

Studies of Interstellar Ion Reactions Using the SIFT Technique: Isotope Fractionation

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Received February 21, 1992

Introduction

It has been known for decades that if an electrical discharge passes through a gas mixture, then gas-phase chemistry occurs which produces new gases. Clearly, dissociation of molecules occurs in such events producing radicals; for example, oxygen and nitrogen atoms are produced in air discharges, which react to produce ozone and oxides of nitrogen. But what is the contribution to the overall chemistry of the positive ions, negative ions, and free electrons which are also produced in such discharges? The general answer to this question is that it depends on several different factors, such as the degree of ionization of the gas, the gas pressure and temperature, and the chemical nature of the ions and the neutral gas with which they can react. The most obvious example of this is the gas-phase chemistry of the terrestrial atmosphere. In the high-pressure lower atmosphere—the troposphere and the lower stratosphere—neutral radical reactions dominate the chemistry, and ion chemistry is only a very minor contributor to the overall chemistry because the degree of ionization is so very low ($\sim 10^3$ positive and negative ions per cm^3). However, in the upper atmosphere—the ionosphere—where solar photons produce a much higher degree of ionization in a much more tenuous atmosphere, ion chemistry dominates and produces a wide variety of complex positive and negative ions.¹

Much is known about the ion chemistry of the ionosphere. Understanding began when ionospheric plasma was first sampled using rocket-borne mass spectrometers and it was noted that several exotic ion types were present. Qualitative ion chemical models were formulated to explain these observations, and then laboratory experiments were conceived and exploited to study ionic reactions in the gas phase under appropriate conditions of temperature and pressure, in order to provide data on reaction products and kinetics to quantitatively substantiate the models. The rapid progress in understanding this ion chemistry was the direct result of the conception and exploitation of the flowing afterglow (FA) technique by Ferguson, Fehsenfeld, and

Schmeltekopf in Boulder, Colorado, in the early 1960s.² What was so important about the development of the FA technique was that, using it, the rate coefficients and product ions could be determined for a very large number and variety of reactions under precisely controlled temperature conditions and over a wide temperature range (~ 80 – 900 K). Thus, using the FA, the ion chemistry of the ionosphere was elucidated. In essence, the FA technique involves the creation of ionization (e.g., by an electrical discharge) in the upstream region of a fast-flowing inert (carrier) gas (usually helium), which results in the creation of a thermalized afterglow plasma consisting of carrier gas ions and electrons in the downstream region of the flow. The temperature of the carrier gas, and hence that of the ions and electrons, can be readily varied and their reactions studied by the addition of controlled amounts of reactant gases to the carrier gas and by sampling the reactant and product ions by a downstream pinhole orifice/differentially pumped mass spectrometer system. The addition of more than one gas to the flow allowed the creation of complex ions which could not be produced by electron impact on a parent gas. This “chemical versatility” of the FA was a major reason for its great value and productivity. Using it, the understanding of ion–neutral reactions grew at a very rapid rate. It should, however, be noted that the parallel development and exploitation of the ion cyclotron resonance (ICR) technique³ also contributed greatly to the growth in understanding of the kinetics, energetics, and mechanistics of ion–molecule reactions.

Further impetus was brought to the study of gas-phase reactions in the early 1970s with the discovery by radio astronomers of a variety of molecular species in the cold, tenuous interstellar gas clouds which pervade the Milky Way.⁴ Immediately the question arose as to how these molecules could be synthesized from their composite elements in such harsh regions. Conventional neutral gas-phase chemistry could not be the answer since it is well known that neutral–neutral reactions, including many such reactions involving radicals, usually require “activation energy” and they must therefore be very slow at the low temperatures of these interstellar clouds, which can be as low as ~ 10 K. However, it was quickly realized that the reactions of positive ions with neutrals could be the answer, in that such reactions rarely require activation energy and are thus generally efficient even at very low temperatures. Limited quantitative ion chemical models based on the

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(1) Smith, D.; Adams, N. G. *Top. Curr. Chem.* 1980, 1–43.

(2) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. *Adv. At. Mol. Phys.* 1969, 5, 1–56.

(3) Kemper, P. R.; Bowers, M. T. *Techniques of Chemistry*; Farraran, J. M., Saunders, W. H., Eds.; Wiley: New York, 1988; Vol. 20, pp 1–59.

(4) Duley, W. W.; Williams, D. A. *Interstellar Chemistry*; Academic Press: London, 1984. *Molecular Astrophysics*; Hartquist, T. W., Ed.; Cambridge University Press: Cambridge, 1990.

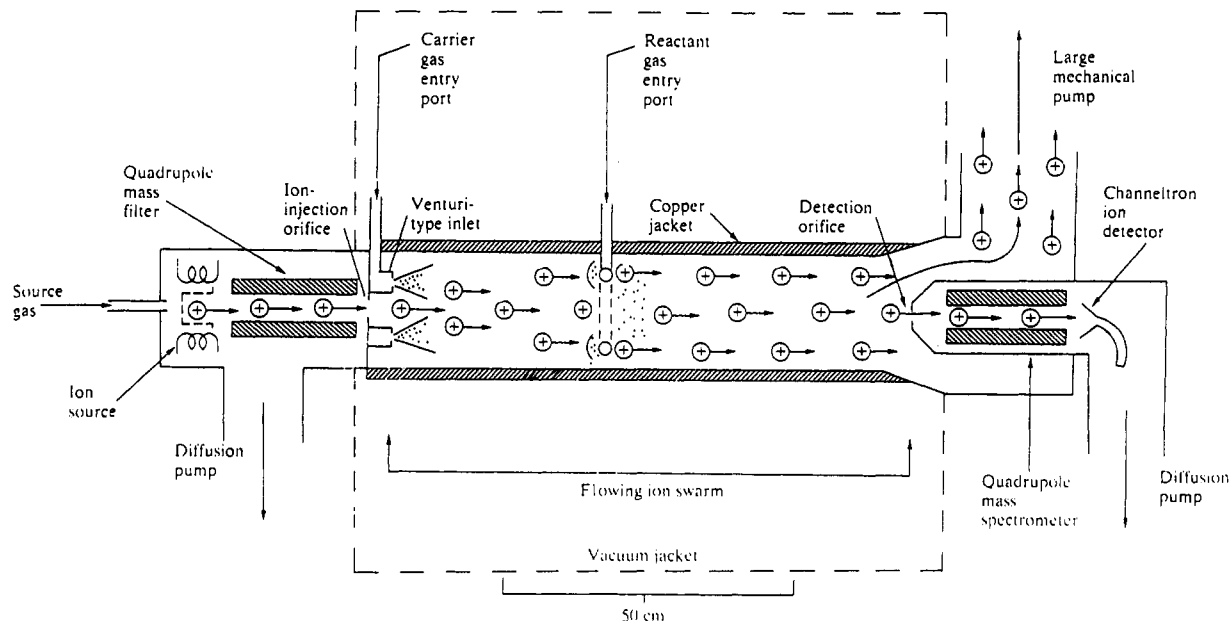


Figure 1. Schematic representation of a selected ion flow tube (SIFT). In this apparatus, ions are created in a remote ion source, selected according to their charge-to-mass ratio by a quadrupole mass filter, and injected into a fast-flowing carrier gas, whence they are convected along the flow tube and detected by a downstream quadrupole mass spectrometer/channeltron detection system. Both of the quadrupoles are differentially pumped against carrier gas flow through the injection and detection orifices. Reactions of the ions are studied by adding controlled amounts of reactant gases via the gas entry port. A copper jacket to which copper pipes have been brazed surrounds the flow tube. Refrigerant liquids such as liquid nitrogen can be sent through the pipes to cool the flow tube. Ohmic heaters are also connected to the copper jacket to facilitate experiments at high temperatures. Only an outline is shown of the vacuum jacket which encloses the flow tube and thermally insulates it.

available relevant experimental data (mostly from FA and ICR experiments at the time) indicated that gas-phase ion chemistry could indeed be responsible for the production of some of the less complex molecules. Further progress was inhibited by the lack of experimental data on relevant gas-phase ionic reactions, especially relating to the very reactive hydrocarbon ions and other "organic" ions which were presumed to be involved in the chemistry because of the increasing number of organic molecules that were being detected in the interstellar clouds. Unfortunately, FA could not provide the required experimental data because it is in the nature of the FA method that the primary (reactant) ions are usually very reactive with the "ion source gas" from which they are derived, which is present in the flow tube. Thus the determination of rate coefficients and product ions for the reactions of the primary ions with added reactant gases is often complicated to the point of impossibility. The ICR method provided some useful data, but it too suffered from similar problems, and doubts also arose as to the relevance of ICR data to interstellar (low temperature) chemistry because of the suprathreshold energies of ions in ICR cells. Thus, the selected ion flow tube (SIFT) technique was conceived.⁵

The SIFT technique is a variant of FA, i.e., a fast flow tube technique, but with the vital difference that the primary reactant ions are generated in a conventional ion source outside the flow tube as is indicated in Figure 1. The primary ions are mass selected using a differentially pumped quadrupole mass filter and then injected into the carrier gas via a venturi-type inlet, which greatly limits the backflow of carrier gas into the mass filter (which must operate at low pressure). Thus a

current of ions of a given mass-to-charge ratio is introduced into the carrier gas (pressure typically 1 Torr) where they quickly thermalize in collisions with carrier gas atoms to the gas temperature and are convected downstream. The reactions of these primary ions can then be studied with reactant gases which are introduced into the flow tube via an entry port such as that shown in Figure 1 in the same way as for the FA method. However, the crucial difference is that the source gas from which the primary ions are derived is completely excluded from the flow tube, and thus a serious complication is avoided. This has allowed the reactions of numerous ion types to be studied with a great variety of reactant neutral species, some over the wide temperature range 80–600 K, and thus heralded a new chapter in chemical kinetics. The very large amount of data obtained from SIFT experiments in several laboratories around the world has contributed greatly to the better understanding of ion-neutral reactions and to the rapid growth in understanding of interstellar ion chemistry.

We briefly discuss the basic elements of interstellar ion chemistry below as a prelude to discussing the main topic of this Account: "isotope fractionation" in interstellar molecules. Many interstellar molecular species have been detected containing also the rare (heavy) isotopes of some elements, e.g., D, ^{13}C , ^{15}N , etc., and so the abundance ratios of particular molecules containing the common and rare isotopes can be obtained (e.g., HCN/DCN , $^{12}\text{CO}/^{13}\text{CO}$). Thus the exciting discovery was made that the isotopic ratios D/H, $^{13}\text{C}/^{12}\text{C}$, etc. in interstellar molecular are usually greater than the solar-terrestrial ratios.⁶ Why should this be

(5) Adams, N. G.; Smith, D. J. *Mass Spectrom. Ion Phys.* 1976, 21, 349–359. Smith, D.; Adams, N. G. *Adv. At. Mol. Phys.* 1988, 24, 1–49.

(6) Winnewisser, G.; Churchwell, E.; Walmsley, C. M. *Modern Aspects of Microwave Spectroscopy*; Chantry, G. W., Ed.; Academic Press: New York, 1979; pp 313–501.

Table I
Molecules Observed in Diffuse and Dense Interstellar Clouds and in Circumstellar Shells (Marked with Asterisk)

2-atomic	H ₂ , CH, OH, C ₂ , CN, CO, NO, HCl, CS, SiO, PN, SN, AlF*, SO, NaCl*, SiS, AlCl*, KCl*
3-atomic	H ₂ O, C ₂ H, HCN, HNC, HCO, HNO, H ₂ S, SiC ₂ *, C ₂ S, OCS, SO ₂
4-atomic	NH ₃ , C ₂ H ₂ *, H ₂ CO, I-C ₃ H, c-C ₃ H, HNCO, H ₂ CS, C ₂ CN, C ₃ O, HNCS, C ₂ S
5-atomic	CH ₄ *, CH ₂ NH, SiH ₄ *, c-C ₃ H ₂ , CH ₂ CN, CH ₂ CO, NH ₂ CN, HCO ₂ H, C ₄ H, HC ₂ CN
6-atomic	C ₂ H ₄ *, CH ₃ OH, CH ₃ CN, CH ₃ NC, NH ₂ CHO, CH ₃ SH, HC ₂ CHO, C ₆ H
7-atomic	CH ₃ NH ₂ , CH ₃ C ₂ H, CH ₃ CHO, C ₂ H ₃ CN, C ₆ H, HC ₄ CN
8-atomic	CH ₃ C ₂ CN, CH ₃ CO ₂ H
9-atomic	C ₂ H ₅ OH, CH ₃ OCH ₃ , C ₂ H ₅ CN, CH ₃ C ₄ H, HC ₆ CN
10-atomic	CH ₃ COCH ₃ , CH ₃ C ₄ CN
11-atomic	HC ₈ CN
13-atomic ions	HC ₁₀ CN CH ⁺ , SO ⁺ , HCO ⁺ , HCS ⁺ , N ₂ H ⁺ , H ₃ O ⁺ , HCO ₂ ⁺ , H ₂ CN ⁺

so? A possible reason for this is that the interstellar cloud material as a whole is enriched in the rare isotopes due to their different nuclear history compared to that of the solar system. However, it now seems certain that this is not the case, but rather the heavy isotopes of the elements are enriched in the interstellar molecules by the phenomenon of isotope fractionation in ion-neutral reactions. This phenomenon has been studied in some detail using the SIFT technique, the only technique by which such studies can be conducted with acceptable accuracy. It is this particularly exciting area of gas-phase ionic reactions on which this Account is largely focused.

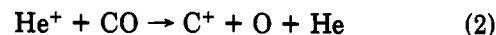
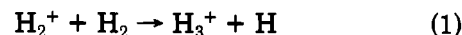
A Brief Overview of Interstellar Chemistry

The objective of interstellar cloud chemistry is to establish how the molecules observed in the clouds are synthesized from their composite elements, which are initially presumed to be in the atomic form. By far the most abundant molecule is H₂; the next most abundant is CO, which is 10⁻⁴ less abundant than H₂, this being roughly in accordance with the cosmical abundances of H relative to C and O. All other molecules are less abundant than CO, the lower limit of detectability being molecules with abundances ~10⁻¹⁰ of H₂. A list of the observed interstellar molecules is given in Table I. The highest order polyatomic molecule positively identified to date is the 13-atomic HC₁₀CN, one of the series of cyanopolyalkynes, HC_nCN (*n* = 2, 4, 6, 8, 10, ...).

So how are these molecules formed? The gas number densities in these clouds are very low by terrestrial standards, being about 10² cm⁻³ in the so-called *diffuse clouds* and about 10⁴ cm⁻³ in the so-called *dense clouds*. Gas-phase reactions can be only bimolecular (two-body) since the probability of a termolecular (three-body) interaction is negligible, even on a time scale comparable to the lifetime of the universe! However, heterogeneous (catalytic) reactions can occur on the surfaces of the micron-sized "dust" grains which exist in association with the gas, particularly in the dense clouds. It is on these grains that H₂ is considered to be formed from the combination of two H atoms which adsorb onto a grain and subsequently desorb into the gas phase as H₂. While it is now accepted that the majority of the other interstellar molecular species are formed in gas-phase ionic reactions, it is ironical that no quantitatively

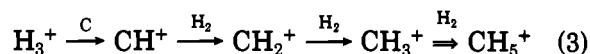
acceptable gas-phase mechanism has been identified for the production of H₂!

Diffuse clouds, as the name implies, are partially transparent to visible and ultraviolet radiation of longer wavelengths than the threshold wavelength for ionization of H atoms (a major constituent). Since the ionization energy of the relatively abundant C atoms is less than that of H atoms, then photoionization of C atoms can occur, producing reactive C⁺ ions and free electrons. Galactic cosmic rays can, of course, penetrate these clouds, and since they are nonselective in the species they ionize, they produce mostly H⁺, H₂⁺, and He⁺ from the most abundant species H, H₂, and He. Dense clouds are opaque to ultraviolet radiation, and so it is the galactic cosmic rays that produce the initial ions, again mostly H⁺, H₂⁺, and He⁺. Two very rapid reactions then occur in both diffuse and dense clouds:



Both reactions occur on every collision between the reactants as many laboratory measurements, including FA, ICR, and SIFT measurements, have shown. The H₃⁺ and C⁺ species so formed (and the C⁺ formed by photoionization of C) are the important precursor ions to most other ions formed in interstellar clouds; we shall be particularly concerned with the reactions of these species (and also CH₃⁺) when we discuss isotope exchange in ion-molecule reactions in the next section.

Hydrocarbon ions can now be formed in the following sequence of reactions:⁷

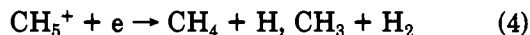


The first reaction involves proton transfer from H₃⁺ ions to C atoms. Proton transfer is known to be facile when it is exothermic (i.e., when the proton affinity (PA) of the acceptor species (C atoms in this case) exceeds the PA of the donor (H₂ in this case)), although it must be said that the H₃⁺ + C reaction has not yet been studied in the laboratory. The next two steps are H-atom abstraction reactions which are also very rapid, as many SIFT measurements have shown. The final step, indicated by the thick arrow, is a bimolecular association reaction, in which the excited complex (CH₅⁺)* is stabilized against unimolecular decomposition back to CH₃⁺ and H₂ by the emission of a photon. This process, known as radiative association, is uncommon in the relatively high-pressure laboratory environment, where the analogous process of third-body stabilized association is much more probable. However, radiative association is considered to be quite common in the low-pressure, low-temperature environment of interstellar clouds. So CH₃⁺ + H₂ → CH₅⁺ + hν is an interstellar reaction; CH₃⁺ + H₂ + M → CH₅⁺ + M* is a laboratory reaction. Extensive studies of three-body association reactions have been carried out from which inferences have been made as to which analogous radiative association reactions will occur in interstellar clouds,⁸ and now careful measurements of bimolecular (radiative) association are being made.

(7) Smith, D.; Adams, N. G. *Int. Rev. Phys. Chem.* 1981, 1, 271-307. *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1988.

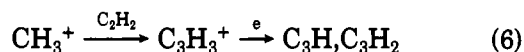
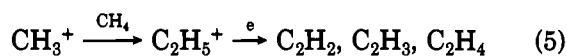
(8) Herbst, E.; Adams, N. G.; Smith, D. *Astrophys. J.* 1983, 269, 329-333. Gerlich, D.; Horning, S. *Chem. Rev.*, in press.

The slow radiative association reactions of C^+ with H and H_2 , generating CH^+ and CH_2^+ , are also involved in the initial phases of interstellar chemistry. However, they are too slow for their rate coefficients to be measured accurately, and so theoretical values of their rate coefficients are usually used in interstellar ion chemical models. The CH^+ and CH_2^+ molecules formed in these reactions react rapidly with H_2 to finally form CH_3^+ . It is important to note that each of the hydrocarbon ions formed in reaction sequence 3 can react with a free electron in the cloud, producing neutral fragments:



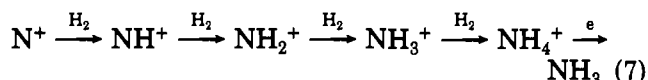
This process, known as dissociative recombination, is largely responsible for converting molecular ions to neutral molecules in ionized gases and is an essential step in the production of the observed neutral interstellar molecules.⁹

Higher order hydrocarbons can now be formed:



In this way, the carbon chain length can be increased and ring molecules can be generated. In fact, reaction sequence 6 is thought to generate the cyclic forms of both C_3H and C_3H_2 , which have been detected in interstellar clouds (see Table I).

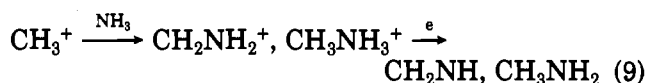
The most abundant nitrogen-bearing interstellar molecule is NH_3 , which can be formed in the following reaction sequence:



The NH_3 can then react with C^+ to form CN-bearing molecules:



The ion-molecule reactions in the above reaction sequences have been studied in detail using the SIFT technique, some over a wide range of temperature. In the $C^+ + NH_3$ reaction 8, the SIFT measurements reveal that two products are formed, as indicated. The reactions which lead to amino compounds have also been studied:



The above are just a few examples of the very many ionic reactions that occur to produce the wide variety of observed interstellar molecules. Other sequences have been identified leading to the production of other interstellar molecules. For example, one which is similar to reaction sequence 7 begins with O^+ and leads to the production of H_3O^+ and then H_2O .

The validity of the ion chemical models which utilize a large amount of laboratory data on gas-phase ionic reactions is seen when the model predictions of the relative abundances of the various observed species are compared to astronomical measurements. The agreement is good for many of the species, although some

Table II
Molecules Detected Containing the Rare Stable Isotopes as Indicated

D	$H_2, H_2O, HCO^+, N_2H^+, HCN, HNC, NH_3, H_2CO, CH_3OH, c-C_3H_2, HC_2CN, HC_4CN$
^{13}C	$CO, CS, HCN, HNC, HCO^+, OCS, H_2CO, c-C_3H_2, HC_2CN, CH_3CN, CH_3OH$
^{15}N	HCN, HNC, NH_3, N_2H^+
^{17}O	CO, HCO^+
^{18}O	$CO, OH, H_2O, HCO^+, H_2CO$
^{29}Si	SiO, SiS
^{33}S	CS
^{34}S	CS, SO, SO_2, OCS, SiS

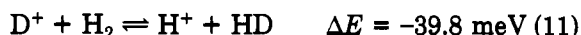
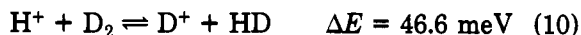
Table III
Rate Coefficients ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$) for the Reactions Indicated at the Temperatures Indicated

	205 K	295 K	k_L
$H^+ + D_2 \xrightarrow{k_{10}} HD + D^+$	2.1 ± 0.2	3.6 ± 0.3	23
$H^+ + HD \xrightarrow{k_{11}} H_2 + D^+$	1.1 ± 0.2	1.7 ± 0.2	24
$D^+ + H_2 \xrightarrow{k_{11}} HD + H^+$	22 ± 1	17 ± 1	21
$D^+ + HD \xrightarrow{k_{10}} D_2 + H^+$	12 ± 1	9.5 ± 1	19

discrepancies remain. For example, the observed abundances of CH^+ in diffuse clouds¹⁰ and NH_3 in dense clouds¹¹ are significantly greater than their predicted abundances. This area of research remains extremely active! Further discussions of interstellar ion chemistry are given in the review papers.^{12,13}

Fractionation of Rare Isotopes into Interstellar Molecules

As was previously mentioned, many interstellar molecules are seen to be enriched in the rare (heavy) isotopes of some elements. This is particularly so for deuterium, which is enriched by as much as a factor of 10^3 in some molecules relative to its cosmic abundance. Similarly, ^{13}C is enriched by about a factor of 2 in most molecules in which it is detected. A list of the molecules in which rare isotopes are observed is given in Table II. It is now clear that the enrichment is due to the phenomenon of "isotope fractionation", which is best exemplified by the following reactions:



The ergicities of the reactions as given (in millielectronvolts) have been calculated from the vibrational zero-point energies of H_2 (0.2702 eV), HD (0.2344 eV), and D_2 (0.1917 eV) and the recombination energies of H^+ (13.595 eV) and D^+ (13.602 eV). Thus reaction 10 is endothermic to the right and reaction 11 is exothermic to the right. What does this imply a priori about the kinetics of these reactions? The simple answer is nothing, except that reaction 11, for example, will be much faster in the forward (exothermic) direction than in the reverse (endothermic) direction at low temperatures (i.e., $T < \Delta E/k_b$, where k_b is the Boltzmann constant). Fortunately, the SIFT technique is

(10) Dalgarno, A.; Black, J. H. *Rep. Prog. Phys.* 1976, 39, 573.

(11) Hartquist, T. W.; Flower, D. R.; Pineau des Forets, G. *Molecular Astrophysics*; Hartquist, T. W., Ed.; Cambridge University Press: Cambridge, 1990; pp 99-112.

(12) Smith, D. *Philos. Trans. R. Soc. London* 1987, A323, 269-286.

(13) Smith, D.; Adams, N. G. *J. Chem. Soc., Faraday Trans. 2* 1989, 83, 1613-1630.

(9) *Dissociative Recombination*; Mitchell, J. B. A., Guberman, S. L., Eds.; World Scientific Publishing Co. Ltd.: Singapore, 1989.

eminently suited to the study of such reactions, and thus the forward and reverse rate coefficients have been measured for both reactions 10 and 11 at 205 and 295 K.¹⁴ The results obtained are reproduced in Table III since they beautifully illustrate the essential features of all such isotope exchange reactions.

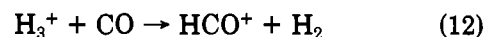
Before interpreting the data given in Table III, a note is required about the rate coefficients (or rate constants) referred to. The Langevin rate coefficient, k_L , is the gas kinetic rate coefficient, calculated according to the equation $k_L = 2\pi q(\alpha/\mu)^{1/2}$ in cgs units, where q is the charge on the ion, α is the polarizability of the reactant molecule, and μ is the reduced mass of the reactants. Thus k_L is the upper limit value of the rate coefficient, and therefore k/k_L indicates the reaction efficiency (where k is the measured rate coefficient). Note then the low efficiencies of the endothermic reactions of H^+ with D_2 and HD, and also note that they are less efficient at 205 K than at 295 K (a manifestation of their endothermicities). Notice, also, that the measured k values for the two reactions at both temperatures differ by almost precisely a factor of 2, which is a manifestation of the influence of statistical factors (or symmetry numbers). Simply stated, the reaction of H^+ with D_2 is approximately twice as likely to produce D^+ than is the reaction of H^+ with HD at the same temperature. Now the exothermic reactions of D^+ with H_2 and HD are much more efficient, increasingly so as the temperature is reduced, and again the influence of statistical factors is clear in that the k value for the $D^+ + H_2$ reaction is about twice that for the $D^+ + HD$ reaction.

These kinetic data can now be used to obtain values for the thermodynamic quantities ΔH and ΔS for reactions 10 and 11. The ratios of the rate coefficients k_{10}/k_{-10} and k_{11}/k_{-11} are equivalent to the equilibrium constants, K , for the reactions at each temperature. Thus, for example, $K_{11} = k_{11}/k_{-11}$. Now, using the standard thermodynamic relations $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$, we can obtain the familiar van't Hoff equation, $\ln K = \Delta S/R - \Delta H/RT$. So from the experimental values of K_{10} and K_{11} at 205 and 295 K, values of ΔH and ΔS can be obtained for reactions 10 and 11. Thus for reaction 10, $\Delta H = 45$ meV and $\Delta S = R \ln 2.2$, and for reaction 11, $\Delta H = -40$ meV and $\Delta S = R \ln 2.1$. The ΔH values are in good agreement with those given above calculated from zero-point energies, although it must be said that significant error figures should be placed on the experimentally derived values.¹⁴ As for the ΔS values, if only statistical factors were important in determining the entropy change, then ΔS would be equal to $R \ln 2$ for both reactions. The values derived from the SIFT data are indeed quite close to $R \ln 2$. However, it is well appreciated that mass factors and rotational effects also contribute to ΔS which must be calculated from total partition functions. When this is done, the ΔS values obtained are $R \ln 2.45$ (reaction 10) and $R \ln 1.73$ (reaction 11).¹⁴

What are the implications of these results for interstellar chemistry? One is that, in cold interstellar clouds, reaction 11 ensures that most of the deuterium will be contained in HD. This follows because at low temperatures k_{11} is very close to k_L for the reaction (see Table III), and $k_{-11} (\approx k_{11} \exp(-\Delta H/RT))$ as obtained

from the above thermodynamic relations) must be very small in view of the large ΔH values for the reverse (endothermic) reaction. (At a gas cloud temperature of 20 K, $k_{-11} \approx 10^{-10}k_{11}$!). Since the cosmic abundance ratio $D/H \approx 10^{-5}$, then it follows that in cold clouds $HD/H_2 \approx 10^{-5}$. Of course, this does not preclude the inclusion of some deuterium in many other interstellar molecules because they are present in much lower abundance than HD.

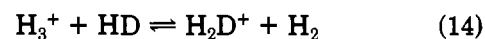
It was indicated in the previous section that H_3^+ was a very important initial ion in interstellar chemistry. This ion is very likely to transfer a proton to most molecules in view of the relatively low proton affinity of H_2 (see the discussion in the previous section). For example, the proton-transfer reaction with CO,



occurs on every collision at room temperature and below and must be facile in interstellar clouds, producing the ubiquitous interstellar ion HCO^+ . Many SIFT studies have shown that proton transfer from H_3^+ to many different molecules occurs at the gas kinetic rate and that when the reactions are very exothermic (i.e., when $PA(\text{acceptor}) \gg PA(H_2)$) then total or partial dissociation of the protonated molecule occurs:



Clearly, therefore, if the H_3^+ were deuterated, then the analogous reaction of (say) H_2D^+ would also involve the transfer of a deuteron to produce deuterated products, and so it became important to study the reactions of H_3^+ with the most abundant deuterium-containing molecule, HD. This was carried out in the context of a SIFT study of the reactions of H_3^+ , H_2D^+ , HD_2^+ , and D_3^+ with H_2 , HD, and D_2 at 300 and 80 K.¹⁵ It was found that H/D exchange was indeed facile in the reaction



The forward (exothermic) reaction rate coefficient, k_{14} , approached k_L at low temperatures and, as expected, the reverse (endothermic) reaction rate coefficient, k_{-14} , decreased with decreasing temperature. Thus the interstellar implication is clear. Fractionation of D will occur into H_3^+ to produce H_2D^+ , the subsequent reactions of which will result in deuterated interstellar ions (and neutral molecules following dissociative recombination) which are also fractionated in deuterium. Quantitative calculations of the degree of fractionation of D into H_2D^+ via reaction 14 require a value of the enthalpy change, ΔH , in the reaction. Calculations of ΔH are straightforward since the rotational energy states of H_3^+ , H_2D^+ , H_2 , and HD are accurately known. Such calculations show that ΔH varies with temperature, with a maximum value of -20 meV at 0 K falling to a minimum value of -10 meV at 115 K and increasing again to a high-temperature value of -13 meV.¹⁶

It was also indicated in the previous section that CH_3^+ was a very important ion in the chemistry of in-

(15) Adams, N. G.; Smith, D. *Astrophys. J.* 1981, 248, 373-379. Adams, N. G.; Smith, D. *Reactions of Small Transient Species*; Fontijn, A., Clyne, M. A. A., Eds.; Academic Press: London, 1983; pp 311-385.

(16) Smith, D.; Adams, N. G.; Alge, E. *Astrophys. J.* 1982, 263, 123-129. Giles, K.; Adams, N. G.; Smith, D. *J. Phys. Chem.*, in press.

(14) Henchman, M. J.; Adams, N. G.; Smith, D. *J. Chem. Phys.* 1981, 75, 1201-1206.

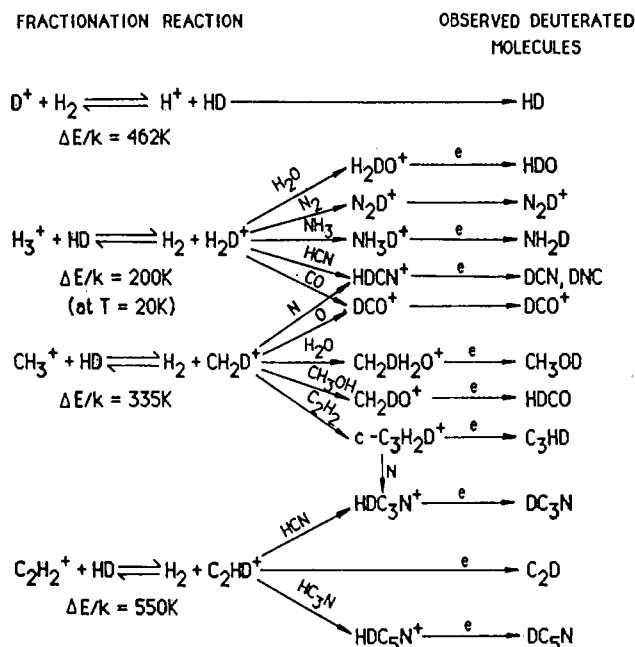


Figure 2. Deuterium fractionation in interstellar molecules.

terstellar clouds, since from it many other molecules originate. It follows again, therefore, that CH_2D^+ , if present in significant concentrations, would be an important precursor to many deuterated molecules. Thus a SIFT study was performed of the reactions of CH_3^+ , CH_2D^+ , CHD_2^+ , and CD_3^+ with H_2 , HD , and D_2 ¹⁷ in which the following reactions received particular attention:



The forward and reverse rate coefficients were determined for these reactions at 295, 205, and 80 K, and a van't Hoff plot was obtained, from which values of ΔH and ΔS were obtained as -29 meV and $R \ln 1.5$, respectively. Again, the forward rate coefficient, k_{15} , approached k_L at low temperature. The large ΔH values for the reactions ensure that the reverse reaction will be very slow at low temperatures. Hence, considerable fractionation of D into CH_3^+ will occur, and so CH_2D^+ will be an important precursor ion to many deuterated interstellar molecules.

SIFT studies of many other H/D exchange reactions of special interest to interstellar chemistry have been carried out, including the $C_2H_2^+ + HD$ ¹⁸ and the $HCO^+ + D$ and $DCO^+ + H$ ¹⁹ reactions, the last two being particularly challenging experimentally since D and H atoms are the neutral reactants. The inescapable conclusion to be drawn from all of these SIFT studies of D/H exchange reactions is that the observed enhancement of D in many interstellar molecules must indeed be largely due to gas-phase isotope fractionation as summarized in Figure 2. This conclusion is based largely on the results of the many SIFT experiments and is undoubtedly one of the major triumphs of the SIFT technique.

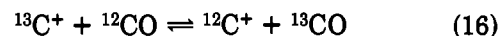
(17) Smith, D.; Adams, N. G.; Alge, E. *J. Chem. Phys.* 1982, 77, 1261-1268.

(18) Herbst, E.; Adams, N. G.; Smith, D.; DeFrees, D. *J. Astrophys. J.* 1987, 312, 351-357.

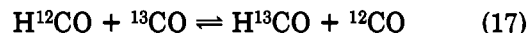
(19) Henchman, M. J.; Paulson, J. F.; Smith, D.; Adams, N. G.; Lindinger, W. *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1988; pp 201-207.

SIFT studies of D/H exchange in ion-molecule reactions continue, since they can also produce insight into the mechanisms of such reactions at thermal energies. A recent paper²⁰ describes a study of exchange in the reactions $CH_5^+ + CD_4/CD_5^+ + CH_4$, $NH_4^+ + ND_3/ND_4^+ + NH_3$, and $H_3O^+ + D_2O/D_3O^+ + H_2O$ and discusses the "shuttling" of protons and deuterons within the proton (deuteron) bound dimers (which are the intermediate complexes in these reactions). This results in the mixing of H and D within the reaction products. Such complex experiments can only be carried out with meaningful results because of the separation of the reactant ions from their parent gas which is such an important feature of the SIFT technique.

Fractionation of the heavy isotopes of other elements is also evident in some interstellar molecules, notably ¹³C in CO. This results from the following reaction:



The enthalpy change in the forward reaction (left to right) is -3.0 meV as calculated from the zero-point energies of ¹²CO and ¹³CO. The SIFT measurements of k_{16} and k_{-16} at 80, 200, 300, and 500 K²¹ provided a value for ΔH of $-(3.5 \pm 0.4)$ meV and $\Delta S \approx 0$, as expected. Again, in common with the H/D exchange reactions, the forward rate coefficient (k_{16}) approached k_L at low temperatures. The last observation and the accurate laboratory kinetic data obtained allow both k_{16} and k_{-16} to be obtained at any temperature below 500 K. Thus the expected enhancement of ¹³CO (relative to ¹²CO) in interstellar clouds can be estimated and shown to be in acceptable agreement with the astronomical measurements. ¹³CO exchange also occurs in the following reactions:



SIFT studies of these reactions²¹ indicated that $\Delta H \approx -1$ meV in the forward reaction, so that fractionation of ¹³C into HCO^+ via this reaction would only be important at very low temperatures.

Concluding Remarks

Isotope fractionation in ion-molecule reactions is facile at the low temperatures of interstellar clouds, especially so for deuterium because of the large change in zero-point energy that results when an H atom is replaced by a D atom in a molecule. Thus the isotope ratios D/H, ¹³C/¹²C, ¹⁵N/¹⁴N, ¹⁸O/¹⁶O, etc. in interstellar molecules will not be representative of the isotope ratios in the cloud material as a whole. This is of some disappointment to astrophysicists who wish to know what the isotope ratios of the common elements are around the Milky Way (and other galaxies) since they would give an indication of the nuclear history of remote regions. However, all is not lost in this regard because there remains hope that, given sufficient understanding of the phenomenon of isotope fractionation (kinetics and energetics), careful modeling of the ion chemistry in particular regions (clouds) would provide estimates of isotope ratios in the cloud as a whole. This area of research remains a very active one with many interesting programs and problems being pursued.

(20) Henchman, M. J.; Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Processes* 1991, 109, 105.

(21) Smith, D.; Adams, N. G. *Astrophys. J.* 1980, 242, 424-431.

More than a dozen SIFT apparatuses are being used in laboratories around the world, and the experiments are becoming more ambitious and sophisticated. For example, a major effort is being undertaken to discover how the larger molecules detected in interstellar clouds are synthesized. The larger the molecule the more isomeric forms are possible; both open-chain and cyclic isomeric ions are often energetically allowed products of some ion-molecule reactions which can be identified by their (often) very different reactivities with particular molecules, e.g., CO.^{22,23} Studies of interstellar molecules and interstellar ion chemistry also provide critical data from which the physical conditions and the

(22) Bohme, D. K. In *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1988.

(23) Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Processes* 1987, 76, 307-317.

chemical history of interstellar clouds can be deduced, and thus the laboratory studies of gas-phase ion chemistry outlined in this paper are a significant contribution to astrophysics as well as to astrochemistry.

Of course, the studies of the reactions of ions in the gas phase extend beyond the area of interstellar chemistry to include the ion chemistry of, for example, planetary atmospheres, laboratory etchant plasmas, and gaseous laser plasmas. Much thermochemical data are obtained from such studies, as well as a deeper insight into the mechanisms of ionic interactions (for this isotopic labeling is particularly profitable). No doubt research into gas-phase ions will continue for a very long time to come.

We are most grateful to Professor Michael Henchman for the continuous stimulus and insight he has provided and the interest he has shown in the isotope exchange work.

Layered Metal Phosphates and Phosphonates: From Crystals to Monolayers

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Received March 23, 1992

Although metal salts of phosphoric acid have been known for over a century, research on layered metal phosphates and their derivatives began only in the late 1950s, when it was recognized that some of these salts could be useful as cation exchangers in radioactive waste streams.¹ Because of the extremely low solubility product of the tetravalent metal phosphates, these materials were available at that time only in the form of amorphous gels, and it was not until Clearfield and Stynes² prepared the first crystalline compounds in 1964 that their structures and chemical reactivity began to be clearly understood. Layered solids of this type have since been studied extensively as inorganic ion exchangers.³ They have also enjoyed significant interest as catalysts and catalyst supports due in part to the success of one member of their family, (VO)₂P₂O₇,

in catalyzing the selective air oxidation of butane and butenes to maleic anhydride.⁴

Organic phosphates and phosphonates of the tetravalent metals, which were first made in the 1970s by Yamanaka⁵ and Alberti,⁶ have structures that are very closely related to their inorganic analogues. These compounds have two endearing properties that have stimulated an extensive exploration of their chemistry over the past several years. First, unlike many solid-state materials they are made at low temperatures, often from aqueous solutions. Most solid-state reactions require high temperatures for interdiffusion of ions and/or dissolution of precursor phases, and so the bond connectivity of the final product usually bears little resemblance to that of the starting materials. However, when the temperature of synthesis and crystal growth is low, it is possible to make well-ordered solid materials in which the bonding within the reactant molecules is

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(1) (a) Kraus, K. A.; Phillips, H. O. *J. Am. Chem. Soc.* 1956, 78, 644. (b) Kraus, K. A.; Phillips, H. O.; Carlson, T. A.; Johnson, J. S. *Proc. Int. Conf. Peaceful Uses At. Energy*, 2nd 1958, 28, 3. (c) Vesely, V.; Pekarek, V. *Talanta* 1972, 19, 219.

(2) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* 1964, 26, 117.

(3) (a) Alberti, G. *Acc. Chem. Res.* 1978, 11, 163. (b) Clearfield, A. *Chem. Rev.* 1988, 88, 125.

(4) Centi, G.; Trifiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* 1988, 88, 55.

(5) (a) Yamanaka, S. *Inorg. Chem.* 1976, 15, 2811. (b) Yamanaka, S.; Koizumi, M. *Clays Clay Miner.* 1975, 23, 477. (c) Yamanaka, S.; Tsujimoto, M.; Tanaka, M. *J. Inorg. Nucl. Chem.* 1979, 41, 605. (d) Yamanaka, S.; Matsunaga, M.; Hattori, M. *J. Inorg. Nucl. Chem.* 1981, 43, 1343.

(6) Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* 1978, 40, 1113.