Interstellar organic chemistry and other applications of gas phase ion-molecule chemistry

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<u>Abstract</u> - Over 60 molecules and ions, most of them organic, have been detected in interstellar space and most are thought to be formed by gas phase ion - molecule reactions. The unique features of reactions of this type, which allow them to proceed readily under the extreme conditions of space and yet exhibit great selectivity and otherwise resemble reactions in solution, are discussed and illustrated.

INTRODUCTION

Among the most remarkable astronomical discoveries of the last few decades has been the observation of complex organic molecules as major constituents in interstellar clouds (ref. 1). At the present time over 60 molecules and ions, most of them organic, have been detected in space, including the ubiquitous compound cyclopropenylidene, C₃H₂ (ref. 2). A representative sample of interstellar molecules is given in Table 1.

TABLE 1: Representative Interstellar lons and Molecules

CH +	HCN	H ₂ CO	CH3OH	HCOOCH3
CO	H ₂ O	C ₃ H	CH3CN	CH3OCH3
C ₂	HĈO +	нсоон	CH3CHO	C ₂ H ₅ OH
HC = C - C = C - C = C - C = C - C = N				

It is generally believed that the formation of these molecules involves gas phase reactions between ions and neutral molecules. The study of organic gas phase ion-molecule chemistry, of which interstellar organic chemistry is just one example, has made remarkable progress in the last decade, with important implications for other branches of organic chemistry. Yet there are some important conceptual points about these reactions which often seem to prevent their incorporation into the general body of organic knowledge. In this lecture I would like to illustrate these unique features and to explain why, in spite of them, gas phase ion reactions usually closely resemble those in solution. At the same time I would like to show how the particular properties of gas phase ion reactions make them especially suitable for the synthesis of organic molecules in the unusual environment of space.

THE FLOWING AFTERGLOW

Before discussing the reactions themselves, I will describe how we carry out our experiments to give some idea of the very many different types of ions which can be produced and the great number of different kinds of experiments which can be performed. Most physical organic chemists will be acquainted with ion cyclotron resonance spectrometry (ICR), and its newer cousin fourier transform mass spectrometry (FT-MS). In these experiments ions are trapped for relatively long periods of time at very low pressure in static electric and magnetic fields and allowed to react with neutrals. Fewer are aware of the instruments we use, the flowing afterglow (FA) (ref. 3) and the selected ion flow tube (SIFT) (ref. 4).

The FA is shown in Fig. 1. It consists of a meter-long by 7 cm diameter stainless steel tube through which helium buffer gas is pumped rapidly (0.01 sec/meter) and at relatively high pressure (0.3 - 1.0 torr). Ions are produced by any of several methods at the beginning of the flow tube and immediately removed from the ionizing region by

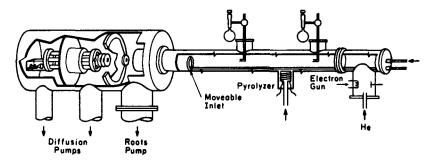


Fig. 1. The flowing afterglow apparatus.

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entrainment in the helium. Because of the high pressures, the ions are rapidly cooled to room temperature, an important feature of the FA technique. Reactant molecules are added through various ports along the flow tube, well away from the ionizing region, and ion-molecule reactions are allowed to proceed. At the end of the flow tube the ions are sampled through a 0.5 mm orifice into a low pressure region where they are separated in a quadrupole mass filter and detected by an electron multiplier.

In a FA the ionization and reaction regions are separated spatially and temporally. Sequential reactions can be performed as the ions traverse the flow tube. Ion-molecule reactions can be used to synthesize ions of interest, whose chemical reactions can in turn be explored. Or the structure of the ions produced in an ion-molecule reaction can be probed by further reactions. For example, the parent ion of allene can be produced cleanly by the use of metastable argon atoms. Methyl acetylene can be added downstream and the ionic products detected. Alternatively, methyl acetylene can be ionized and allene added downstream. Both experiments yield C₆H₇+ ions among the products. However when D₂O is added still further downstream, the C₆H₇+ ions produced in the latter but not the former reaction undergo hydrogen - deuterium exchange, a reaction characteristic of protonated benzene.

Carbanions as well as carbocations can be easily studied in the FA. Usually a highly basic anion (HO^- or NH_2^-) is produced by electron impact and used to generate the carbanion by proton abstraction. For example the diazomethyl anion is produced by adding vapors of diazomethane to a flow tube which contains hydroxide ions.

$$N=N=0$$
 $\xrightarrow{\theta^{-}}$ $O^{-} + N_{2}$
 $O^{-} + CH_{4}$ \longrightarrow $HO^{-} + CH_{3}$
 $HO^{-} + CH_{2}=N=N$ \longrightarrow $CH==N=N$ $+$ $H_{2}O$

If CO₂ is now added further downstream a rapid addition reaction occurs. However in the gas phase the exothermicity of such an addition reaction cannot be transferred to the solvent as it can in solution, and so remains within the molecule. If no other reaction pathways are available to the adduct, it will dissociate to reactants. In this case, however, energy can be released by loss of N₂. The resulting carbene anion can be detected, but also reacts rapidly with the excess CO₂ in the flow tube.

CH=N=N +
$$CO_2$$
 - O_2 C-CH=N=N O_2 C-CH=N=N O_2 C-CH: + O_2 C-CH:

Amide and hydroxide ions are strong enough bases to abstract a proton from nearly all unsaturated organic molecules. Carbanions can also be produced at a specific site within a molecule, a site at which a carbanion might not be formed by proton abstraction, by allowing a trimethylsilyl derivative to react with F⁻ (ref. 5).

In this way the chemistry of unusual carbanions of synthetic interest can be explored.

THE SELECTED ION FLOW TUBE

The flowing afterglow is a versatile instrument, but it has some limitations. For example, while the parent ion of allene can be generated cleanly, more vigorous ionization of allene produces a mixture of C₃H_n⁺ ions of almost equal intensity (Fig. 3a). Since all of these ions are present in the flow tube at the same time, it is impossible to study the ion chemistry of any one of them. The presence of an excess of neutral reagent in the flow tube can also cause complications, as the reaction of the carbene anion with excess CO₂ demonstrates. These and other limitations of the conventional FA are overcome in the selected ion flow tube. In our laboratory we have constructed a SIFT which uses a flowing afterglow as an ion source (FA-SIFT) (ref. 6). This instrument, which is shown in Fig. 2, consists of two flow tubes connected by a quadrupole mass filter. Ions are produced in the first FA either by direct ionization or by a sequence of ion-molecule reactions. At the end of this FA they are sampled into the quadrupole, the neutrals removed by pumping, and ions of a single m/z are selected and injected into the second FA, where their chemistry can be investigated in the absence of other ions, neutrals, photons and electrons. For example from the mixture of ions in Fig. 3a the C₃H₂+ ion (m/z 38) can be separated (Fig. 3b) and its reaction with OCS investigated. As the spectrum in Fig. 2c shows, it reacts to give primarily a single ion C₃H₂S+. The rate of this sulfur atom abstraction reaction can easily be determined by examining the extent of reaction as a function of distance along the flow tube at which the OCS is introduced, since in a flow system time and distance are related (Fig. 3d).

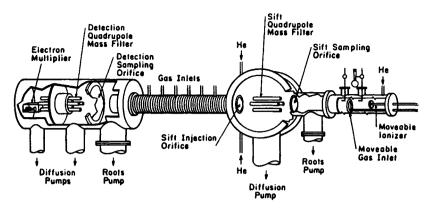


Fig. 2. The selected ion flow tube (SIFT).

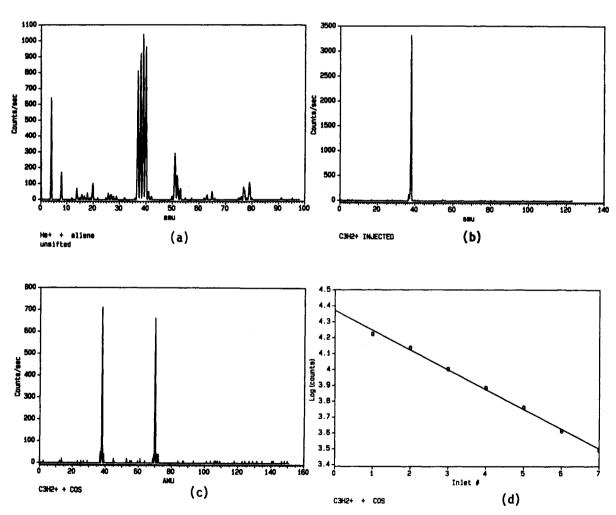


Fig. 3 (a) The mass spectrum of allene; (b) the m/z 38 ion, C₃H₂+, injected in the SIFT;
 (c) Spectrum of the product (C₃H₂S+, m/z 70) of the reaction of C₃H₂+ with OCS;
 (d) the intensity of the C₃H₂+ ion as a function of the inlet through which the OCS is introduced.

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The SIFT also provides an additional way of producing interesting and unique ions. In order to inject ions from the low pressure region of the quadrupole into the high pressure region of the second flow tube, they must be given kinetic energy. Ordinarily ions survive this injection without destruction. For example the simple ion H₃SiO can be produced and injected.

$$C_6H_5SiH_3 + HO^- \rightarrow H_3SiO^- + C_6H_6$$

However if the injection energy is increased one can bring about its collision-induced dissociation to HSiO⁻. Its chemistry can be studied by introducing reagent gases into the second flow tube.

The chemistry of this silaformyl anion can then be investigated.

$$H-Si=0$$

RCH₂O + SiO

 CO_2

HSiO₂ + CO

From studies of its ability to transfer a hydride and of its basicity we have been able to estimate such fundamental properties as its heat of formation and that of its parent, silaformaldehyde.

Our reaction flow tube has been constructed so that an electric field (drift) may be applied to the ions, giving them kinetic energy with respect to the neutrals (ref. 7). As a result, reactions may be studied which are either too slow to be observed at room temperature or which are endothermic. For example C₃H₂+ reacts only very slowly with H₂ to form C₃H₃+ because of a small kinetic barrier (ref. 8). The application of a small drift field induces the reaction to proceed readily. As another example, ammonia is several kcal/mol stronger an acid than is ethylene and so the reaction of amide ion with ethylene to form the vinyl anion is several kcal/mol endothermic. However amide ion injected in a SIFT can be given kinetic energy and completely converted into the vinyl anion in the presence of ethylene.

$$NH_2^-$$
 + $CH_2=CH_2$ $\xrightarrow{\text{kinetic}}$ NH_3 + $CH_2=CH^-$

CHARACTERISTICS OF ION-MOLECULE REACTIONS

The rates of gas phase ion - molecule reactions are typically very fast. Many have bimolecular rate constants greater than 10¹² l/mol sec, which corresponds to a rate faster than that for the collision of two neutral molecules in the gas phase. Despite this high rate, many ion reactions are highly selective. Indeed a hydrogen - deuterium isotope effect of 6 is observed in the following gas phase E2 reaction (ref. 9).

Gas phase ion-molecule reactions are so fast because the ion and neutral are attracted to one another by ion-dipole and ion-induced dipole forces which typically amount to 10 - 20 kcal/mol by the time they reach reaction distances. Some or all of this kinetic energy can be converted into internal energy and used to overcome reaction barriers or to drive endothermic reactions. Eventually, however, it must be recovered, reconverted to kinetic energy, and used for the separation of the ion and neutral. Gas phase H - D exchange in both anions and cations illustrates this dramatically (ref. 10). If the benzyl anion is produced in the FA by proton abstraction from toluene it appears not to react with H₂O. However rapid H - D exchange of the benzylic protons for deuterium is observed with D₂O. The initially formed ion-dipole complex contains about 15 kcal/mol excess energy. Part of this can be used to fuel the 10 kcal/mol endothermic proton transfer to form toluene - d₁ and DO - . Proton transfer generates the monodeuterated benzyl anion. A second exchange can occur within a single complex; indeed we have shown that an average of six proton transfers can occur during a single encounter of some carbanions and D₂O.

$$[C_6H_5CH_2^-. D_2O] \iff [C_6H_5CH_2D \cdot DO^-] \iff [C_6H_5CHD^- \cdot HOD]$$

Experiments of this type demonstrate that ion - dipole complexes may have relatively long lifetimes, sometimes > 10⁻⁷ sec for large organic ions.

Yet ion - molecule reactions can be selective for the very reason that energy is put into the reaction in this unique way. Consider a reaction with an activation energy of 15 kcal/mol. To get such a reaction to go very rapidly in solution, one would have to heat the reactants, creating a high-temperature Boltzman distribution of energies. At high temperatures many molecules would have energies far in excess of 15 kcal/mol, and it is these highly energetic species which react indiscriminately. In the gas phase the situation is different. One starts with a room temperature Boltzman distribution of energies and 15 kcal/mol of ion - dipole complexation is given to each reacting pair. Thus one has a narrow energy distribution centered just around the activation energy. The high - energy, randomly reacting components are not present.

INTERSTELLAR ORGANIC SYNTHESIS

The unique properties of ionic reactions occurring in the gas phase make them ideal candidates for interstellar synthesis. According to current theories, only the elements hydrogen, helium and deuterium were formed in the initial "Big Bang"; all other elements are formed in stars and ejected into space when stars explode. The first products of nuclear synthesis are the elements carbon, oxygen and nitrogen. The major constituents of space are those given in Table 2. All other elements and compounds are at leastan order of magnitude lower in abundance.

TABLE 2: Typical Composition of Interstellar Clouds

H, H ₂	1	
c, c T	2 x 10 ⁻⁴	
0	5 x 10 -4	
N	7 x 10 ⁻⁵	
CO	1 x 10 ⁻⁶	

Interstellar clouds are divided into two types, <u>diffuse clouds</u>, into which light can penetrate, and <u>dense clouds</u>, which are opaque. In diffuse clouds, which contain $10^2 - 10^3$ particles/cc and have temperatures of about 100 K, only simple ions and molecules are observed, since larger ones would be decomposed by stellar radiation. In this region synthesis is believed to begin by photoionization of carbon atoms to C⁺, since among the abundant constituents only carbon has an ionization potential lower than that of the hydrogen atoms, whose great abundance effectively screens N and O from photoionization. In diffuse clouds almost all the carbon atoms are in the form of C⁺.

The carbon ions can, of course, combine with H, N, and O atoms, but, because there is no way of getting rid of the exothermicity of such reactions, the adducts dissociate.

Reaction of C+ with H_2 to form CH+ and a hydrogen atom is endothermic. The key reaction which initiates interstellar synthesis is thought to be the association of C+ with H_2 to form CH₂+ followed by emission of a photon to remove the reaction exothermicity. This is a very slow reaction, one whose rate is still being disputed. At the most only one collision out of 10^6 is effective in forming CH₂+ (ref. 11).

$$C^+ + H_2$$
 $CH_2^+ + W$
 $CH_2^+ + W$
 $CH_2^+ + W$
 $CH_2^+ + W$

If one believes, as some astronomers have speculated, that life originated from interstellar organic matter deposited on earth, then this reaction may well be the rate determining organic reaction in the universe!

Once CH₂⁺ has been formed, other reactions can proceed more rapidly, since the ejection of a hydrogen atom can remove energy from the system.

$$CH_2^+$$
 + O \longrightarrow HCO^+ + H CH_2^+ + H_2 \longrightarrow CH_3^+ + H

Neutral molecules are assumed to form by the combination of a cation with an electron, the energy of the recombination being removed by fragmentation.

In dense clouds (10^3 - 10^6 particles/cc, 20 K), large molecules can build up because they are shielded from photodissociation. Ionization is thought to be initiated by cosmic rays, which form H+, H₂+, and He+. The latter ion is known to react with the abundant carbon monoxide to form C+, which can, in turn, react with other organic molecules. Even at temperatures as low as 20 K an ion-molecule reaction can proceed rapidly because there is still the approximately 15 kcal/mol ion-dipole complexation energy available. For example C+ reacts rapidly with acetylene to form HC₃+.

The most probable steps from HC_3^+ to cyclopropenylidene have been worked out by David Smith and Nigel Adams of Birmingham University (ref. 12). Insertion into H_2 will form an adduct with > 100 kcal/mol internal energy. This is sufficient energy to allow rearrangement to the more stable cyclic form of $C_3H_3^+$, which is postulated to become stable by photon emission.

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Recombination of this ion with an electron and loss of a hydrogen atom would be expected to form the observed cycloprepenylidene. It should be emphasized, however, that the identities and structures of the neutral products from ion - electron recombination reactions are in general not known. This is an area of active investigation at the present time.

SUMMARY

In summary, gas phase ion - molecule reactions share many similarities with ionic reactions in solution. However there are a few important differences which must be taken into account. The activation energy for reaction is generated by the attraction between the ion and the neutral, so that ion - molecule reactions can occur rapidly even at very low temperatures. It is difficult for the exothermicity of an addition reaction to be dissipated, so that simple adducts are seldom observed as reaction products. Reactions proceed through long - lived ion - dipole complexes in which several sequential reactions may occur. Once these special circumstances are recognized, the results obtained from the study of gas phase ionic reactions can often be applied to analogous reactions in solution.

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