

## Negative Ions

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## Negative ions

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During the last few years, improvements in ionization techniques have revived interest in negative ion mass spectrometry and its applications. Ion sources that operate at pressures of up to 1 Torr (133 Pa) produce high concentrations of low energy electrons which may react directly with suitable sample molecules to form negative molecular and fragment ions. Alternatively, a reagent gas may be used to generate negative chemical ionization mass spectra which, in general, exhibit less fragmentation than many positive chemical ionization mass spectra. The sensitivity of the electron attachment processes may be very high for compounds containing electronegative elements and it may be enhanced for other compounds by making use of fluorinated derivatives. Under chemical ionization conditions, reagent ions which react as Brønsted bases frequently give  $[M-H]^-$  ions in great abundance. Use of selected ion monitoring leads to sub-picogram detection levels in favourable cases. The gas phase ion chemistries of such ions as  $O^-$  and  $O_2^-$  exhibit several unusual types of reaction which reveal further structural and mechanistic information, examples of which are discussed.

### INTRODUCTION

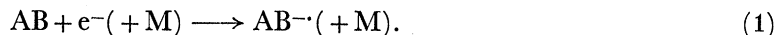
For many years, little use was made of negative ion mass spectrometry for the investigation of structural and analytical problems and our knowledge of the mechanisms of negative ion reactions in the gas phase was very limited. This neglect of negative ions could be attributed to several factors associated with irreproducibility, low sensitivity and inappropriate instrumentation. The production of negative ions from a given sample is usually dependent both on the electron energy and the ion source temperature; slight variations in either of these parameters can lead to marked changes both in the total number of negative ions formed and in the relative abundances of ions given by the sample. A further problem until quite recently was that most commercial mass spectrometers could not readily be operated in the negative ion mode. At the electron energies normally employed to obtain positive ion spectra, the sensitivity for the production of negative ions is two or three orders of magnitude less than that for positive ion production. However, in many instruments, modifications to the electron multiplier electronics are necessary if any negative ions are to be detected.

The introduction of alternative methods of ionization, in particular chemical ionization (Field 1973), revived interest in negative ions, and electron capture spectra and negative chemical ionization spectra are proving increasingly useful in a wide variety of applications (Jennings 1977). Concurrently, a growing body of information on the thermodynamics, kinetics and mechanisms of negative ion reactions is being built up from results obtained by the use of techniques such as high pressure source mass spectrometry, ion cyclotron resonance spectrometry and the flowing afterglow and related techniques. This paper aims to give a brief survey of our current state of knowledge of negative ion gas phase chemistry and its applications.

## THE PRODUCTION OF NEGATIVE IONS

Primary negative ions are produced by one of three general processes:

(i) Resonance capture or three-body attachment:



At low pressures this is a bimolecular process that occurs only over a very narrow range of electron energies, provided AB has a positive electron affinity. In the presence of a third body at higher pressures it may become an important process for electrons having energies within the range 0–10 eV.

(ii) Dissociative resonance capture:



If no stable molecular anion is formed, a fragment ion may be formed if the neutral fragment has a positive electron affinity; this process is often important at low pressures for electrons having energies within the range 0–15 eV.

(iii) Ion pair production:



This differs from the above two processes in that it is a non-resonant process that can occur with electrons having a wide range of energies above about 10 eV. It is the only process that can occur at 70 eV but processes (i) and (ii) may occur if secondary electrons of appropriate energies are formed either at metal surfaces or by collision with a buffer gas (Dougherty & Weisenberger 1968).

## NEGATIVE CHEMICAL IONIZATION MASS SPECTROMETRY

Chemical ionization mass spectrometry is normally carried out in an ion source capable of operating at a pressure of about 1 Torr (133 Pa) in which reagent ions produced by electron impact from a suitable reagent gas react with a much lower partial pressure of sample molecules. Positive chemical ionization mass spectrometry is based largely on the gas phase ion chemistry of Brønsted acids, several of which are commonly used as reagent ions. Over the last few years, it has been shown in several laboratories that at source pressures of about 1 Torr, sufficient electrons of appropriate energies are produced to give high yields of negative ions if suitable reagent gases are used (Dougherty *et al.* 1975; Smit & Field 1977; Harrison & Jennings 1976; Hunt *et al.* 1976). The advantages of positive chemical ionization mass spectrometry are retained in that a range of reagent gases can be used to produce specific reagent ions, many of which react as Brønsted bases. Alternatively, the reagent gas can act as a buffer gas, leading to electron attachment mass spectra of samples that contain electronegative elements. In favourable cases, the sensitivity attainable with electron attachment mass spectrometry is two or three orders of magnitude greater than that obtainable by using positive ion electron impact or either positive or negative chemical ionization mass spectrometry.

Reagent ions that react as Brønsted bases abstract a proton from a sample molecule:

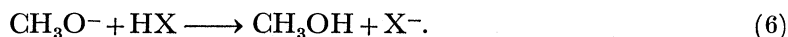


Much of the exothermicity of this type of reaction frequently appears as vibrational energy

of the newly formed bond, i.e. in the neutral product HB, so that fragmentation of the newly formed ion,  $A^-$ , is often very limited. Reagent ions of this type are therefore particularly suitable for single ion monitoring of traces of substances in mixtures.

Nitrogen, methane and isobutane have been used as buffer gases in the production of electron capture spectra. True negative chemical ionization spectra can be produced by using hydrogen as the reagent gas; this gives  $H^-$  ions at electron energies of about 3 eV in a dissociative electron capture process and at energies above 15 eV by ion pair formation. Because of its very high proton affinity,  $H^-$  reacts as a strong Brønsted base. At electron energies of about 6.5 eV, water gives  $H^-$  ions which react further to give  $OH^-$  ions. The  $OH^-$  ion is also a strong Brønsted base but its production in this reaction is not very convenient because of interference from hydrated ions. Alcohols give low yields of  $RO^-$  (alkoxide) ions but the yield can be increased considerably by adding a trace of water when  $RO^-$  ions are formed in proton abstraction reactions of  $OH^-$  ions. Interpretation of results is again complicated by the presence of solvated ions, however.

A general method of producing Brønsted bases as reagent ions makes use of a reagent gas mixture consisting of  $CH_4$  containing 1%  $CH_3ONO$  and 5% HX (where HX =  $(CH_3)_2CO$ ,  $C_2H_2$ ,  $CH_3NO_2$ , RSH,  $c-C_5H_6$ , etc.) (Hunt *et al.* 1976). The methane acts as a buffer gas to produce electrons of energies suitable for initiating the reaction sequence



In practice, HX is added to the reagent gas mixture until the signal for the  $m/z = 31$  ion just disappears. This method can in principle be used to produce Brønsted bases having proton affinities less than that of the  $CH_3O^-$  ion, 1577 kJ mol<sup>-1</sup>. A few representative proton affinities (in kilojoules per mole) are as follows:

|       |        |           |          |        |             |               |
|-------|--------|-----------|----------|--------|-------------|---------------|
| $H^-$ | $OH^-$ | $CH_3O^-$ | $C_2H^-$ | $SH^-$ | $CH_3COO^-$ | $C_6H_5COO^-$ |
| 1673  | 1632   | 1577      | 1561     | 1468   | 1443        | 1406          |

Several laboratories have reported spectra obtained by the use of  $O_2^-$  as the reagent ion. Since filament life is very short in the presence of high partial pressures of oxygen, the  $O_2^-$  has been generated by using mixtures of reagent gases or by using other sources of electrons. Nitrogen containing 10%  $N_2O$  and a small percentage of oxygen gives  $O_2^-$  as the major ion and similar results are obtained by using a mixture of hydrogen and oxygen (R. K. Mitchum, A. J. V. Ferrer Correia, A. G. Harrison & K. R. Jennings 1978, unpublished). Alternatively, they may be produced by passing oxygen through a Townsend discharge (Hunt *et al.* 1975) or in an atmospheric pressure ionization instrument by means of radiation from a <sup>63</sup>Ni foil or a corona discharge (Dzidic *et al.* 1974). In the latter instrument,  $O_2^-$  is the major ion given by a reagent gas of nitrogen containing 1.5% oxygen at 100 °C.

Nitrous oxide is a useful reagent gas that forms the  $O^-$  ion by dissociative electron capture:

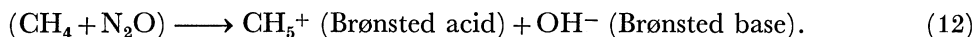
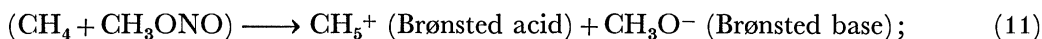
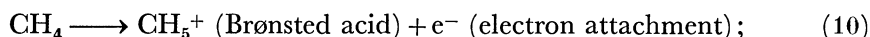
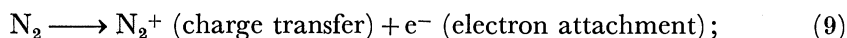


The subsequent reaction to form  $NO^-$  can be largely suppressed by using an  $N_2-N_2O$  mixture (Harrison & Jennings 1976). At high partial pressures of  $N_2O$ , ions formed from organic

substrates may react further with  $N_2O$  (see below). If methane is added to  $N_2O$ , with or without helium as a diluent, high yields of  $OH^-$  ions free from hydrated species are given (Smit & Field 1977).

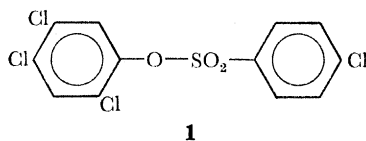
A recent development has been the use of pulsed positive-negative chemical ionization mass spectrometry with the use of a quadrupole instrument (Hunt *et al.* 1976). Positive and negative spectra are recorded in rapid succession by pulsing the source accelerating voltage and associated lens voltages at 10 kHz. Packets of positive and negative ions are analysed by the mass filter, the operation of which is independent of the sign of the charge on the ions. Ions of opposite charge are detected by applying potentials of opposite polarity to the first dynodes of two electron multipliers placed at the exit of the mass filter.

The various types of positive and negative ion spectra that may be obtained by working with different reagent gases are exemplified by the following schemes:

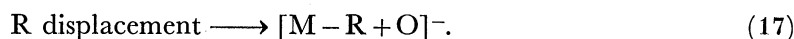
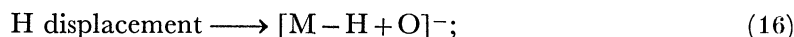
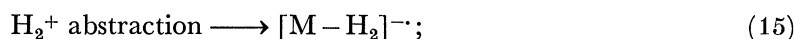
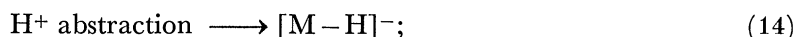
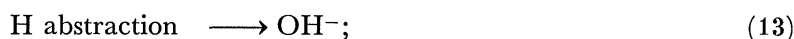


If electronegative elements are present in a molecule, high yields of  $M^-$  ions are often produced under electron attachment conditions and sensitivity can often be increased by suitable derivatisation, e.g. by the use of  $C_6F_5COCl$  with phenols and  $C_6F_5CHO$  with amines. The sensitivity under negative ion operation may be two to three orders of magnitude greater than that obtained in the positive ion mode. For example, the pentafluoropropionic anhydride derivative of melatonin gives an  $[M+H]^+$  ion at  $m/z = 361$  with methane as reagent gas in the positive ion mode and the base peak in the negative ion mode,  $[M-2HF]^-$ ,  $m/z = 320$ , is approximately 150 times as intense. The intensity of the latter ion has been shown to be linear in sample pressure over a range of sample sizes of 2–500 pg (Markey *et al.* 1977).

Major reactions of the  $O_2^-$  ion are proton abstraction to give an  $(M-H)^-$  ion which may fragment, chlorine displacement to give an  $[M-Cl+O]^-$  ion possibly with fragmentation and addition to weakly acidic substances to give the  $[M+O_2]^-$  ion (Hunt *et al.* 1975; Dzidic *et al.* 1975; Levonowich *et al.* 1975). For example, the product of the chlorine displacement reaction given by the acaricide **1** is 20 times as abundant as the molecular anion under atmospheric pressure ionization conditions (Dzidic 1977).



The reactions of the  $O^-$  reagent ion have been studied with a wide range of compounds (Jennings 1977) and the major reaction types may be summarized as follows:



Reactions 14–17 may be accompanied by fragmentation. In general, the  $\text{OH}^-$  ions react further to provide an additional route for the formation of  $[\text{M}-\text{H}]^-$  ions at all but the lowest sample partial pressures. Further details of some of these reactions are considered below.

Negative chemical ionization mass spectrometry is now established as a useful analytical technique having a sensitivity and versatility comparable with its positive ion counterpart. A range of reagent ions is being developed to explore particular structural features and these will be added to as our knowledge of gas phase negative ion chemistry increases. An interesting example of the different types of negative ion spectra that can be given under different conditions is provided by the behaviour of the nitrosamine  $(\text{C}_2\text{H}_5)_2\text{NNO}$  (M. D. Friesen & K. R. Jennings 1978, unpublished). The electron attachment spectrum gives the  $[\text{M}-45]^-$  ion as the most abundant ion, formed either by the loss of  $(\text{CH}_3 + \text{NO})$  or  $(\text{C}_2\text{H}_5 + \text{O})$ . When  $\text{OH}^-$  ions are used as reagent ions, the  $[\text{M}-29]^-$  ion gives the only significant peak, presumably due to the loss of  $\text{C}_2\text{H}_4$  from the  $[\text{M}-\text{H}]^-$  ion which is not observed. When the reagent ion is  $\text{O}^-$ , the only significant peak is the  $[\text{M}-32]^-$  ion, attributed to the loss of  $\text{NO}$  from the  $[\text{M}-2\text{H}]^-$  ion which is not observed.

#### STUDIES OF THE MECHANISMS OF NEGATIVE ION REACTIONS

Detailed mechanistic studies of the reactions of  $\text{O}^-$  ions have revealed a number of interesting features. The production of an ion of  $m/z = 26$  in its reactions with ethylene was originally ascribed to the formation of  $\text{CN}^-$  from impurities since the formation of  $\text{CHCH}^-$  was unlikely because acetylene does not possess a positive electron affinity. Reaction with  $\text{CH}_2\text{CD}_2$  gives products of  $m/z = 26$  and 28 but not 27, suggesting that the ion is formed by abstraction of  $\text{H}_2^+$  from a single carbon atom to form the ion  $\text{CH}_2\text{C}^-$  (Goode & Jennings 1974). Similar reactions are observed with many 1-olefins such as  $\text{CH}_2\text{CF}_2$ ,  $\text{CH}_3\text{CFCH}_2$  and  $\text{CH}_2=\text{C}=\text{CH}_2$ , but they are not observed if other reactions predominate, as in reactions with propene and isobutene.

Provided the  $\text{CH}_2$  group is suitably activated,  $\text{H}_2^+$  abstraction is found to be a fairly general reaction. For example,  $\text{CF}_2^-$  and  $\text{CHCN}^-$  ions may be formed in reactions with  $\text{CH}_2\text{F}_2$  and  $\text{CH}_3\text{CN}$  (Dawson & Jennings 1976), and in reactions with ketones (Harrison & Jennings 1976), deuterium labelling experiments show that  $\text{H}_2^+$  abstraction occurs at the carbon atom  $\alpha$  to the carbonyl group. This is consistent with the observation that  $(\text{M}-2\text{H})^-$  ions are formed in the reaction of  $\text{O}^-$  ions with di-*n*-propyl ketone but not with di-isopropyl ketone.

In the  $\text{N}_2\text{O}-(\text{C}_2\text{H}_5)_2\text{O}$  system, the major product is  $\text{OH}^-$  which reacts further with a diethyl ether molecule to give an ion of  $m/z = 63$ , formulated as  $[\text{C}_2\text{H}_5\text{O H}_2\text{O}]^-$ . This was shown to arise by the attack of the  $\text{OH}^-$  ion on the ether linkage coupled with a  $\beta$ -hydrogen transfer with elimination of an ethylene molecule (J. H. Stapleton, A. J. V. Ferrer Correia & K. R. Jennings 1978, unpublished). In the  $\text{N}_2\text{O}-\text{CH}_3\text{CD}_2\text{OCH}_2\text{CH}_3$  system,  $\text{OH}^-$  and  $\text{OD}^-$  ions are formed and give rise to products of  $m/z = 63-66$ ; there is more than one route to the formation of ions of  $m/z = 64-66$ , but that at  $m/z = 63$  is best understood as being formed by the  $\beta$ -hydrogen transfer mechanism. This is consistent with results obtained with the unsymmetrical ethers *n*- $\text{C}_4\text{H}_9\text{OCH}_3$  and *n*- $\text{C}_4\text{H}_9\text{OC}_2\text{H}_5$ , only the latter of which gives the ion  $m/z = 91$ , formulated as  $[\textit{n}\text{-C}_4\text{H}_9\text{O H}_2\text{O}]^-$ .

In its reactions with esters of monocarboxylic acids, the  $O^{\cdot-}$  ion gives three major products:

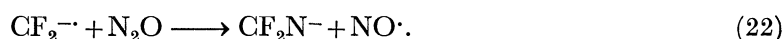
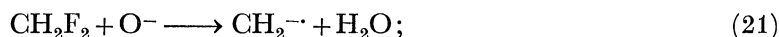


Reactions 18 and 20 therefore give information on the acid group present in the ester and on the molecular mass, respectively (M. J. Farmer & K. R. Jennings 1978, unpublished). The specificity of the position of attack of the  $O^{\cdot-}$  ion was demonstrated in the reaction with  $(CH_3)_2CHO.CO.CH_3$ . Use of  $(CD_3)_2CHO.CO.CH_3$  and  $(CH_3)_2CDO.CO.CH_3$  showed no incorporation of deuterium in the major products,  $CH_3COO^-$  and  $CH_2COO^{\cdot-}$  but indicated that the  $[M-H]^-$  ion is formed exclusively by the abstraction of the secondary hydrogen atom. In the reactions of  $O^{\cdot-}$  ions with  $\beta$ -diketones,  $\beta$ -ketoesters and malonic esters, all of which contain the grouping  $(-CO-CH_2-CO-)$ , an important product is the  $[M+14]^-$  ion, which is presumably the ion  $[M+O-2H]^-$ . Labelling experiments indicate that it is the two hydrogen atoms of the central  $-CH_2-$  group that are eliminated and it is possible that the reaction proceeds through the enol forms of the compounds.

In its reaction with the unsubstituted aromatic compounds benzene and pyridine, the  $O^{\cdot-}$  ion gives as its major products the ions  $[M-2H]^-$  and  $[M-H+O]^-$ , corresponding to reactions 15 and 16 (Bruins *et al.* 1978). In these cases, however,  $H_2^+$  abstraction cannot occur from a single carbon atom and experiments with labelled benzene suggest that hydrogen atoms from adjacent carbon atoms are removed. In the reaction with 4-deuteropyridine, a marked preference for displacement of the deuterium atom was displayed, indicating positional selectivity in hydrogen atom displacement reactions since other observations ruled out the presence of a kinetic isotope effect. This was consistent with observations made on products given by the reaction of  $O^{\cdot-}$  ions with various methyl pyridines in which there was a marked reduction in the formation of the  $[M-H+O]^-$  ion when there was a methyl group in the 4-position.

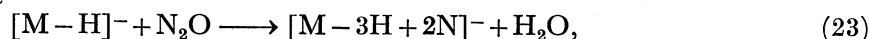
In the reactions of  $O^{\cdot-}$  ions with the three isomeric xylenes, the  $[M-2H]^-$  ion was of low abundance in the products given by the *ortho*- and *para*-isomers but was responsible for the base peak in the spectrum given by the *meta*-isomer. Labelling experiments showed that a hydrogen atom was removed from each of the methyl groups in this reaction (Bruins *et al.* 1978). It therefore appeared that the observation of an intense peak due to  $[M-2H]^-$  ions might be diagnostic of two methyl groups *meta*- to each other in aromatic compounds but results obtained with dimethylpyridines and dimethylnaphthalenes do not bear this out (M. D. Friesen & K. R. Jennings 1978, unpublished).

Nitrous oxide has been used in a number of experiments, either as a source of  $O^{\cdot-}$  ions or of  $OH^-$  ions, and there is increasing evidence that it will undergo several different types of reaction with organic anions. Ions formed by  $H_2^+$  abstraction from an activated methylene group react by abstracting a nitrogen atom (Dawson & Jennings 1976), e.g.



Alkylbenzenes yield  $[M-H]^-$  ions in great abundance when reacted with  $O^{\cdot-}$  or  $OH^-$ , and

in the presence of  $N_2O$  these ions react further to give ions of  $m/z = [M + 25]^-$  which arise in reactions of the type



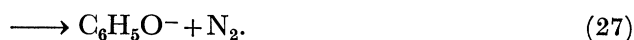
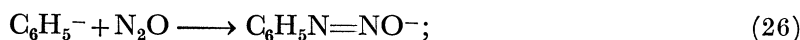
the products of which are believed to contain heterocyclic rings (Smit & Field 1977). A similar reaction has recently been observed in a flowing afterglow system for the allyl anion (Bierbaum *et al.* 1977):



In contrast, the anion formed by proton abstraction from 1,3-butadiene reacts with  $N_2O$  to give the same product but with the loss of a formaldehyde molecule:



The above reactions presumably occur by the formation of an initial adduct which rapidly rearranges with the elimination of a small neutral molecule. A system in which the adduct is observed and which also demonstrates a further reaction type is given by the phenide ion:

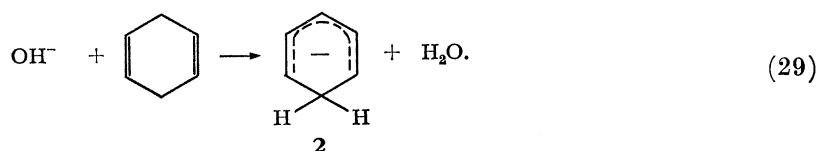


Although solution analogues of the diazo transfer reactions of  $N_2O$  are known, no reaction analogous to the oxygen transfer reaction (27) has been observed in solution.

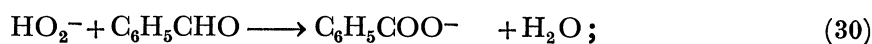
An even more reactive molecule with gas phase anions is  $CO_2$  (Bierbaum *et al.* 1977) which, in a manner entirely analogous with reactions observed in solution, adds to many anions:



Although many gas-phase ion reactions are of the acid-base type, the variety of reactions observed for organic anions is rapidly increasing and several potentially useful reagent ions have recently been reported (De Puy *et al.* 1978) which facilitate the study of gas-phase oxidation and reduction reactions. In a flowing afterglow system,  $OH^-$  ions react with 1,4-cyclohexadiene to give the  $C_6H_7^-$  ion, **2**:



This species is a useful reducing agent and acts as a hydride donor towards a number of substrates: for example, benzaldehyde gives the benzyl alcohol anion, acrolein gives the  $C_3H_5O^-$  ion and nitric oxide reacts to give another useful hydride donor,  $HNO^-$ . The ion, **2**, does not react with  $N_2O$  and simply adds to  $CO_2$  but the  $HNO^-$  ion acts as a hydride donor towards both species and yields the  $HN_2O^-$  and  $HCOO^-$  ions; hence **2** can be used to produce a very good gas phase reducing agent,  $HNO^-$ . Equally well, it reacts rapidly with oxygen by hydride transfer to give the  $HO_2^-$  ion which is a strong oxidizing agent in the gas phase, as in solution. Its potential may be judged from the reactions

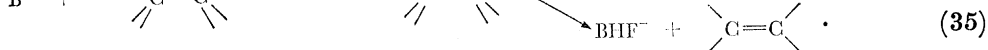
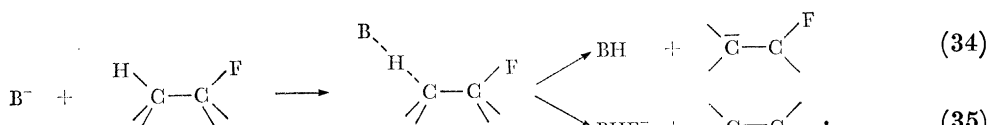




Although proton abstraction reactions may complicate observations in some systems, reactions of ions such as  $\text{HNO}^-$  and  $\text{HO}_2^-$  with organic substrates should prove of considerable interest.

By exposing a basic anion to an excess of  $\text{D}_2\text{O}$  or  $\text{CH}_3\text{OD}$ , the number and type of hydrogen atoms exchanged in the ion can be controlled. For example, in a high pressure source with  $\text{N}_2\text{O}-\text{D}_2\text{O}$  as the reagent gas, the  $[\text{M}-\text{H}]^-$  ions formed from xylenes exchange up to five hydrogen atoms, i.e. all six hydrogen atoms of the methyl groups are removed or exchanged (D. F. Hunt 1977, personal communication). Similarly, the use of  $\text{N}_2\text{O}-\text{CH}_3\text{OD}$  as reagent gas leads to the exchange of the four hydrogen atoms on the carbon atoms adjacent to the carbonyl group in ketones. Hydrogen-deuterium exchange reactions of a large number of carbanions in a flowing afterglow apparatus have been used to distinguish structures of isomeric anions having different numbers of potentially exchangeable hydrogen atoms (Stewart *et al.* 1977). The exchange is postulated as occurring in a complex between the organic anion and the  $\text{D}_2\text{O}$  molecule in which deuterium addition followed by proton abstraction occurs, after which the complex can separate. Although the  $[\text{M}-\text{H}]^-$  ions given by acetone, acetaldehyde and 3-pentanone do not exchange with  $\text{D}_2\text{O}$ , all exchange with the more acidic  $\text{CH}_3\text{OD}$ , and with the still more acidic  $\text{CF}_3\text{CH}_2\text{OD}$ , deuterium abstraction to form  $\text{CF}_3\text{CH}_2\text{O}^-$  predominates.

Another type of reaction analogous to a well known solution reaction is the base-induced elimination reaction. These reactions may be looked upon as occurring by the interaction of a strong base, by hydrogen-bond formation, with a labile proton such as in fluoroethane (Ridge & Beauchamp 1974). In addition to proton transfer, HF elimination may occur and in a detailed study of the influence of base strength on reaction products with a series of fluoroethanes (Sullivan & Beauchamp 1977), it was found that in each case there was a minimum base strength below which no proton transfer occurs, although HF elimination occurs with a base as weak as  $\text{CN}^-$ .



A similar type of reaction has been observed (Dawson & Jennings 1977) in the reaction of fluoroalcohols:



Throughout this review, use has been made of proton affinities and gas phase acidities of both neutral species and anions and it is perhaps of interest to indicate how these quantities are derived. An approximate method that has been widely used to bracket proton affinities is to look for the occurrence or non-occurrence of proton transfer reactions. If the anion  $\text{X}^-$  will abstract a proton from a molecule HA but not from a molecule HB, the proton affinity of  $\text{X}^-$  is greater than that of  $\text{A}^-$  but less than that of  $\text{B}^-$ . If the proton affinities of  $\text{A}^-$  and  $\text{B}^-$  are known, limits can be set on the proton affinity of  $\text{X}^-$  and the accuracy with which this is known is dependent on finding two species  $\text{A}^-$  and  $\text{B}^-$  the proton affinities of which lie just above and just below that of  $\text{X}^-$ . More accurate data are obtained from the study of ion-molecule equilibria by ion cyclotron resonance spectrometry (McIver & Miller 1974), pulsed high pressure source methods (Yamdagni & Kebarle 1973, 1974) or use of the flowing afterglow technique (Bohme *et al.* 1974). The equilibrium constant is measured either over a range of temperatures, giving  $\Delta H^\circ$  directly, or at a single temperature, coupled with an estimate of  $\Delta S^\circ$ , to calculate

$\Delta H^\circ$ . This gives a direct measure of the difference in proton affinities of the two anions and allows one to construct a table of relative proton affinities which are put on an absolute basis by independent determinations of one or more proton affinities. When combined with other thermochemical data, these values can be used to draw up a table of gas-phase acidities, defined as  $(D_{\text{AH}} - A_{\text{e,A}})$  kJ mole<sup>-1</sup>, where  $D_{\text{AH}}$  is the dissociation energy of AH and  $A_{\text{e,A}}$  is the electron affinity of A. Some typical values are as follows (in kilojoules per mole):

| acid              | NH <sub>3</sub> | H <sub>2</sub> | H <sub>2</sub> O | CH <sub>3</sub> OH | HF  | H <sub>2</sub> S | C <sub>6</sub> H <sub>5</sub> OH | CH <sub>3</sub> COOH | HCl |
|-------------------|-----------------|----------------|------------------|--------------------|-----|------------------|----------------------------------|----------------------|-----|
| gas-phase acidity | 372             | 359            | 322              | 267                | 238 | 154              | 139                              | 133                  | 83  |

### CONCLUSION

Ten years ago, there would have been little or nothing to discuss about the gas phase ion chemistry of organic anions. The subject is now one of the most rapidly developing in the field and great strides have been made in developing techniques for the study of negative ions and in putting their study on a firm thermodynamic basis. The study of mechanisms of negative ion molecule reactions has barely begun and much of interest undoubtedly remains to be discovered on this topic. Negative ions have already demonstrated their value in analytical applications and their reactions should continue to prove of interest to many chemists and biochemists.

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