kinetic studies, we have reversed the exchange reaction (*27*). Using the SIFT, we inject DO^- into the flow tube in the absence of D_2O or HO^- and allow it to react with molecules (hydrogen, amines, and vinyl and aryl compounds) that are less acidic than water. All H-D exchanges demand that an endothermic proton transfer occurs in the reaction complex (for example, from benzene to DO^-), and the energy for this transfer must come from the ion-induced dipole attractive energy of the complex (Eq. 8).

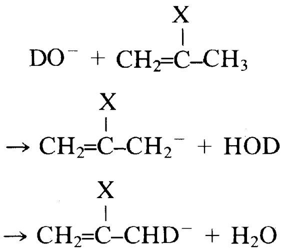
$$DO^- + C_6H_6 \rightarrow [DOH + C_6H_5^-] \rightarrow HO^- + C_6H_5D \qquad (8)$$

Exchange rates for neutrals with similar acidity correlate well with estimated relative ion-neutral attractive energies. For example, ammonia exchanges rapidly with DO^-, even though it is 13 kcal/mole less acidic than water. Since ammonia is polarizable and has a dipole moment, there is a large amount of attractive energy available in the reaction complex, and an otherwise endothermic proton transfer is easily possible. Hydrogen is more acidic than ammonia (10 kcal/mole less acidic than water), but exchanges only very slowly because it has no dipole moment and is only slightly polarizable; there is insufficient energy in the complex for rapid exchange. Similar considerations apply to organic molecules. For example, ethylene does not exchange, but attaching a polarizable *tert*-butyl group (that is, *tert*-butylethylene) brings about moderately rapid exchange.

Studies of H-D exchange can also be revealing about the site of reaction within ions. For example, the pentadienyl anion exchanges four protons rapidly, demonstrating that proton addition occurs more rapidly at the ends of the conjugated system than in the middle (*26*).

$$H_2C{=}CH{-}\bar{C}H{-}CH{=}CH_2 \xrightarrow{ROD} D_2C{=}CH{-}\bar{C}H{-}CH{=}CD_2 \qquad (9)$$

Finally, H-D exchange can provide some information about the lifetimes of ion-molecule complexes. For example proton abstraction from 2-substituted propylenes by DO^- gives appreciable amounts of deuterated allyl anion, showing that multiple proton transfers occur within a single complex (*28*).



$$DO^- + CH_2{=}\overset{X}{\overset{|}{C}}{-}CH_3 \rightarrow CH_2{=}\overset{X}{\overset{|}{C}}{-}CH_2^- + HOD \rightarrow CH_2{=}\overset{X}{\overset{|}{C}}{-}CHD^- + H_2O \qquad (10)$$

The Electron Affinity of $HO_2\cdot$

The study of gas phase ion-molecule reactions can also contribute to the determination of fundamental thermochemical data, including gas phase acidities, basicities, electron affinities, ionization potentials, and bond dissociation energies. We recently made the first experimental determination of the electron affinity of the hydroperoxy radical [$EA(HO_2\cdot)$] (*29*) defined as the enthalpy change for Eq. 11.

$$HO_2\cdot + e^- \rightarrow HO_2^- \qquad (11)$$

The hydroperoxy radical is an important species in the atmosphere and in a host of chemical and biological processes. For this measurement, the chemical synthesis of ions in the flowing afterglow was especially useful. To complete a thermochemical cycle and calculate $EA(HO_2\cdot)$, we needed an accurate determination of the proton affinity of HO_2^-. However, HO_2^- is a strong oxidant and reacts with many neutrals by oxidation rather than by proton transfer (Fig. 8). Indeed, it even reacts with H_2O_2 by disproportionation (Eq. 12), so that H_2O_2 cannot be used as the source of the hydroperoxy anion.

$$HO_2^- + H_2O_2 \rightarrow HO^- + H_2O + O_2 \qquad (12)$$

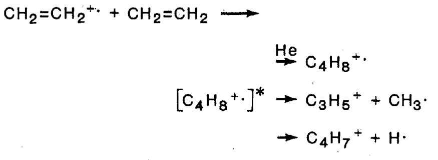


Fig. 10. Reaction of the ethylene cation with ethylene neutral proceeds through a chemically activated complex that decomposes by three pathways. Competition among these channels can be studied as a function of ion kinetic energy in drift experiments.

It can, however, be made by hydride transfer from organic molecules, as mentioned earlier. The experiment also required two acids of known standard enthalpy change (ΔH°_{acid}) that would not be oxidized by HO_2^- and so could be used to bracket the basicity of HO_2^-. Fluoroform and hydrofluoric acid proved to be ideal for this purpose.

$$HO_2^- + HCF_3 \rightleftarrows CF_3^- + H_2O_2 \qquad (13)$$

$$HO_2^- + HF \rightleftarrows F^- + H_2O_2 \qquad (14)$$

From experimental measurement of the equilibrium constants for these acid-base reactions and known heats of formation, we determined $EA(HO_2\cdot)$ to be 1.16 ± 0.15 eV, considerably lower than previous estimates (1.85 to 4.6 eV). Threshold photodetachment spectroscopy was subsequently performed to determine the more precise value of 1.19 ± 0.01 eV (*29*).

Reactions as a Function of Ion Kinetic Energy

Very recently we have begun drift studies to examine some fundamental reactions as a function of ion kinetic energy. Ions are injected in the SIFT and then accelerated relative to the reagent and buffer gases by an electric field. They quickly reach a constant velocity defined by the magnitude of the applied electric field and the neutral gas density. Although ion energies as high as 10 eV have been reported (*30*), our initial studies have been confined to energies below 2 eV. The flow drift therefore provides data in the energy regime between thermal and that conveniently accessed by tandem mass spectrometry and ion beam techniques.

Our preliminary results reveal some important advantages of the drift technique. For example, drifting allows the anions to react like stronger bases. Although HO^- does not react with ammonia at zero field, reaction to form H_2N^- readily occurs in our drift tube. This opens up a method for the generation of carbanions, which are considerably less acidic than water. Because ethylene is even less acidic than ammonia, the gas phase chemistry of the vinyl anion has not been studied. Ethylene does not even exchange with DO^- in the gas phase. However, in our drift experiments, DO^- with kinetic energy $[DO^-(KE)]$ reacts with ethylene to produce large signals of the vinyl anion as well as HO^- by exchange (Eq. 15).

$$\begin{aligned} DO^-(KE) + CH_2{=}CH_2 & \\ &\rightarrow HO^- + CHD{=}CH_2 \qquad (15) \\ &\rightarrow CH_2{=}\overline{C}H + DOH \end{aligned}$$

Once formed in this way, chemical reactions of this anion can be studied. For example, the vinyl anion adds to CO_2 and also reacts with N_2O and O_2.

Drifting DO^- can also induce new reaction pathways, even for highly reactive neutrals (*31*). For example, DO^- displaces chloride ion from methyl chloride at every collision at zero field. In a drift field, two new reaction channels, proton abstraction and H-D exchange, appear (Eq. 16).

$$\begin{aligned} DO^-(KE) + CH_3Cl & \\ &\rightarrow Cl^- + CH_3OD \\ &\rightarrow \overline{C}H_2Cl + DOH \qquad (16) \\ &\rightarrow HO^- + CH_2DCl \end{aligned}$$

Thus, by using the drift technique, we are able to examine the chemistry of anions that cannot be generated by proton abstraction with H_2N^- in a conventional flowing afterglow.

Although most of our work has involved anions, cations can also be generated and studied in the flowing afterglow and SIFT. One reaction that has been extensively studied in many different types of instruments is that between the parent positive ion of ethylene and ethylene itself. The products are the simple adduct and the adduct in which a methyl radical or hydrogen atom has been lost (Fig. 10). At low pressure—for example, in an ion cyclotron resonance spectrometer—no simple adduct is seen; the exothermicity of the reaction is removed by fragmentation. In a flowing afterglow, as in a high-pressure mass spectrometer, all three product ions are seen, since energy can be removed from the addition product by the buffer gas. In the drift mode, the addition product is formed with more and more energy as the kinetic energy of the reactant ion is increased, and the variation in product ratios is studied as a function of ion energy. As expected, more fragmentation is seen as this energy increases. It is clear that careful studies of the variations in production ratios as a function of ion kinetic energy will provide new insights into how ion-molecule reactions occur.

Concluding Remarks

An understanding of the chemistry and reactivity of ions in the gas phase is important to a variety of diverse fields—from the synthesis of molecules in interstellar space to the most familiar of reactions in solution. A number of experimental techniques have been successfully applied to the study of gas phase ion-molecule chemistry. The flowing afterglow, with selected ion flow tube and flow-drift capabilities, provides a versatile approach to the generation and study of a host of ions, both organic and inorganic, both common and previously unknown. These techniques have allowed us to examine rates, products, mechanisms, and thermochemistry of a wide variety of reactions, both at room temperature and as a function of ion kinetic energy. The traditional tools of organic chemistry are also valuable in the gas phase: the kinetics of reactions (for example, displacement on carbon versus silicon) allows us to assign mechanisms; isotopically labeled reactants allow us to probe intramolecular rearrangements; and hydrogen-deuterium exchange allows us to distinguish structures. Moreover, the underlying conceptual framework of synthetic organic chemistry appears to apply as well to carbanions in the gas phase as it does to those in solution. Shorn of their solvent molecules, gas phase anions—both organic and inorganic—react rapidly, but usually by familiar pathways. This makes the occasional dramatic differences between reaction in the gas phase and in solution all the more interesting, since these differences must owe their origin to solvation or to some fundamental change in reaction mechanism in the two phases. Indeed, as is usual in science, it is the deviation from expected behavior that can reveal the most about natural processes. The study of anions in the gas phase is still a relatively young field, and rapid progress and new insights are to be expected in the future, aided by new instrumental developments as well as by our increasing ability to recognize the similarities and differences between solvated and unsolvated ions.

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