An introduction to the gas phase chemistry of anions

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1. Introduction

Since most mass spectrometry involves the chemistry of cations, why is gas phase anion chemistry such an active field of research? Primarily because the most useful synthetic organic reactions involve anions. Substitution and elimination reactions, Grignard additions, and aldol condensations, hydrolysis of esters, and the great majority of the most common synthetic reactions involve anions. Anions are favored over cations because they seldom rearrange; a Grignard reagent derived from a primary halide remains primary, while a primary cation instantly rearranges. Physical organic chemists, who have unraveled the mechanisms of many of these anionic reactions in solution, were attracted to their study in the gas phase in the hopes that complicating factors due to solvation or the presence of counter ions could be eliminated, and that more intimate details about these important species could be revealed.

2. Instrumentation

Most experiments in the field of gas phase carbanion chemistry have been carried out using ion-cyclotron resonance (Fourier transform mass spectrometry) spectrometers [1] or flowing afterglow (FA) devices

[2]. A major experimental problem is that carbanions of interest to organic chemists are seldom formed in useful amounts by conventional ionization techniques. Instead a strong base must first be formed by using one of these ionization methods and then the desired anion (e.g. an enolate, benzyl or allyl anion) generated by a bimolecular proton transfer or other reaction. The chemistry of the resulting anion must then be probed by further bimolecular reactions. Since the concentration of both the ions and the neutral reactants are extremely low ($\sim 10^{-12}$ mol L^{-1} for the ions and $\sim 10^{-8}$ for the neutrals) bimolecular collisions are relatively improbable. It is only because ion-molecule reactions have such large rate coefficients (as large as 10^{12} L mol^{-1} s^{-1}) that they can be observed at all in these instruments. In the FA there is also helium (0.5 Torr, 2.5×10^{-5} mol L^{-1}) so that the ions are cooled to room temperature by frequent collisions with the bath gas before they encounter the neutral reactant. In the ion-cyclotron resonance (ICR) an inert gas is sometimes added to the reaction cell to cool the ions, then removed before the neutral reactant is added.

Anions have also been studied in sector instruments. Particularly important have been equilibrium studies carried out in high pressure pulsed ion sources. In a typical experiment some ion that can be made by electron impact (e.g. chloride ion) is generated in the presence of a high pressure of neutral reagents and a buffer gas. An equilibrium mixture of
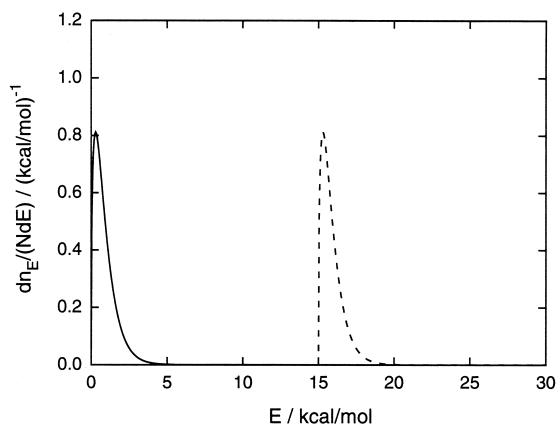
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Fig. 1. Plots of the kinetic energy distribution of molecules at room temperature (solid line) and of ion–dipole complexes with 15 kcal/mol complexation energy (dashed line). The area under each curve is 1.

complexes of the ion with the neutrals present is quickly established and then the relative ion concentrations are obtained by sampling the ions into the mass spectrometer. Since the source can be heated or cooled, reactions can easily be studied as a function of temperature.

3. Energetics of gas phase ion–molecule reactions

Gas phase ion–molecule reactions have the remarkable property of being both extremely fast and yet highly selective, and hence they seemingly violate the reactivity-selectivity principle so central to physical organic chemistry. For example an S_N2 reaction between an anion and a methyl halide can react 10^{12} or more times faster in the gas phase than it does in solution, yet can exhibit a secondary isotope effect as large as that in solution. To understand this apparent contradiction it is necessary to understand the peculiar energetics of ionic reactions in the gas phase [3].

Suppose we have an ion and a reactive neutral in solution at room temperature, and that a reaction between them has an activation energy of 15 kcal/mol. The reactants thus have a room temperature Maxwell-Boltzmann distribution of energies as approximated by the solid line shown in Fig. 1. For a reaction to occur, the reactants must come together with a total energy of 15 kcal/mol or more in order to have sufficient energy to surmount the activation barrier. But only very, very few of the reactants in solution have this amount of energy, so that nearly all encounters between the ion and neutral are unproductive.

In the gas phase the reactants also start with a room temperature distribution of energies. However, an ion and a neutral are attracted to one another by ion–dipole and ion–induced dipole forces which increase as they approach one another and which amount typically to 12–18 kcal/mol by the time they reach reaction distance and enter an ion–dipole complex. For example the complexation energy for chloride with methyl bromide is 12.7 kcal/mol and for chloride with *t*-butyl bromide 17.5 kcal/mol [4]. We will assume an average value of 15 kcal/mol in our discussions. In solution this energy is removed by the surrounding solvent molecules, but in vacuum it remains within the reaction complex. Therefore each time an ion and a neutral come within reaction distance in the gas phase they have their original small room temperature energy plus about 15 kcal/mol of ion–dipole and ion–induced dipole energy (dashed line in Fig. 1).

Initially this additional energy is in the form of translation as the reactants approach one another, but as they collide it becomes equilibrated among the various vibrational and rotational energy levels within the system, resulting in a fairly long-lived ion–dipole complex. If no reaction occurs this complex will dissociate once the energy is re-concentrated into relative translational energy. The lifetime of such complexes varies depending upon the structure of the reactants, but is generally much less than 10^{-7} s, the average time before collision with a helium atom in a flowing afterglow apparatus where the total pressure of buffer gas is about 0.5 Torr. As an example, the lifetime of a chloride/methyl bromide complex has been measured to be 10^{-12} s in a high pressure mass spectrometry experiment [4]. If a reaction is possible with an activation energy smaller than the complexation energy, then the energy can be concentrated along the reaction coordinate and the reaction can proceed.

We can identify three regions of activation energies of importance in Fig. 1. If the activation energy is below the complexation energy, every complex will have sufficient energy to react. If it is well above the complexation energy, no reaction will be observed under the experimental conditions. But in the crucial range where the activation energy is at or somewhat above the complexation energy, the reaction rate will change rapidly as the activation energy changes. It is in this region where a small change in structure, for instance isotopic substitution, can have a measurable effect on the rate. This range is relatively small, because reaction rates can only be measured accurately in the gas phase over a range of about four orders of magnitude.

It is sometimes alleged that gas phase ion–molecule reactions are "hot" reactions (and hence unselective) because a collection of molecules with an average energy content of 15 kcal/mol would have a temperature of many thousands of degrees. But this is misleading, because what is important is the excess energy in the transition state of the reaction, not in the complex before reaction. In a reaction with a complexation energy of 15 kcal/mol and an energy at the top of the barrier of the same amount, the transition state is at room temperature because the complexation energy is being used to traverse the barrier. This is the same total energy that the reaction in solution would have. Only if the energy at the top of the barrier is much less than the complexation energy is there "excess" energy in the transition state and we shall see how even this limitation can sometimes be overcome.

The energy generated by complexing an ion and a neutral can be "borrowed" for use in other ways than traversing a reaction barrier of the type one finds, e.g. in an S_N2 reaction. It may instead, for example, be used to "fuel," temporarily, an endothermic proton transfer of the type (B^-HA) to (BH^-A). If we assume that the complexation energy of the two ions is 15 kcal/mol, then this will be sufficient to fuel a proton transfer that is as much as 15 kcal/mol endothermic. In the process of this endothermic proton transfer the complex cools down by the amount of the endothermicity, but maintains its room temperature energy distribution. Of course the complex no longer has

sufficient energy to dissociate and must regain the needed energy by a reverse proton transfer by the same (or an equivalent) proton. Or the two processes may be combined; part of the complexation energy may be used for an endothermic proton transfer and part of the remaining energy used to surmount a barrier that is inaccessible in the original complex. We will see examples of each of these types of reactions.

4. Formation of gas phase anions

Simple anions, of the type used in organic synthetic reactions in solution, can seldom be formed in the gas phase by the standard methods of ionization commonly used in mass spectrometry. Fortunately a few strong bases, in particular NH_2^-, HO^-, and CH_3O^-, can be formed by electron impact on suitable precursors, and these ions can in turn be used to abstract a proton to generate ions of interest. Amide ion, the most basic ion which can easily be generated in the gas phase, is produced by electron impact on ammonia, whereas hydroxide ion, by far the most commonly employed base, results from electron impact on a mixture of nitrous oxide and methane as shown in Eq. (1)

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

The initially produced oxygen radical anion rapidly abstracts a hydrogen atom from methane. Methoxide ion results from electron impact on methyl nitrite (CH_3ONO). One or another of these bases is capable of abstracting a proton from nearly all organic neutrals with the exception of alkanes.

Proton transfer reactions have the drawback that there may be more than one acidic site in a molecule, so that either an undesired anion or a mixture of anions results. To circumvent this problem, the reaction of a trimethylsilyl (TMS) derivative with fluoride ion may be used to place the charge at a specific site [5]. For example the methyl hydrogens of acetaldehyde are much more acidic than the aldehydic hydro-

gen, and reaction with a base generates only the enolate. However the isomeric acyl anion can be prepared by allowing acetyl trimethylsilane to react with fluoride ion [6] [Eq. (2)]

$$CH_3\overset{O}{\overset{\|}{C}}-Si(CH_3)_3 \xrightarrow{F^-} CH_3\overset{O}{\overset{\|}{C}}- + Si(CH_3)_3F \quad (2)$$
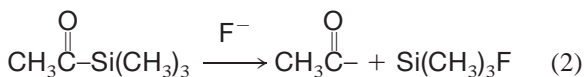
In addition to these more or less standard methods, there are numerous special methods that have been used to prepare unusual anions. For example the oxide radical anion often abstracts both a proton and a hydrogen atom from a neutral to form a radical anion, as shown for its reaction with ethylene [7] in Eq. (2)

$$CH_2=CH_2 + O^{-\cdot} \longrightarrow CH_2=C^{-\cdot} + H_2O \quad (3)$$

Anions can also sometimes be prepared by collision-induced dissociation (CID) of more easily prepared anions. For example the neopentyl anion has been prepared in this way [8]; neopentane is too weak an acid for the anion to be formed in a more conventional reaction.

$$(CH_3)_3CCH_2COO^- \xrightarrow{CID} (CH_3)_3CCH_2^- + CO_2$$

$$(4)$$
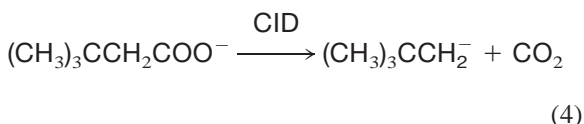
In order to form stable ion–dipole cluster ions, energy must be removed from a collision complex before dissociation can occur. An effective way to accomplish this is to generate a third body in the reaction itself; this neutral molecule can depart, taking energy with it. An example is the Riveros reaction [9] [Eq. (5)]

$$C_2H_5\overset{O}{\overset{\|}{C}}- \longrightarrow [C_2H_5OH\ CO^-\ OCH_3] \quad (5)$$
$$\longrightarrow C_2H_5O^-HOCH_3 + CO$$
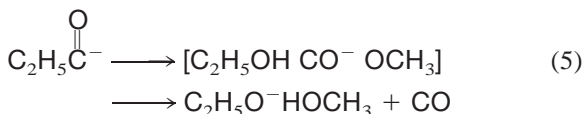
in which a base is allowed to react with a formate ester. After abstraction of a proton from the acetyl carbon, carbon monoxide and methoxide ion are formed. Loss of carbon monoxide leaves the cooled complex behind. As long as the resulting complex has

Table 1
Gas phase acidities of some common molecules (kcal/mol)[a]

Molecule	ΔH_{acid}	ΔG_{acid}
CH_4		409
C_2H_4	409	401
NH_3	404	397
C_6H_6	402	393
H_2	400	394
H_2O	391	384
CH_2CHCH_3	389	383
CH_3OH	382	375
$C_6H_5CH_3$	381	374
C_2H_2	378	370
$CH_3CON(CH_3)_2$	375	368
CH_3COOCH_3	372	365
CH_3COCH_3	369	362
$c\text{-}C_5H_6$	354	348
H_2S	351	345

[a] An up-to-date compilation of thermochemical data including gas phase acidities can be found at http://webbook.nist.gov/chemistry/.

insufficient energy to dissociate, it will be long-lived and will be cooled to room temperature by collisions with the bath gas.

5. Gas phase acidities

The gas phase acidity (GPA) of a molecule RH is defined as the molar Gibbs energy, ΔG, required to dissociate it heterolytically into a proton and an anion

$$RH \underset{PA}{\overset{GPA}{\rightleftharpoons}} R^- + H^+ \quad (6)$$
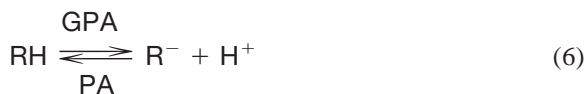
The proton affinity (PA) of the corresponding anion is the enthalpy, ΔH, of the reverse reaction. In the literature GPA and PA values are sometimes used. Hundreds of such gas phase acidities are now known, and those of a number of simple molecules are given in Table 1. It is striking how often the order of acidities within classes of compounds resembles that in solution. Among the hydrocarbons, methane is less acidic than ethylene, which is less acidic than benzene, which in turn is less acidic than acetylene, and the relative order of acidity of other hydrocarbons is just as expected from solution. Similarly the methyl hydrogens of an amide are less acidic than those of an

ester that in turn are less acidic than those of a ketone or aldehyde. Ammonia, water, hydrogen sulfide and hydrogen chloride are in the expected order of acidity. Many other examples of correspondence between solution and gas phase acidities could be given.

It is against this background of general agreement between gas phase and solution acidities that major differences stand out. The most striking, and best known, of these differences is that first pointed out by Brauman and Blair [10]. In the gas phase the relative acidity order of water and the simple alcohols is completely reversed from that in aqueous solution. Water is by far the weakest acid of the group, methanol is much stronger, followed by ethanol, isopropanol and *t*-butyl alcohol. This increase in acidity with an increase of methyl groups near the anionic center is attributed to polarizability; methyl groups stabilize a negative charge, just as they stabilize a positive charge in carbocations. The inverse order in aqueous solution is ascribed to a solvent effect in which the methyls prevent the close approach of solvent molecules to the charged center.
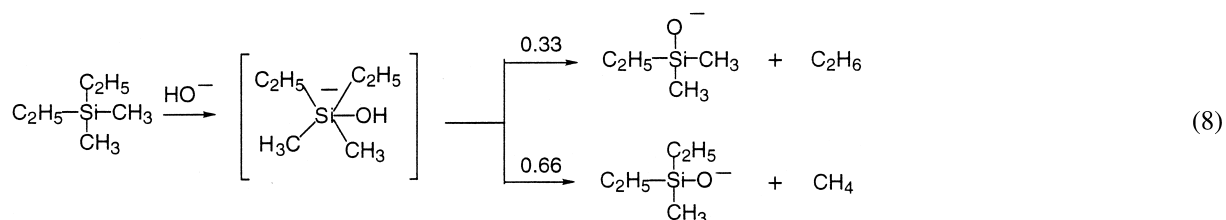
6. Measurement of gas phase acidities

The obvious way to measure the gas phase acidity of a neutral, RH, is to establish an equilibrium with another acid, R′H, of known acidity and to measure the concentrations of the two anions at equilibrium. Many acidities have been determined this way, especially in the ICR. In the FA it is sometimes difficult to be sure that equilibrium conditions have been established during the short residence time of the ions in the flow tube, and it is more common to measure the rate constants of the forward and reverse reactions, providing each anion can be prepared separately. The rate constant ratio is the equilibrium constant. A common, semiquantitative method for determining acidities is called the "bracketing technique." In this method an anion is prepared and allowed to react with a series of increasingly strong acids until one or more is found for which proton transfer occurs. For example, if an anion fails to react with methanol to generate methoxide ion, reacts slowly with ethanol to form

ethoxide ion, and reacts rapidly with *t*-butyl alcohol to form the *t*-butoxide ion, its acidity is said to be bracketed at about that of ethanol. This method is especially useful for an ion (e.g. O_2^-) whose conjugate acid (HO_2) cannot be readily obtained for kinetic or equilibrium studies. Proton transfer reactions occur at nearly every collision if the reaction is exothermic, and the rate drops off rapidly when it becomes endothermic providing that at least one of the partners is an alcohol or amine. Unfortunately, proton transfer reactions between carbon centers are usually slow in the gas phase, as they are in solution, and some regions of the acidity scale do not have standard acids suitable for this method to work well.

The kinetic method of Cook and Kruger [11] is another powerful way of obtaining the relative acidity of two acids. First an ion–dipole complex is formed, perhaps by the Riveros reaction [Eq. (5)] between an acid (e.g. methanol) and the conjugate base of a second acid (e.g. ethoxide ion). The complex is then subjected to collision-induced dissociation [Eq. (7)]. The ethoxide/methoxide ion ratio observed in the resulting mass spectrum is a measure of the relative acidity of the two alcohols. Although the acidities of these two alcohols are already well known, their ratio observed under a particular set of instrumental conditions can be used to calibrate the measurement. The acidity of an unknown alcohol can then be determined from dissociation of its complex with methoxide or ethoxide ion under the same conditions [12].

$$[R\text{-}H\text{-}R']^- \xrightarrow{CID} \begin{array}{c} RH + R'^- \\ R^- + R'H \end{array} \tag{7}$$
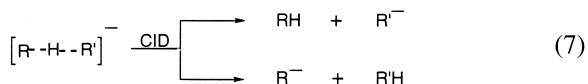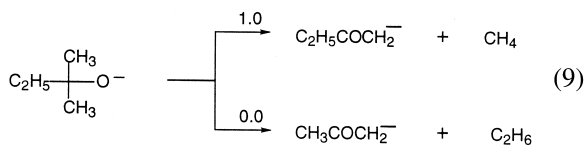
A particular challenge is to determine the acidity of the alkanes, since these hydrocarbons are such weak acids that there is no gas phase base sufficiently strong to abstract a proton. Therefore kinetic methods have also been devised to probe their acidity. In one method silanes are used, but allowed to react with HO^- rather than F^- [see Eq. (2)] [13]. The mechanisms of the two reactions are assumed to be analogous, with the base adding exothermically to the silicon atom and the resulting adduct attempting to

$$
\begin{array}{c}
\underset{\overset{\displaystyle C_2H_5}{|}}{\overset{\displaystyle C_2H_5}{C_2H_5-Si-CH_3}}
\xrightarrow{\ HO^-\ }
\left[
\begin{array}{c}
\underset{\overset{\displaystyle H_3C}{}}{\overset{\displaystyle C_2H_5}{}}
\overset{\displaystyle -}{Si}
\overset{\displaystyle C_2H_5}{\underset{\displaystyle CH_3}{}}
-OH
\end{array}
\right]
\end{array}
$$

0.33 → $C_2H_5\overset{\overset{O^-}{\|}}{\underset{CH_3}{Si}}CH_3$ + C_2H_6

0.66 → $C_2H_5\overset{C_2H_5}{\underset{CH_3}{Si}}O^-$ + CH_4

$$(8)$$

eject a carbanion. Alkyl anions are so strongly basic that there is insufficient energy in the adduct to accomplish this completely, so that with F^- no alkyl anions are produced. In the reaction with HO^-, as negative charge builds up on the alkyl group it reacts with the proton on the hydroxyl group to form an alkane, leaving the siloxide ion behind. The carbon best able to accommodate the negative charge in the transition state is lost in the greater amount. By examining the ratio of the siloxide ions produced, the relative acidity of the alkyl anions can be inferred. For example when diethyl dimethyl silane is allowed to react with hydroxide ion, twice as much methane as ethane is lost, indicating that methane is a stronger acid than ethane [Eq. (8)]

Among the simple, acyclic hydrocarbons studied in this way, neopentane was found to be the most acidic, just as its oxygen analog, tertiary.butyl alcohol, is the most acidic alcohol. Cyclopropane, as expected, is the most acidic of the simple, cyclic hydrocarbons. The greater acidity of methane than ethane, while somewhat surprising, has been predicted computationally [14].
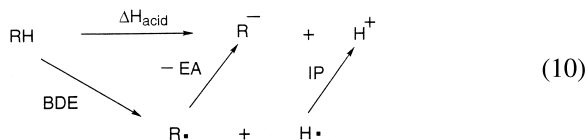
A related infrared multiphoton dissociation method has also been applied to determining alkane acidities [15]. In these ICR experiments an unsymmetrical alkoxide is heated by the absorption of many infrared photons until it dissociates to a hydrocarbon and an enolate.

$$
\underset{\overset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{C_2H_5-C-O^-}}
\longrightarrow
\begin{array}{c}
\xrightarrow{1.0} C_2H_5COCH_2^- + CH_4\\[2ex]
\xrightarrow{0.0} CH_3COCH_2^- + C_2H_6
\end{array}
\qquad (9)
$$

As mentioned above, in the transition state negative charge develops on the alkyl group, which abstracts a proton from the ketone to form an enolate. The

relative amounts of the two ions formed, corrected for statistical effects, reflects the relative acidities of the two hydrocarbons lost. In the example, only methane is lost, again showing that ethane is a weaker acid than methane. In this method a greater degree of negative charge builds up in the transition state on the departing alkyl group than is the case in the silane cleavage reaction, leading to a greater selectivity in the loss of alkyl groups. The silane method covers a larger range of acidities and can be anchored to the known acidity of benzene. Although there are some differences in the relative hydrocarbon acidities predicted by the two methods, the general trend is the same in both experiments, and they nicely complement one another.

All of the methods described determine the relative acidity of two acids. To obtain absolute acidities, one needs standard acids whose acidities are known by some other method. Fortunately several key absolute acidities have been determined. This is possible because a thermodynamic cycle [Eq. (10)] relates the bond dissociation energy (BDE) of the R–H bond, the electron affinity (EA) of the resulting radical, and the ionization potential (IP) of the hydrogen atom to the acidity of RH. Since the EA, BDE, and IP are all enthalpies, the acidity of RH must also be expressed as ΔH of ionization. If the first three values are all known, as they are for methane, ammonia, water and several other molecules, then the absolute gas phase acidity can be calculated. These molecules then serve as anchors for the whole acidity scale.

$$
\begin{array}{c}
RH \xrightarrow{\ \Delta H_{acid}\ } R^- + H^+ \\[1ex]
\searrow_{BDE} \quad \nearrow_{-EA} \quad \nearrow_{IP} \\[1ex]
R\cdot + H\cdot
\end{array}
\qquad (10)
$$

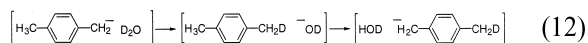## 7. Proof of structure of gas phase ions

Because ions repel one another, it is extremely difficult to obtain them in sufficiently high concentrations for spectroscopic analysis. Therefore a number of chemical reactions have been developed as aids in structural analysis. Of the methods available for identifying an ion, its proton affinity is an obvious starting point, and the bracketing technique and the kinetic method of Cook and Kruger are commonly used for this purpose. Among more "chemical" methods, hydrogen/deuterium exchange reactions are especially useful [16]. For example when the benzyl anion is allowed to react with D_2O, the two benzylic hydrogens are replaced by deuterium. The mechanism for this exchange makes use of the endothermic proton transfer step fueled by the complexation energy that was described previously

$$\left[\text{Ph—CH}_2^-\ \ D_2O\right] \longrightarrow \left[\text{Ph—CH}_2D\ \ ^-OD\right] \longrightarrow \left[\text{Ph—C}^-HD\ \ HOD\right] \quad (11)$$
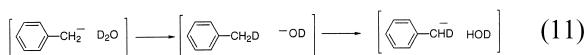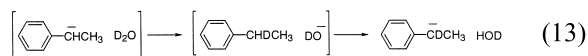
The first intermediate is an ion–dipole complex between the benzyl anion and D_2O which contains in the neighborhood of 15 kcal/mol complexation energy. An endothermic deuteron transfer reaction then occurs to form a new complex between deuterated toluene and DO^-. Since toluene is 10 kcal/mol more acidic than water, this proton transfer reaction can occur and the resulting complex is cooled by 10 kcal/mol. Dissociation of this second complex into its components is endothermic; they must remain together until energy is regained by abstraction of a proton to reform the original complex, with the benzyl anion now deuterated. The complex can now dissociate into labeled benzyl anion and HOD and a second deuterium can be introduced by an encounter with another D_2O molecule. It is also possible to introduce two deuterium atoms into the benzyl anion in a single encounter with D_2O, since before dissociation of the complex containing a single deuterium on carbon, a second deuterium transfer followed by a second proton transfer may occur leading to the formation of H_2O [17].

It is important to recognize that in an ion–dipole

complex the ion and the neutral are not covalently bonded, and can move easily with respect to one another. This is illustrated for the case of H/D exchange between the *p*-xylyl anion and D_2O where all five benzylic hydrogens can be replaced by deuterium. After the initial deuteron transfer to the benzyl carbon DO^- can migrate to the para position and abstract a proton from the para methyl group [Eq. (12)]

$$\left[\text{H}_3\text{C—}\bigcirc\text{—CH}_2^-\ \ D_2O\right] \longrightarrow \left[\text{H}_3\text{C—}\bigcirc\text{—CH}_2D\ \ ^-OD\right] \longrightarrow \left[\text{HOD}\ \ ^-\text{H}_2\text{C—}\bigcirc\text{—CH}_2D\right] \quad (12)$$

Eventually, after additional reactions with D_2O, all five benzyl protons can be exchanged for deuterium. In contrast, the isomeric anion from ethyl benzene exchanges only a single hydrogen for deuterium [Eq. (13)]

$$\left[\text{Ph—C}^-\text{HCH}_3\ \ D_2O\right] \longrightarrow \left[\text{Ph—CHDCH}_3\ \ DO^-\right] \longrightarrow \text{Ph—C}^-\text{DCH}_3\ \ HOD \quad (13)$$
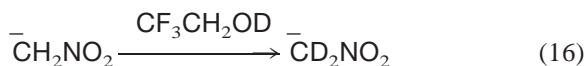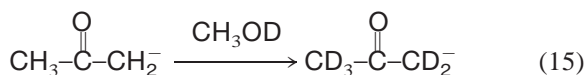
thus allowing the two isobaric ions to be distinguished. By an analogous mechanism, double bond isomerization can occur in the course of H/D exchange. For example in the anion derived from 1-pentene, all seven hydrogens exchange for deuterium. In the process of exchange the double bond migrates along the carbon skeleton so that eventually each hydrogen becomes allylic and hence exchangeable. The isomerization process is shown in Eq. (14).
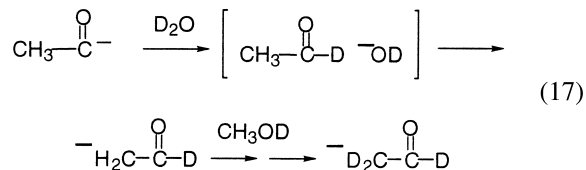
$$(14)$$
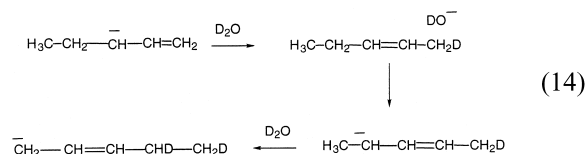
Vinylic hydrogens are too weakly acidic to exchange so that the allyl anion only exchanges four hydrogens since the central hydrogen can never become allylic.

The energy required to fuel the initial endothermic proton transfer comes from the complexation energy of the two species. If the endothermicity is too great, no exchange will occur. Acetone is 22 kcal/mol more acidic than water; this endothermicity exceeds the approximately 15 kcal/mol complexation energy between the acetone enolate and D_2O, and so no exchange is observed. However the enolate does exchange all five of its hydrogens for deuterium if CH_3OD is used as the exchange reagent, since acetone is only 11 kcal/mol more acidic than methanol. Deuterated methanol, in turn, will not exchange with the nitromethyl anion (difference in acidity 24 kcal/mol) but CF_3CH_2OD (4 kcal/mol difference in acidity) will exchange both hydrogens. Both the number of hydrogens which exchange and the exchange reagent which brings about exchange give valuable clues to the structure of an ion.

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2^- \xrightarrow{\ CH_3OD\ } CD_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CD_2^- \qquad (15)$$

$$\overset{-}{C}H_2NO_2 \xrightarrow{\ CF_3CH_2OD\ } \overset{-}{C}D_2NO_2 \qquad (16)$$

These energetics can be combined in revealing and informative ways. For example the acyl anion [Eq. (2)] exchanges a single proton with D_2O. A deuteron is added to the strongly basic acyl carbon and a proton is then abstracted from the acidic methyl group. Exchange then stops. If deuterated methanol is next added, further exchange takes place.

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-} \xrightarrow{\ D_2O\ } \left[CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}D \ \ ^-OD \right] \longrightarrow$$

$$\overset{-}{}H_2C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}D \xrightarrow{\ CH_3OD\ } \overset{-}{}D_2C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}D \qquad (17)$$

By analogous steps anions derived by proton abstraction from compounds with separated double bonds can be brought into conjugation by allowing them to react with H_2O, at which point exchange with D_2O stops [18]. An estimate of the degree of separation of the original double bonds can be made from the number of deuteriums incorporated with D_2O. Further H/D exchange can then be induced, and further structural information obtained, by exchange with CH_3OD. Indeed the very act of abstracting a proton by HO^- or DO^- can lead to partial or complete isomerization of a double bond because of multiple proton transfer reactions within the initially formed long-lived ion–dipole complex [17]. This is further evidence for the usefulness of the TMS/F^- method for forming anions if their structural integrity is important, for rearrangements during their formation do not occur in this reaction.

If D_2O can exchange its deuterons with an ion which is 15 kcal/mol less basic than DO^-, a hydrocarbon, RH, which is as much as 15 kcal/mol less acidic than D_2O should exchange with DO^-. Indeed benzene, which is 11 kcal/mol less acidic than water, will rapidly convert DO^- to HO^- by the same steps as those by which the benzyl anion exchanges with D_2O [19].

$$C_6H_6 + DO^- \longrightarrow C_6H_5D + HO^- \qquad (18)$$
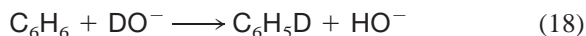
This reaction is obviously not useful in determining ion structure since the charge remains on the wrong moiety, but it can be combined with the previous examples in the following way. Suppose we begin with the phenyl cyclopropyl anion and allow it to react with D_2O. Since the benzylic carbon carries no hydrogen atoms, no exchange would be expected, yet the anion exchanges five hydrogens for deuterium [20]! The mechanism for this at first sight surprising exchange is shown in Eq. (19).

The initial deuteron transfer to the cyclopropyl carbon is only slightly endothermic, so that nearly the entire 15 kcal/mol complexation energy remains within the complex. This is sufficient for the DO^- to exchange its deuterium for hydrogen on the benzene ring in analogy with Eq. (18). It then regains its initial energy by abstracting the benzyl deuterium that was initially transferred. Further reactions with D_2O exchange the remaining aryl hydrogens. The cyclopropyl hydrogens do not exchange because they are too weakly acidic. An analogous exchange of aryl hydrogens cannot occur in the benzyl anion because the initial 10

(19)
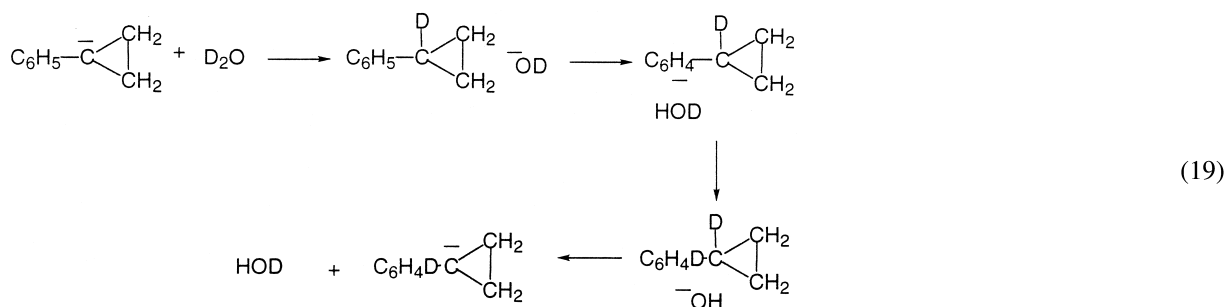
kcal/mol endothermic deuteron transfer reaction leaves only 5 kcal/mol in the complex, insufficient energy to fuel the second, 11 kcal/mol endothermic proton transfer needed for exchange of the ring protons.

Alcohol exchange reagents cannot induce this "extraordinary" exchange because they bring only a single deuterium into the complex. This difference between the two reagents is best illustrated for anions which have proton affinities between approximately 380 and 376 kcal/mol since they can exchange with both D_2O (391) and CH_3OD (381). An example is the anion from *o*-difluorobenzene. D_2O exchanges all three hydrogens, while CH_3OD exchanges only one [21, 22] [Eq. (20)]

(20)
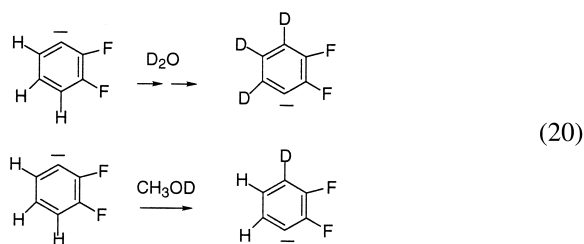
There are a number of molecules other than D_2O that have come to be used as diagnostic reagents because of their characteristic reactions with organic anions. Reactions that lead to fragmentation of the anion are particularly informative, since they help to locate the position of the reactive center within the molecule. One such cleavage reaction is that between allenyl anions or their analogs and carbon disulfide or carbon oxysulfide [23]
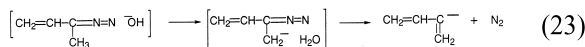
$$H_2C=C=\overline{C}H \xrightarrow{CS_2} H_2C=C=S + H\overline{C}=C=S \quad (21)$$
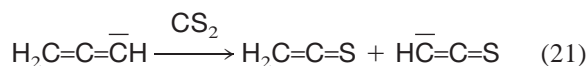
Other anions with cumulative double bonds (e.g. ketenyl) undergo the same type of reaction [24], which proceeds by initial addition followed by cyclization through a four-membered ring containing sulfur, followed by fragmentation. With non-allenic anions sulfur atom transfer is commonly observed with both CS_2 and COS [25]. Nitrous oxide, N_2O, is by far the most versatile reagent used to probe ion structure [26]. Depending upon the structure of the anion with which it reacts, N_2O can transfer N, N_2, NO, or O, oxidize the anion by removing two hydrogen atoms or give rise to even more bizarre reaction products. For example, if the anionic carbon center is primary (e.g. in the allyl anion) a diazo anion results

(22)
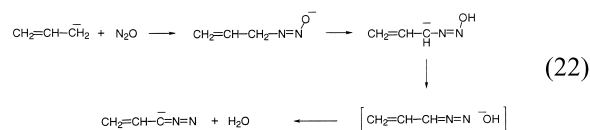
if it is secondary oxidation is common, and if it has no hydrogens on the carbanionic carbon addition of an oxygen atom to form an alkoxide ion may occur. The diazotransfer reaction is typical of condensation reactions in general in the gas phase. Addition of the anion to the terminal nitrogen occurs followed by intramolecular proton transfer and loss of hydroxide ion. Although the reaction is sufficiently exothermic to allow dissociation to HO^- and the neutral diazo compound, the ion–dipole complex has a sufficient lifetime to allow the hydroxide ion to find an acidic

proton and abstract it, leaving the anionic center on the organic molecule. If the diazo compound has no hydrogen on the diazocarbon, beta elimination of N_2 occurs to form a vinyl anion. This is a good gas phase synthetic method for the preparation of vinyl anions, which can be difficult to form by other methods because of their great basicity [27,28]

$$\left[CH_2=CH-C\overset{\underset{\textstyle CH_3}{|}}{=}N=N \;\; \bar{O}H \right] \longrightarrow \left[CH_2=CH-C\overset{\underset{\textstyle CH_2^-}{|}}{=}N=N \;\; H_2O \right] \longrightarrow CH_2=CH-C\overset{\underset{\textstyle CH_2}{||}}{}^- \; + \; N_2 \qquad (23)$$

Perfluorobenzene and perfluoropropylene are also useful reagents for probing the structure of anions and for determining the site of reaction of ambient anions [29]. In particular, when the acetone enolate is allowed to react with C_6F_6, perfluorophenoxide ion results from attack of the oxygen atom, while a condensation product results from carbon attack. Since m/z is different for these two product ions, the relative amount of reaction at oxygen versus that at carbon can be determined.

8. S_N2 and E2 reactions

By far the best studied gas phase anion reaction mechanisms are those of nucleophilic substitution (S_N2) and elimination (E2), two reactions which have also been widely investigated in solution so that comparisons between the two phases can be made. The S_N2 reaction was first studied in the gas phase by Bohme and Young [30]. It is a classic example of the double well potential model developed by Olmstead and Brauman [3] for ion–molecule reactions in general and S_N2 reactions in particular. In Fig. 2 we show an energy diagram for the reaction of chloride ion with methyl bromide as determined by McMahon and co-workers [4]. The initial ion–dipole complex has a lifetime of approximately 10^{-12} s during which it can either dissociate to reactants or cross the S_N2 barrier to a second ion–dipole complex, that between Br^- and methyl chloride. This second complex is more weakly bound (10.9 kcal/mol) and in addition it contains the reaction exothermicity of 6.7 kcal/mol. Dissociation of this complex leads to the products. It
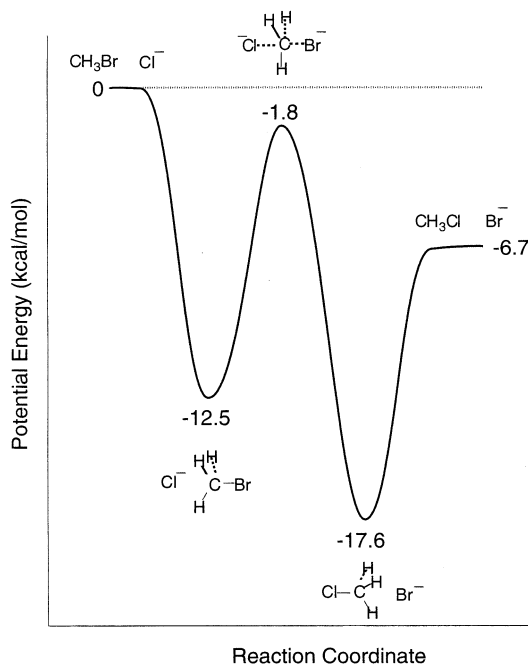

Fig. 2. Potential energy diagram for the reaction of chloride ion with methyl bromide. The data are from [4].

is important to note that the total energy of the system remains constant, since no energy is removed during the reaction; the graph represents the equilibrium energy of the various structures. However the individual complexes can be prepared separately if we bring into the reaction a third body which can be lost to remove energy. In the Riveros reaction [Eq. (5)] this third body was carbon monoxide, brought in by the neutral formate ester. In the S_N2 reaction it is commonly brought in complexed to the anion. For example SO_2Cl_2 is ionized to produce SO_2Cl^- which, when allowed to react with methyl bromide, forms the initial complex with loss of SO_2. The cooled complex is then sufficiently long-lived to be brought to room temperature by collisions with the bath gas. This complex has been shown spectroscopically to have the chloride ion tucked neatly at the rear of the carbon–bromine bond [31]. When prepared in this way, the chloride–methyl bromide and bromide–methyl chloride complexes do not interconvert.

A typical ion–molecule reaction that proceeds at a rate which is slower than the collision rate will have

an energy profile in which the energy at the barrier is above the lowest energy of the reactants. Since the reagents have a room temperature distribution of energies, some will have sufficient energy to cross the barrier, while others will not. A striking feature of the chloride ion-methyl bromide S_N2 reaction illustrated in Fig. 2 is that, whereas the barrier for the S_N2 reaction is nearly 2 kcal/mol below the energy of the reactants, the overall reaction is still slow. Only slightly over 1 in 50 encounters between chloride ion and methyl bromide actually lead to S_N2 products. Results like these show that the entropy of the reaction as well as the enthalpy contributes to the overall rate. To understand this, consider the complex as it is formed in the reaction as a highly excited molecule that has sufficient energy either to cross the S_N2 barrier or to dissociate to reactants. The S_N2 transition state is highly structured, with tight constraints on the position of the atoms. In contrast there are few such constraints on dissociation. Consequently dissociation is highly favored entropically over reaction across the barrier, with the transition state entropy acting as a bottleneck along the S_N2 pathway. As the energy of the transition state is lowered relative to the energy of the reactants, the transition state become less of a bottleneck and it is easier to cross the barrier, whereas the dissociation rate remains unaffected, and the S_N2 reaction speeds up. One way to lower the barrier is to increase the exothermicity of the reaction, for example by starting with a stronger base. The dissociation rate is not much affected but lowering the energy of the products pulls down the transition state energy and the reaction goes faster. Increasing the steric hindrance of the neutral halide raises the central barrier without necessarily changing the reaction exothermicity. For the reaction of chloride ion with isopropyl bromide the barrier is 2.9 kcal/mol above the energy of the reactants while the exothermicity of the reaction remains essentially unchanged; reaction is very slow and is seen only at high temperature.

For any given alkyl halide there are only a few nucleophiles that react at a slow but measurable rate at room temperature. Thus to study the effect of structure on the rates of the S_N2 reaction one must vary the nucleophile, the substrate and the leaving group in order to find just those combinations which react more slowly than the collision rate but fast enough to be measured [32]. For example HO^- reacts at the collision rate with methyl bromide and chloride, but in only 1 out of 250 collisions with methyl fluoride. From this one can conclude that fluoride is a poorer leaving group than bromide and chloride, but nothing about the relative reactivity of the latter two. To make that comparison one must use a less basic ion, e.g. $CF_3CH_2O^-$, which reacts rapidly with methyl bromide but slowly with methyl chloride and not at all with methyl fluoride. Thus the leaving abilities of the halides are $Br > Cl > F$, as they are in solution. More strongly basic anions react more rapidly with a given alkyl halide, as they usually do in solution, and there is a good correlation between basicity and nucleophilicity in both media. One major difference among nucleophiles in the gas phase and in solution is that of sulfur-containing anions. Sulfur anions are enormously more reactive in solution than would be predicted from their basicity. This is not the case in the gas phase, where their rates are comparable to those of oxy anions of the same basicity. The effect of methyl substitution on S_N2 reaction rates in the gas phase is also the same as that in solution [4,32]. Inverse deuterium isotope effects analogous to those in solution have also been observed for S_N2 reactions of methyl halides in the gas phase [33]. For example CD_3Cl reacts faster than CH_3Cl with fluoride ion.

Bimolecular elimination (E2) reactions are even more difficult to study in the gas phase than substitution reactions because the stereo- and regiochemistry of E2 reactions, which are of primary interest to mechanistic chemists, are usually hidden in the neutral product. Indeed for alkyl halides reacting with most nucleophiles, it is difficult to determine whether substitution or elimination occurs, since the ionic product of the reaction is the same in either case

$$(CH_3)_2CHBr \xrightarrow{\ Nu\ } \begin{array}{l} (CH_3)_2CHNu + Br^- \\ \\ CH_2=CHCH_3 + Br^- + NuH \end{array} \qquad (24)$$
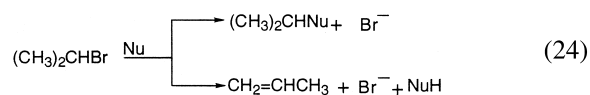
Some qualitative information can be obtained by rate measurements. For instance, isopropyl chloride reacts faster than methyl chloride with a strong base that is capable of inducing elimination, but slower with a base so weak that elimination is endothermic. The simplest explanation is that elimination and substitution compete in the former case while only substitution occurs in the latter. Definite proof of the occurrence of elimination in the gas phase reaction of an alkyl halide was obtained by the isolation of propylene when methoxide ion is allowed to react with *n*-propyl bromide in a FA equipped with a cold finger to trap the neutral products [34]. However, this has not proved to be a method of general utility because of the exceedingly small amounts of neutrals produced in the reactions and the sensitivity of the method to traces of impurities. More fruitful approaches involve elimination reactions designed so that the olefins formed in the reaction are incorporated into an anionic product and can be detected. For example, when the methyl ether shown in Eq. (25)

(25)
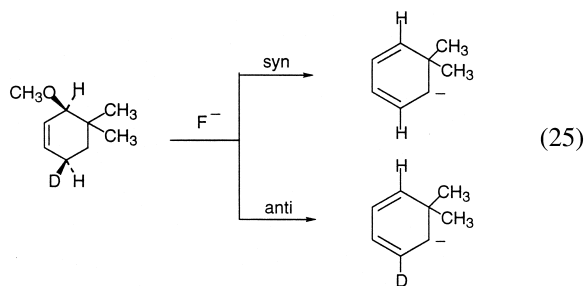
is allowed to react with fluoride ion in the FA, an elimination reaction occurs to produce HF, methoxide ion, and dimethylcyclohexadiene in a product ion–molecule complex. Before leaving the complex the methoxide ion abstracts a proton from the diene, which is more acidic than methanol, thus leaving the isotopic label in the ion. The predominant syn stereochemistry of the elimination can then be detected because the two product ions have different masses [Eq. (25)] [35].

Another strategy to distinguish E2 from S_N2 reactions is to use as the nucleophile a dianion containing one highly reactive and one unreactive site [36], as in

Eq. (26). Such a dianion may be formed by electrospray ionization and was allowed to react with a series of alkyl halides; the S_N2 and E2 product ions differ in mass and the $E2/S_N2$ ratio can be determined. For ethyl bromide this ratio is 1:10, for isopropyl bromide 5:1 and for *t*-butyl bromide >200:1, quite analogous to the trend found in solution

Primary deuterium isotope effects have also been detected in gas phase elimination reactions [37–39].
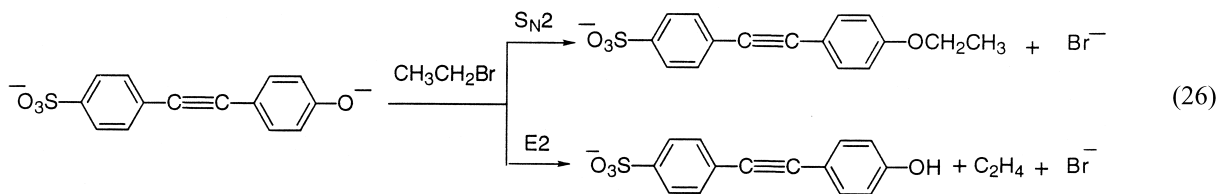
9. Other common reactions

Virtually any reaction of anions that occurs in solution can also be carried out in the gas phase. Oxidation [40] and reduction [40,41] (including stereochemistry [42]), condensation [43], polymerization [44], and ester hydrolysis [45] have all been observed. However, simple addition of an anion to a neutral is usually not observed experimentally at the pressures of the FA or ICR, since the energy generated in the addition cannot be dissipated, and if no further fragmentation occurs the adduct reverts to reactants. As a simple example, O^- appears not to react with CO_2 in the gas phase, but rapid oxygen exchange is observed if $^{18}O^-$ is used as the reactant ion [46]

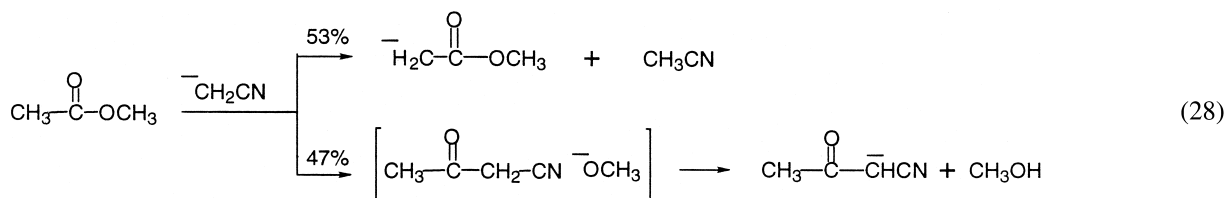$$O^- + CO_2 \rightleftharpoons CO_3^- \qquad (27)$$

At sufficiently high pressure CO_3^- is produced by collisions with buffer gas.

Other typical addition-elimination reactions of carbonyl compounds are observed in the gas phase, but they are often obscured by fast competing proton transfer reactions, for example by the Riveros reaction [Eq. (5)] with formate esters or by formation of the enolate anion with esters containing alpha hydrogens. S_N2 and E2 reactions can also be competitive with carbonyl addition [45]. Frink and Hadad 47] have studied, experimentally and computationally, the reactions of formate and acetate esters with a series of bases and have given a good literature survey of the field. When methyl acetate, for example, is allowed to react with methoxide ion only proton transfer is observed. But when the conjugate base of acetonitrile is the reactant, proton transfer and addition-elimina-
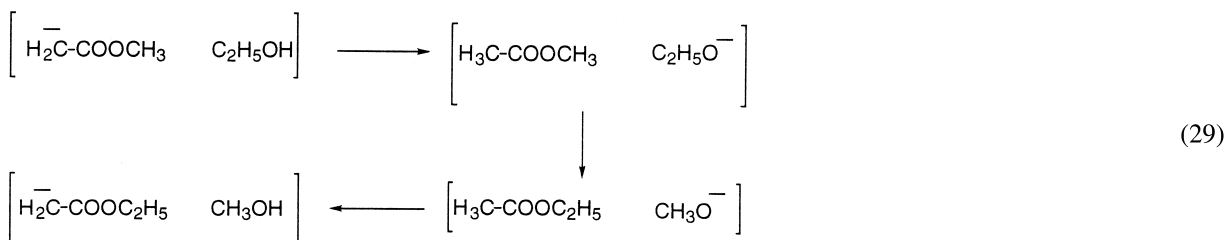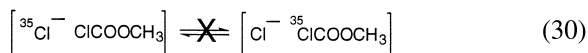
$$\overline{O}_3S\text{—}C_6H_4\text{—}C\equiv C\text{—}C_6H_4\text{—}O^- \xrightarrow[\text{E2}]{\overset{\text{S}_N2}{\text{CH}_3\text{CH}_2\text{Br}}} \begin{cases} {}^-O_3S\text{—}C_6H_4\text{—}C\equiv C\text{—}C_6H_4\text{—}OCH_2CH_3 + Br^- \\ {}^-O_3S\text{—}C_6H_4\text{—}C\equiv C\text{—}C_6H_4\text{—}OH + C_2H_4 + Br^- \end{cases} \quad (26)$$

tion followed by proton transfer are observed in comparable amounts.

$$CH_3\text{—}CO\text{—}OCH_3 \xrightarrow{{}^-CH_2CN} \begin{cases} 53\% \quad {}^-H_2C\text{—}CO\text{—}OCH_3 + CH_3CN \\ 47\% \quad [CH_3\text{—}CO\text{—}CH_2\text{—}CN\ {}^-OCH_3] \longrightarrow CH_3\text{—}CO\text{—}\overline{C}HCN + CH_3OH \end{cases} \quad (28)$$

The cyanomethyl anion is a relatively weak base and one for which proton transfer is expected to be slow because it must occur between two carbon atoms. Hence carbonyl addition can compete with proton abstraction. How, then, can one study ester interchange between methyl acetate and ethoxide ion? By starting, not with the ester and alkoxide, but with the enolate ion and ethanol [48].

energy can be investigated. A fundamental question in the reactions of carbonyl groups is whether an adduct with a tetrahedral carbon is an intermediate or a transition state in any particular reaction. For the case of isotopically labeled chloride ion reacting with an acid chloride shown in Eq. (30).

$$[{}^{35}Cl^-\ ClCOOCH_3] \xcancel{=} [Cl^-\ {}^{35}ClCOOCH_3] \quad (30)$$

$$\begin{array}{ccc} [H_2\overline{C}\text{-COOCH}_3 \quad C_2H_5OH] & \longrightarrow & [H_3C\text{-COOCH}_3 \quad C_2H_5O^-] \\ & & \downarrow \\ [H_2\overline{C}\text{-COOC}_2H_5 \quad CH_3OH] & \longleftarrow & [H_3C\text{-COOC}_2H_5 \quad CH_3O^-] \end{array} \quad (29)$$

After entering an ion–dipole complex an endothermic proton transfer occurs, as in the H/D exchange reaction, and indeed exchange is observed if a deuterated alcohol is used. The complex is cooled by this endothermic reaction. Then ester interchange takes place by the usual mechanism of attack of the ethoxide ion on the carbonyl group. Finally an enolate is reformed by proton abstraction. In this way, reactions with activation energies less than the complexation

Brauman and co-worker have shown that two distinct, non-interconverting ion–dipole complexes separated by a barrier exist on the reaction surface, analogous to results for the S_N2 reaction [49]. These results preclude a single well potential surface in which a tetrahedral adduct is formed directly without a barrier. However, with more basic anions it seems likely that an adduct is formed as an intermediate and exists in a potential minimum. Brauman and co-workers have

shown that a cyclic hemiacetal anion is favored over the open-chain isomer [50], and Nibbering has presented evidence that a methoxide–benzaldehyde adduct is favored over an ion–dipole complex [51]

$$\text{(31)}$$
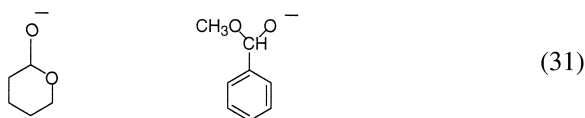
10. Unusual gas phase anions

One of the most exciting aspects of gas phase anion chemistry lies in its ability to generate new, unknown ions which have little or no precedence in solution, and to study their chemistry. Considering how closely gas phase ion chemistry parallels that in solution, one can feel relatively confident that these ions would react analogously were they to be formed in solution. For example Nibbering and co-worker [52] applied the Riveros reaction to the preparation of the previously unknown ion H_3O^- as shown in

$$HO^- + H\overset{O}{\overset{\|}{C}}H \longrightarrow H_2O + H\overline{C}O \longrightarrow H_3\overline{O} + CO \tag{32}$$
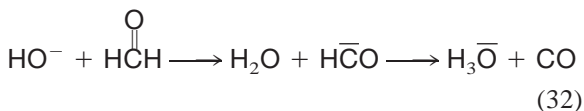
The atomic oxygen radical anion is especially useful as a reagent for generating new anionic species because of its ability to oxidize neutrals by abstraction of the elements of H_2^+ [Eq. (3)]. It reacts with benzene to abstract hydrogens from adjacent carbons to form the radical anion of benzyne [53]
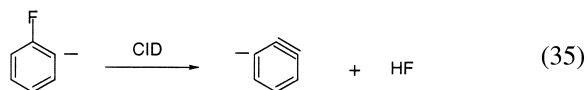
$$\text{(33)}$$
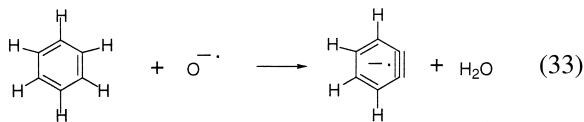
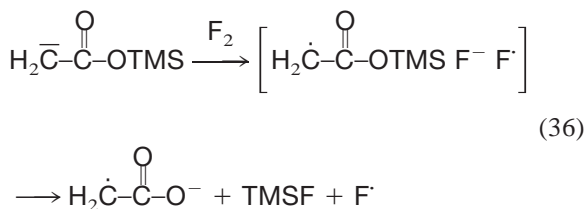and analogously with many other hydrocarbons.

The first example of a cyclopropenyl anion has been found in the gas phase [54]

$$\text{(34)}$$
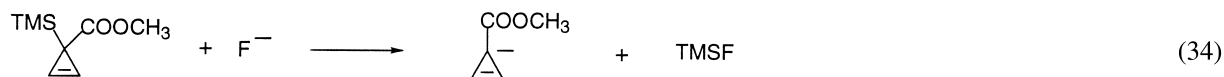
whereas collision-induced dissociation has been used to generate otherwise unknown anions, for example the ion, $C_6H_3^-$, which would result from proton abstraction from benzyne [55]

$$\xrightarrow{\text{CID}} \quad + \quad HF \tag{35}$$

Squires [56] has developed an ingenious method for the preparation of distonic radical anions, ions in which the charge and the radical are on different atoms. The method involves the reaction of an anion with F_2; electron transfer occurs to form F^-, which generates the radical anion by desilylation

$$H_2\overset{O}{\overset{\|}{\overline{C}}}-\overset{O}{\overset{\|}{C}}-OTMS \xrightarrow{F_2} \left[H_2\overset{O}{\overset{\|}{\dot{C}}}-\overset{O}{\overset{\|}{C}}-OTMS \; F^- \; F^\cdot \right] \tag{36}$$

$$\longrightarrow H_2\dot{C}-\overset{O}{\overset{\|}{C}}-O^- + TMSF + F^\cdot$$

These ions undergo reactions characteristic of both anions and radicals. The method is very powerful. For example one can begin with a di-TMS derivative and generate the radical anion directly. Diradical anions also have been formed from tri-TMS derivatives as shown in [57]

$$\xrightarrow{F^-/F_2} \quad \tag{37}$$
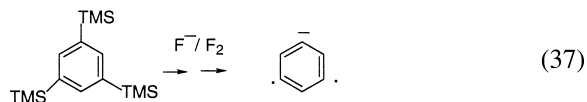
11. Rearrangements of anions

Simple 1,2 rearrangements, which are so common in cations, seldom occur in anions. This difference is readily accounted for by the Woodward Hoffmann rules. In cations the cyclic three-membered transition state for a 1,2 rearrangement contains only the two

electrons of the migrating group; such a transition state is "aromatic" in the sense that it obeys the $4n + 2$ rule for cyclic aromatic systems with $n = 0$. In the case of anions the corresponding transition state contains four electrons and is "antiaromatic"; two of the electrons must go into antibonding orbitals, and hence the barrier to rearrangement is large. At sufficiently high temperatures, however, anions do undergo rearrangements. For example the ring-opening reaction of the phenyl cyclopropyl anion to the 2-phenylallyl anion has been studied in a variable temperature flowing afterglow apparatus at 200 °C by Kass and co-workers and shown to have an activation energy of 26 kcal/mol [58]. In contrast Bartmess and co-workers have shown that the oxy-Cope rearrangement shown in

$$ \text{(38)} $$
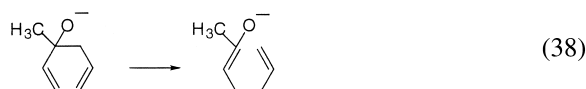
proceeds rapidly at room temperature [59]. In this case the reaction occurs by way of a six-membered cyclic transition state containing an aromatic sextet of electrons. The reactant and the product ions can be distinguished by H/D exchange since the product ion exchanges four hydrogens when allowed to react with CH_3OD, while the alkoxide ion does not exchange under the same conditions.

12. Spectroscopy of gas phase ions

It is difficult experimentally to carry out spectroscopy on gas phase ions because the maximum concentration of such species that can be obtained is so low. Nevertheless, by working in plasmas Saykally and co-workers [60] have obtained infrared spectra of some simple anions, including the azide ion N_3^-. Closed shell anions, like most of those we have been discussing in this review, seldom have bound electronic excited states, so that excitation in the visible and ultraviolet region of the spectrum leads only to electron detachment. However when an anion is
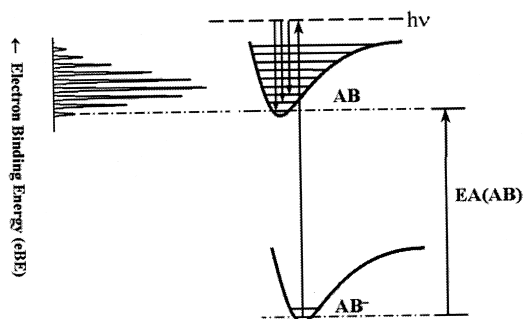

Fig. 3. Photoelectron spectroscopy. See text for discussion.

clustered to one or more neutral molecules the ejected electron may be trapped in a bound dipole state, giving rise to reasonably sharp peaks [61].

Among the most useful chemical information obtained spectroscopically with anions is that from photoelectron spectroscopy (PES) [62]. In these experiments a beam of anions, usually produced in a flowing afterglow ion source to insure that the anions are at room temperature, is crossed with a fixed wavelength laser whose photons have sufficient energy to detach an electron. The detached electrons are collected and separated in an energy analyzer, giving rise to a photoelectron spectrum. The process is illustrated in Fig 3. Note from this figure that the anion is in its ground vibrational state and that the energy of the electron that is ejected depends upon the vibrational state of the neutral molecule which is formed. Thus PES gives mostly information about the neutral product of the detachment rather than about the anion itself. In particular the energy of the peak in the spectrum corresponding to a transition from the ground state of the anion to the ground state of the neutral is the electron affinity of the neutral, and this energy can be measured with great accuracy. The relative intensities of the peaks in the photoelectron spectrum are a measure of the similarity in structure of the anion and the neutral molecule. If they have very similar structures, the anion curve will lie directly under that of the neutral, and detachment will take place to give mainly the ground state of the neutral. In the spectrum which is generated, most of the intensity will be concentrated in the first peak. In the example shown in Fig 3, the two structures differ

enough so that detachment takes place mostly to form excited vibrational states of the neutral.

The combination of gas phase anion chemistry and photoelectron spectroscopy has been developed into an extremely useful method for the determination of bond dissociation energies. We showed in Eq. (11) how the ΔH_{acid} of a molecule RH can be calculated from the EA of R, the BDE of RH, and the IP of the hydrogen atom. Of these four quantities the BDE is usually the most difficult to determine accurately. Therefore if one knows the EA (from PES) and ΔH_{acid} (from ion chemistry) these values can be combined with the IP of hydrogen to obtain the CH bond dissociation energy [63].

Under favorable circumstances PES can also be used to obtain a spectrum of a transition state, a species ordinarily present in too low a concentration to be observed. For example consider the ring inversion of cyclooctatetraene, which is presumed to proceed by way of a planar transition state [64] [Eq. (39)].

(39)
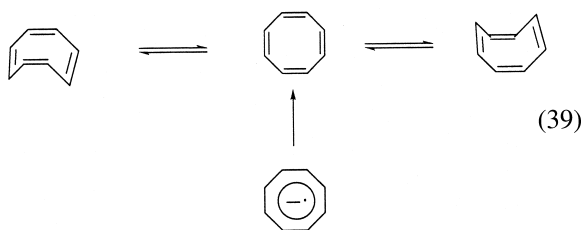
Molecular orbital calculations predict that the radical anion of cyclooctatetraene, which can be obtained by electron attachment to the neutral in a FA source, is also planar. Thus photodetachment of this anion gives structural information about the neutral transition state.

Photoelectron spectroscopy of anions can also give an accurate measure of the difference in energy between the singlet and triplet state of a neutral. This is most easily seen in a simple ion like CH_2^-, where the detaching electron can come from either of two orbitals [Eq. (40)].

to form either neutral singlet methylene or neutral triplet methylene [65]. Two sets of peaks, one for the

(40)
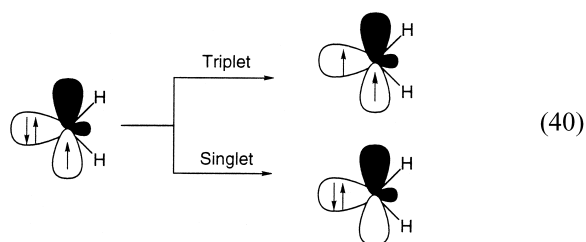
singlet and one for the triplet, are seen, with the difference in electron affinity of the two neutrals giving the energy separation between the two electronic states.

13. Naturally occurring gas phase anions

Anions are relatively fragile species because they can easily lose an electron. As a consequence, they do not occur naturally to the extent that cations do. Yet they do play key roles under certain circumstances. For example H^- is thought to be formed transiently in the photosphere of the sun and affects its opacity [66]. The chemistry of interstellar space is predominantly that of cation reactions, and it has been thought that anions will be detached by radiation. Recently, however, it has been proposed that the ions C_6^-, C_7^-, and C_8^- may be present in space [67]. What role, if any, they may play in the ion chemistry of the interstellar medium remains to be seen.

Anions are also present in the earth's atmosphere [68]. Their primary source is from attachment of electrons to the oxygen molecule [Eq. (41)].

$$e + O_2 \xrightarrow{\text{M}} O_2^{-\cdot} \qquad (41)$$

This attachment requires a third body to remove energy, so that O_2^- only becomes important below 70–80 km where the pressure is sufficiently high. Another, much smaller, source of negative ions is from dissociative attachment to ozone, which also occurs at relatively low altitudes where the ozone concentration builds up

$$e + O_3 \rightarrow O_2^{-\cdot} + O \qquad (42)$$

These anions eventually react to form NO_3^-, HSO_4^-, and other stable ions and their hydrates, and at low altitudes nitrate anions clustered to nitric acid predominate.

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