

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

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**Abstract** - 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,  $C_3H_2$  (ref. 2). A representative sample of interstellar molecules is given in Table 1.

TABLE 1: Representative Interstellar Ions and Molecules

CH <sup>+</sup>	HCN	H <sub>2</sub> CO	CH <sub>3</sub> OH	HCOOCH <sub>3</sub>
CO	H <sub>2</sub> O	C <sub>3</sub> H	CH <sub>3</sub> CN	CH <sub>3</sub> OCH <sub>3</sub>
C <sub>2</sub>	HCO <sup>+</sup>	HCOOH	CH <sub>3</sub> CHO	C <sub>2</sub> H <sub>5</sub> OH
HC≡C-C≡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

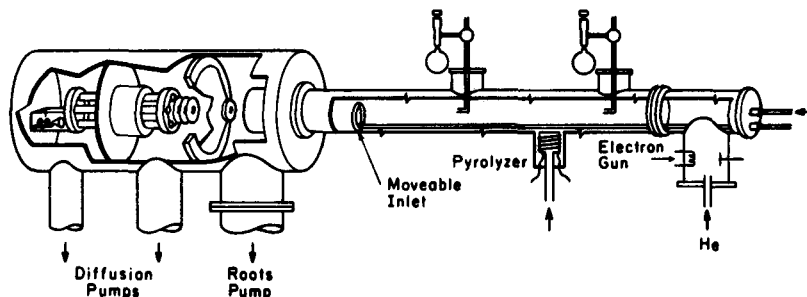


Fig. 1. The flowing afterglow apparatus.



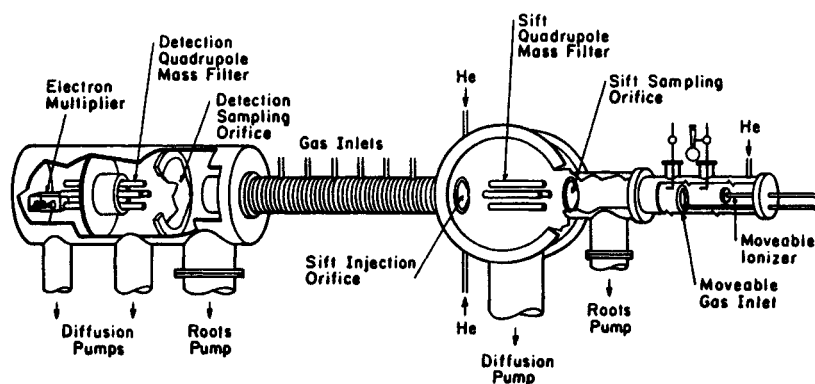


Fig. 2. The selected ion flow tube (SIFT).

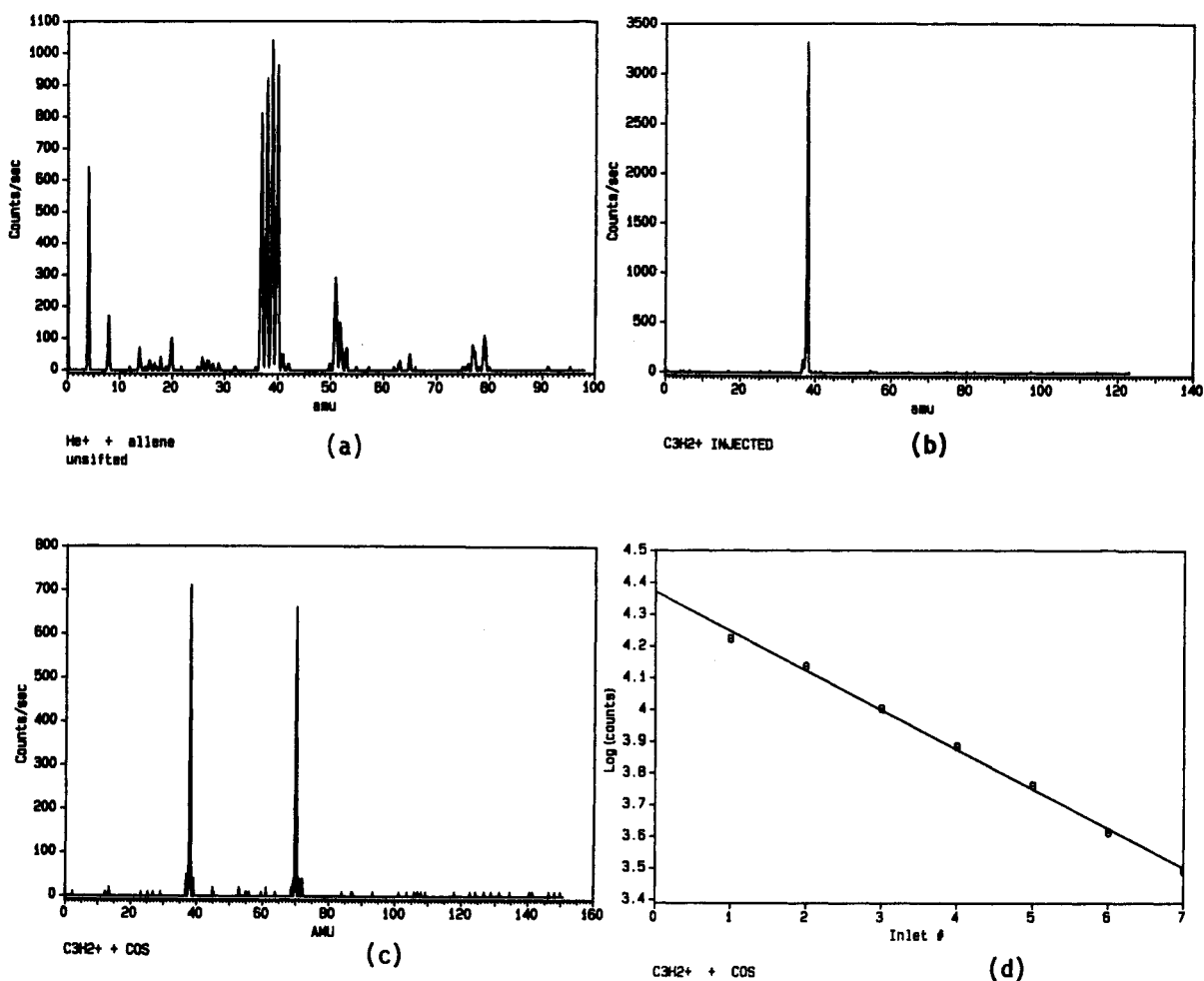
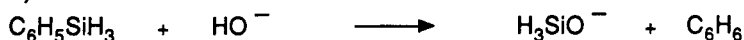


Fig. 3 (a) The mass spectrum of allene; (b) the  $m/z$  38 ion,  $\text{C}_3\text{H}_2^+$ , injected in the SIFT; (c) Spectrum of the product ( $\text{C}_3\text{H}_2\text{S}^+$ ,  $m/z$  70) of the reaction of  $\text{C}_3\text{H}_2^+$  with OCS; (d) the intensity of the  $\text{C}_3\text{H}_2^+$  ion as a function of the inlet through which the OCS is introduced.

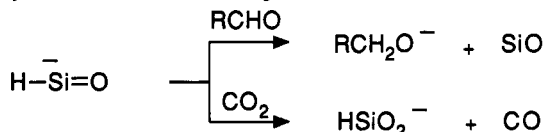
The SIFT also provides an additional way of producing interesting and unique ions. In order to inject ions from the low pressure region of the quadrupole into the high pressure region of the second flow tube, they must be given kinetic energy. Ordinarily ions survive this injection without destruction. For example the simple ion  $\text{H}_3\text{SiO}^-$  can be produced and injected.



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

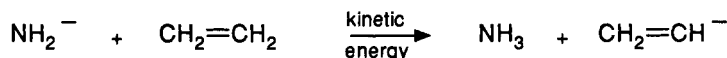


The chemistry of this silaformyl anion can then be investigated.



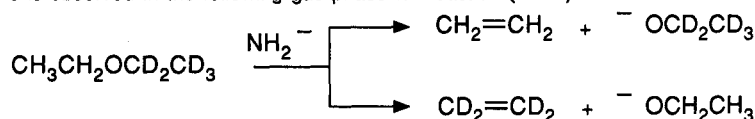
From studies of its ability to transfer a hydride and of its basicity we have been able to estimate such fundamental properties as its heat of formation and that of its parent, silaformaldehyde.

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  $\text{C}_3\text{H}_2^+$  reacts only very slowly with  $\text{H}_2$  to form  $\text{C}_3\text{H}_3^+$  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.

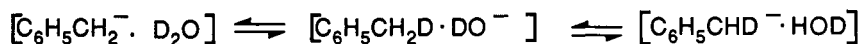


### CHARACTERISTICS OF ION-MOLECULE REACTIONS

The rates of gas phase ion - molecule reactions are typically very fast. Many have bimolecular rate constants greater than  $10^{12}$  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  $\text{H}_2\text{O}$ . However rapid H - D exchange of the benzylic protons for deuterium is observed with  $\text{D}_2\text{O}$ . 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 -  $d_1$  and  $\text{DO}^-$ . 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  $\text{D}_2\text{O}$ .



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

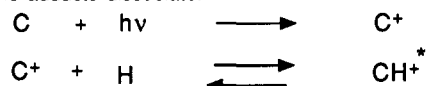
The unique properties of ionic reactions occurring in the gas phase make them ideal candidates for interstellar synthesis. According to current theories, only the elements hydrogen, helium and deuterium were formed in the initial "Big Bang"; all other elements are formed in stars and ejected into space 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 least an order of magnitude lower in abundance.

TABLE 2: Typical Composition of Interstellar Clouds

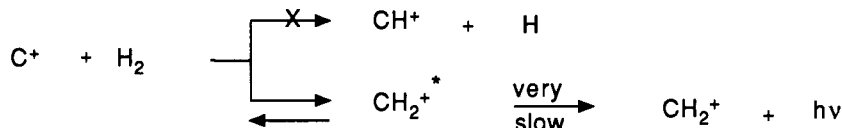
H, H <sub>2</sub>	1
C, C <sup>+</sup>	2 x 10 <sup>-4</sup>
O	5 x 10 <sup>-4</sup>
N	7 x 10 <sup>-5</sup>
CO	1 x 10 <sup>-6</sup>

Interstellar clouds are divided into two types, diffuse clouds, into which light can penetrate, and dense clouds, which are opaque. In diffuse clouds, which contain 10<sup>2</sup> - 10<sup>3</sup> 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<sup>+</sup>, 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<sup>+</sup>.

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.

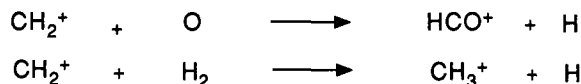


Reaction of C<sup>+</sup> with H<sub>2</sub> to form CH<sup>+</sup> and a hydrogen atom is endothermic. The key reaction which initiates interstellar synthesis is thought to be the association of C<sup>+</sup> with H<sub>2</sub> to form CH<sub>2</sub><sup>+</sup> followed by emission of a photon to remove 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<sup>6</sup> is effective in forming CH<sub>2</sub><sup>+</sup> (ref. 11).

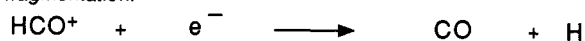


If one believes, as some astronomers have speculated, that life originated from interstellar organic matter deposited on earth, then this reaction may well be the rate determining organic reaction in the universe!

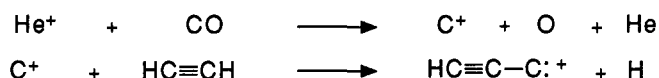
Once CH<sub>2</sub><sup>+</sup> has been formed, other reactions can proceed more rapidly, since the ejection of a hydrogen atom can remove energy from the system.



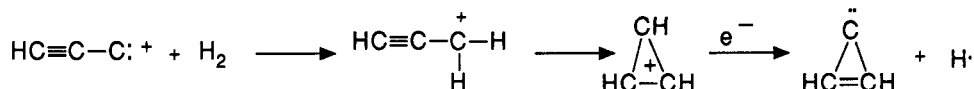
Neutral molecules are assumed to form by the combination of a cation with an electron, the energy of the recombination being removed by fragmentation.



In dense clouds (10<sup>3</sup> - 10<sup>6</sup> 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<sup>+</sup>, H<sub>2</sub><sup>+</sup>, and He<sup>+</sup>. The latter ion is known to react with the abundant carbon monoxide to form C<sup>+</sup>, 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<sup>+</sup> reacts rapidly with acetylene to form HC<sub>3</sub><sup>+</sup>.



The most probable steps from HC<sub>3</sub><sup>+</sup> to cyclopropenylidene have been worked out by David Smith and Nigel Adams of Birmingham University (ref. 12). Insertion into H<sub>2</sub> 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<sub>3</sub>H<sub>3</sub><sup>+</sup>, which is postulated to become stable by photon emission.



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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