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The Ion Chemistry of Interstellar Clouds

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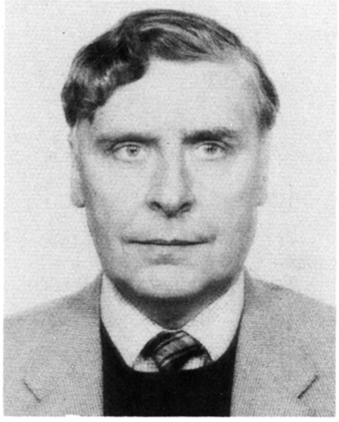
I. Introduction

One of the most interesting events in astronomy during the last few decades has been the discovery of many types of molecules in the *diffuse* and *dense* interstellar clouds which pervade the Milky Way galaxy. This discovery was all the more interesting and exciting because it was quite unexpected, and it immediately posed the question as to how molecules can be formed under such harsh conditions.

The *diffuse* interstellar clouds are so called because they are of very low density consisting mainly of H atoms and H_2 molecules ($\sim 10^2$ cm^{-3}) together with a low but observable concentration of micron-sized "dust" particles and therefore stellar visible and ultraviolet (UV) radiation can penetrate them without total attenuation. It was in such clouds that the first interstellar molecules (i.e. CH, CH^+, and CN) were detected via their characteristic absorption spectra in the visible region of the spectrum by using ground-based telescopes,[1,2] and with the advent of satellite-borne instruments, a wider range of molecules have been detected in diffuse clouds by vacuum UV absorption spectroscopy.[3] Because destructive UV radiation can penetrate and heat diffuse clouds, the molecules which can survive in them are restricted to "simple" diatomic species and the ambient temperature is relatively high ($\sim$100–200 K).

In contrast, the *dense* molecular clouds are of much higher density and consist mostly of H_2 and He ($\sim 10^4$–10^6 cm^{-3}) together with "dust" grains at greater concentrations than exist in diffuse clouds. Thus the interior of these clouds are shielded from destructive stellar radiations, the temperature is consequently much lower (<100 K, and in some clouds $\sim$10 K), and complex polyatomic molecules are detected in them,[4] the most complex detected to date being the 13-atom linear cyanopolyyne molecule, $HC_{11}N$. A compilation of the molecules detected in diffuse and dense clouds and in circumstellar shells is given in Table I.



David Smith was born in Stoke-on-Trent, England. He obtained a B.A. degree in physics and chemistry at the University of Keele in 1959 and a Ph.D. (1962) and a D.Sc. (1974) degrees at the University of Birmingham where he was a member of the academic staff from 1962 to 1990, achieving a Personal Chair in Chemical Physics in 1984. In 1973 he was elected to be a Fellow of the Institute of Physics (London) and in 1988 elected to be a Fellow of the Royal Society. In 1990 he was awarded the degree of D.Sc. (Honoris Causa) by the University of Keele. He is presently University Professor in the Institute for Ion Physics at the University of Innsbruck, Austria, and recently he was awarded the Schrödinger prize for his contributions to atomic and molecular science.

The purpose of this paper is to try to answer the question posed above—at least in general terms—and thus to summarize the chemistry of interstellar clouds which results in the creation of the molecules observed in these regions. It must be said at once that much of this chemistry is reasonably well understood, but problems remain which will be identified and discussed. What is no longer in doubt is that the majority of the molecular species detected to date are synthesized by gas-phase reactions of positive ions with neutral atoms and molecules, which produce a variety of new ions which undergo neutralization reactions, principally with free electrons, producing the observed neutral molecules. This paper will focus on the ion–neutral reactions and the ion–electron dissociative recombination reactions which together largely constitute gas-phase interstellar chemistry, although mention will also be made of positive ion–negative ion mutual neutralization which has been tentatively invoked as an additional neutralization process. Reference will also be made to the laboratory experiments which have provided the necessary kinetic data on ionic and electronic gas-phase

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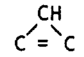
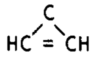
Table I. Molecules Detected in Interstellar Clouds and in Circumstellar Shells (Marked with an Asterisk)[a]

HYDROGEN

H_2

MOLECULES CONTAINING C AND H

CH	$C{\equiv}C$	$C{\equiv}CCH$	$(C{\equiv}C)_2H$	$^*(C{=}C)_2{=}C$	
$\underline{CH^+}$	$C{\equiv}CH$	$H_2C{=}C{=}C$	$H_2C{=}CC{\equiv}C$	$(C{\equiv}C)_3H$	
CH_4	$HC{\equiv}CH$	$H_3CC{\equiv}CH$	$(C{\equiv}C)_2CH$		
	$^*H_2C{=}CH_2$	$^*C{=}C{=}C$	$H_3C(C{\equiv}C)_2H$		

MOLECULES CONTAINING O, C AND H

OH	$(C{\equiv}C)_2CO$	CH_3OH	CH_3CO_2H
H_2O	HCO	HCO_2H	CH_3OCH_3
$\underline{H_3O^+}$	$\underline{HCO^+}$	CH_2CO	CH_3COCH_3
CO	$\underline{HOC^+}$?	CH_3CHO	$HC{\equiv}CCHO$
$C{=}CO$	H_2CO	CH_3CH_2OH	
$C{\equiv}CCO$	$\underline{HOCO^+}$		

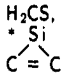
MOLECULES CONTAINING N, C AND H

NH	$\underline{HCNH^+}$	CH_3CN	$H_3CC{\equiv}CCN$
$\underline{N_2H^+}$	CH_2NH	CH_3NC	$H(C{\equiv}C)_2CN$
NH_3	CH_3NH_2	$C{\equiv}CCN$	$H_3C(C{\equiv}C)_2CN$
CN	NH_2CN	$HC{\equiv}CCN$	$H(C{\equiv}C)_3CN$
HCN	$^*HCCN$	$HC{\equiv}CNC$	$H(C{\equiv}C)_4CN$
HNC	CH_2CN	CH_3CH_2CN	$H(C{\equiv}C)_5CN$
		$H_2C{=}CHCN$	

MOLECULES CONTAINING O AND N

NO, HNO, $HNCO$, NH_2CHO

MOLECULES CONTAINING S, Si AND OTHER ELEMENTS

SO, $\underline{SO^+}$, SN, CS, H_2S, SO_2, OCS, $\underline{HCS^+}$, H_2CS,
CH_3SH, $HNCS$, C_2S, C_3S,HCl, PN, SiS, SiO, 
$^*SiC$, $^*SiN$, $^*SiH_4$, $^*c{-}SiC_2$, $^*SiC_4$, $^*CP$, $^*NaCl$, $^*AlCl$, $^*KCl$, $^*AlF$

[a] This list of interstellar molecules has been compiled from several sources, including refs 6, 17, and 29. A particularly valuable compilation of interstellar molecules, which includes the rest frequencies of the microwave transitions which identify the molecules, the clouds in which they have been detected and references to the original papers, is given in ref 95.

reactions, and to the ion-chemical models which utilize the laboratory data to trace the chemistry to predict interstellar molecular abundances. It is the results of these model calculations which give such strong support to the conclusion that gas-phase ion chemistry is the major process by which interstellar molecules are synthesized.

It is not surprising that many of the molecular species detected in dense interstellar clouds are seen to contain the rare isotopes of some elements (e.g. D, ^{13}C, ^{18}O, etc.), but what was at first surprising is that the abundance ratios of some molecules containing the rare and the common isotopes (e.g. DCN/HCN) were in some cases orders of magnitude greater than those expected from the solar–terrestrial (and cosmic) isotopic ratios. Following extensive laboratory studies, it is now understood that this is due to the phenomenon of "isotope fractionation" in gas-phase ion–molecule reactions. This interesting phenomenon will be briefly described in this paper.

It would be remiss not to mention that molecular synthesis can occur on the surfaces of the dust grains which always exist in association with the interstellar gas, especially in dense clouds. This topic has been considered in detail by some researchers (see, for example ref 5) and it will not be discussed in this paper, except to note that it is necessary to invoke grain surface catalysis for the synthesis of the most abundant interstellar molecule, H_2, since no gas-phase processes yet identified is efficient enough! It should be also mentioned for the sake of completeness that molecules have been detected in the atmospheres of some cool (late-type) stars, often termed circumstellar shells. At the higher gas densities and temperatures that are obtained in such atmospheres, neutral–neutral reactions are most important in generating molecules. This interesting chemistry will not be discussed here; rather the reader is referred to ref 6.

This short review is organized as follows. An overview of the ion chemistry of diffuse and dense clouds which leads to the observed molecules is presented first. Then the phenomenon of isotope fractionation and the neutralization processes that convert ions to neutral molecules are discussed. A short note on the laboratory techniques used to provide data on ionic reactions is included, and some concluding remarks are made.

II. Diffuse Cloud Chemistry

Because of the intensity of the interstellar ultraviolet radiation field, a substantial fraction of the matter in diffuse clouds is in the atomic form. Thus the major constituents are H atoms and H_2 molecules, with C, N,

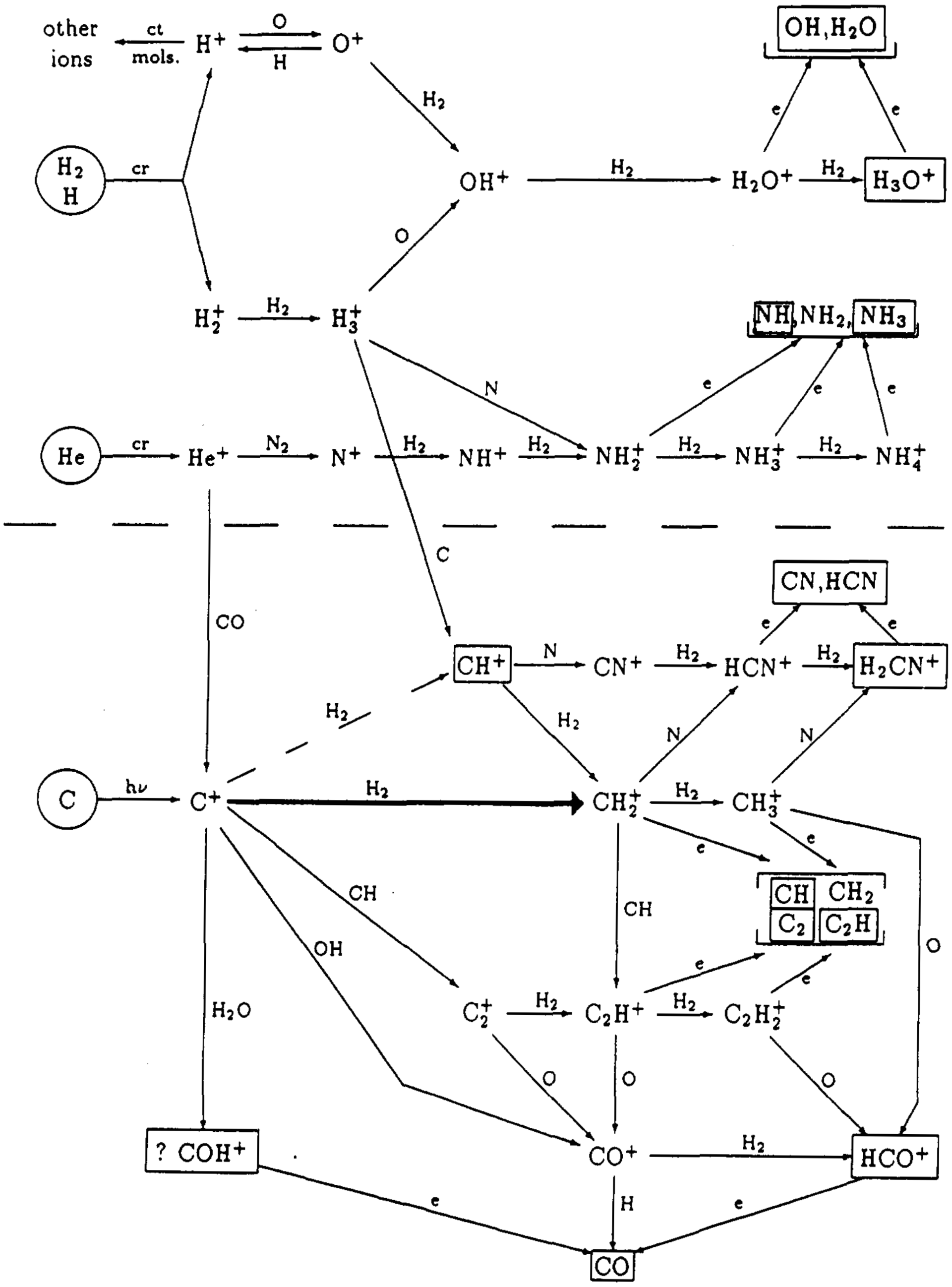


Figure 1. The ion chemistry of diffuse interstellar clouds. The molecules in boxes are known interstellar molecules, but of those only CH^+, CH, C_2, OH, CN, and CO have been detected in diffuse clouds. The remaining molecules in boxes have been detected by millimeter wave astronomy in dense clouds, but they are strongly implicated in diffuse cloud chemistry as the figure indicates. The question mark associated with COH^+ indicates a tentative detection. The thick arrow indicates the radiative association reaction of C^+ with H_2; the dashed arrow indicates the endothermic reaction of C^+ with H_2 (see text). The symbols along the arrows indicate the following: e, dissociative recombination; cr, cosmic ray ionization; ct, charge transfer; *hν*, photoionization.

and O atoms as minor but very important species which play a vital role in the gas-phase ion chemistry. Two distinct ionization processes can be identified: (i) the photoionization of C atoms by stellar UV producing C^+ ions and electrons, and (ii) the ionization of H, H_2, and He by galactic cosmic rays producing H^+, H_2^+, He^+, and electrons. From these positive ions begins the two strands of the gas-phase chemistry illustrated in Figure 1. The chemistry beginning with C^+ is probably more important in the outer parts of the diffuse clouds where the UV is more intense, whereas the chemistry beginning with H^+, H_2^+, and He^+ occurs throughout the clouds because of the great penetrating power of galactic cosmic rays.

The primary H^+ ions can react with O atoms by "accidental resonance" charge transfer producing O^+ ions:[8]

$$H^+ + O \rightleftharpoons O^+ + H - 0.019\ \text{eV} \quad (1)$$

Although this process is slightly endothermic at the temperatures of diffuse clouds, it can result in a significant production rate of O^+ ions, which react rapidly with H_2, producing OH^+. The H_2^+ primary ions react rapidly with H_2, producing H_3^+, which react rapidly with O atoms, producing OH^+. The OH^+ reacts with H_2 to give H_2O^+ which reacts with H_2 to give H_3O^+ in the sequence of H atom abstraction reactions indicated in Figure 1. The closed-shell ion H_3O^+ is at the end of the chain, since it does not react with H_2, but it does undergo dissociative recombination with electrons:

$$H_3O^+ + e \rightarrow H_2O, OH, H \qquad (2)$$

This phenomenon is discussed in section V; it is sufficient to say here that it is known from recent laboratory experiments[7] that OH is the dominant product of reaction 2 and H_2O may be a product also. A similar sequence of H-atom abstraction reactions probably leads to the production of NH (recently detected in diffuse clouds), NH_2, and NH_3. It could begin with the production of N^+ (from the $He^+ + N_2$ reaction) or by the following reaction:

$$H_3^+ + N \rightarrow NH_2^+ + H \qquad (3)$$

Although this reaction is exothermic, it has not been observed in laboratory experiments. However most of the ion–neutral reactions involving H_2, N, and O given in Figure 1 have been studied experimentally and the rate coefficients have been determined.[8] (Note: The N_2 referred to in Figure 1 is probably formed in the reaction of NH radicals with N atoms.)

The hydrocarbon chemistry begins with the slow radiative association reaction of C^+ with H_2, producing CH_2^+, the rate coefficients for which had to be obtained theoretically[9,10] until quite recently when an experimental value (7×10^{-16} cm^3 s^{-1} at 80 K) was obtained by Gerlich and his colleagues[11] which is in acceptable agreement with theory. CH_2^+ reacts rapidly with H_2 to form CH_3^+; dissociative recombination of these ions can produce CH and CH_2 which can themselves react with C^+, CH_2^+, and CH_3^+, producing 2-carbon species as is indicated in Figure 1. Also indicated in Figure 1 is the reaction between C^+ and H_2 producing CH^+. This reaction is endothermic by 0.4 eV, which is far too great to allow the reaction to proceed for thermalized ions in a quiescent diffuse cloud. However, if the interaction energy of C^+ and H_2 is elevated, as would be the case, for example, in shocked regions of the clouds, then the reaction could proceed at a significant rate, and this phenomenon has been invoked to explain the anomalously high abundance of CH^+ observed in diffuse clouds.[12] Also, it is worthy of note that the dissociative charge transfer reaction

$$He^+ + CO \rightarrow C^+ + O + He + 2.2\ \text{eV} \qquad (4)$$

is exothermic by 2.2 eV and thus can only generate the C^+ ions and O atoms in their electronic ground states (no electronically excited states are accessible). So it is very probable that the 2.2 eV of energy appears as kinetic energy which presumably is shared between the C^+ and O in the dissociation of the excited CO^+ ion. Hence the C^+ ions possess about 1 eV of kinetic energy, and so when He^+ reacts with CO in interstellar clouds it produces kinetically excited C^+ ions. This will enhance the probability of their reaction with H_2 to produce CH^+, especially if the H_2 has residual vibrational and/or rotational energy. This then could be a significant source of CH^+ ions in diffuse (and dense) interstellar clouds. Detailed calculations are needed to ascertain whether or not this is a significant effect. A similar argument has been given for the kinetic excitation of N^+ (formed in the reaction of He^+ with N_2) in dense interstellar clouds, which enhances the reaction rate of N^+ with H_2 to form NH^+, a first step in the synthesis of NH_3 in dense interstellar clouds.[13] The kinetic excitation of other ions in interstellar clouds and its likely influence on the ion chemistry has also been discussed.[13,14] The link between the cosmic ray-initiated and the ultraviolet-initiated chemistry is made via reaction 4 and via the proton-transfer reaction:

$$H_3^+ + C \rightarrow CH^+ + H_2 \qquad (5)$$

This reaction has not yet been studied in the laboratory because of the practical problem of producing C atoms in sufficient concentrations. However, it is known from numerous experiments that when proton transfer is exothermic it proceeds rapidly[15] and so reaction 5 is considered to occur efficiently. A detailed theoretical study of reaction 5 has recently been carried out.[16]

The ion-chemical routes to the strongly-bonded CO- and CN-bearing molecules involve the reactions between hydrocarbon ions and O and N atoms respectively (see Figure 1), although neutral–neutral reactions between N atoms and some diatomic molecules (e.g. OH, CH, C_2) may also produce CO and CN.[17] These strongly-bonded molecules are resistant to photodissociation and so can have long lifetimes in diffuse clouds. In contrast, more weakly-bonded molecules (such as NH_3) are unlikely to be present in large concentrations.

Detailed quantitative models of diffuse cloud chemistry have been constructed, and good agreement is obtained between the molecular abundances predicted by these models and the observed abundances for several molecular species.[3] The low predicted abundance of CH^+ remains a problem, although the argument revolving around reaction 4 might offer some hope of a solution. For further details of diffuse cloud chemistry and the modeling, the review by van Dishoeck is useful.[17]

III. Dense Cloud Chemistry

Dense clouds consist largely of H_2, He, and dust grains, and chemically-active minor constituents including H, C, N, O, and S atoms. The ion chemistry is initiated by the action of cosmic rays on the major constituents producing H^+, H_2^+, and He^+. As before, H_2^+ is rapidly converted to H_3^+, but in contrast to diffuse clouds, the major source of C^+ ions is considered to be via reaction 4 since the interior of dense clouds is shielded by dust and grains from ionizing stellar radiation. The lower temperatures, higher gas number densities and the much weaker radiation field in dense clouds are conducive to the synthesis of larger molecules, as are indeed observed. So the chemically-active primary ions are H_3^+ and C^+, and the initial chemistry is similar to that of diffuse clouds in which the reactions of H_3^+ with O atoms finally produces OH and H_2O and with C atoms produces CH_3^+, and NH_3 production starts from N^+ ions (but see the concluding section of this paper for cautionary remarks).

A glance at the types of interstellar molecules given in Table I reveals that there are three major groupings, i.e. carboxy molecules, cyano and amino molecules, and hydrocarbon molecules. There are obviously many fewer species comprising N–O bonds, which is quite consistent with the wide-ranging laboratory studies of a very large number of ion–molecule reactions of interstellar interest which reveal that N–O-bonded ionic products are relatively rare.[8,18] This is the justification for representing the ion chemistry of dense clouds by Figure 2 in which the left-hand, central, and right-hand columns roughly summarize the carboxy, hydrocarbon, and cyano/amino chemistries, respectively, which will now be briefly described beginning with the hydrocarbon chemistry (one eye should be kept on Figure 2).

1. Hydrocarbon Molecules

The hydrocarbon chain develops with the radiative association reaction of CH_3^+ with H_2:

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \tag{6}$$

in which the excited $(CH_5^+)^*$ product is stabilized against unimolecular dissociation to reactants by the emission of a photon. This is the analogue of three-body association in which the excitation energy of the (CH_5^+) (in this example) is removed by a collision with a chemically inert third body (often a helium atom in laboratory experiments). The likely importance of radiative association reactions in interstellar chemistry was realized from studies of three-body association reactions of CH_3^+ ions with several known interstellar gases, including of course H_2 and CO, and polar gases such as H_2O, NH_3, HCN, CH_3OH, and CH_3CN.[19] Much has been written on this topic. (See, for example, the review article[20] and the article by Gerlich and Horning in this special issue of *Chemical Reviews*.) It is sufficient to say here that it is almost certainly a very effective process in cold interstellar[21] clouds resulting in the production of CH_5^+ via reaction 6 which undergoes dissociative recombination probably producing CH_4 (and probably CH_3).[22] (We briefly discuss the products of dissociative recombination reactions in section V.1.) Certainly, proton transfer will occur from CH_5^+ to CO thus generating CH_4 (and HCO^+). Recombination of CH_3^+ can produce CH and CH_2, and so all the small hydrocarbon molecules, CH, CH_2, CH_3, and CH_4 are probably generated. Reactions of these small hydrocarbons with C^+ and CH_3^+ now produce molecules with two carbon atoms (by the process of "carbon insertion"). For example, the reaction

$$C^+ + CH_4 \rightarrow C_2H_2^+ + H_2,\ C_2H_3^+ + H \tag{7}$$

results in both $C_2H_2^+$ and $C_2H_3^+$ ions. A selected-ion flow tube (SIFT) study has recently been carried out on the reactions of these ions[23] which shows that $C_2H_2^+$ has a propensity to undergo charge-transfer reactions with many interstellar molecules, and $C_2H_3^+$ shows a propensity to transfer a proton to many interstellar species. In both cases, the neutral product is C_2H_2 which must indeed be an abundant interstellar species. Although C_2H_2 cannot be detected by its rotational emissions (i.e. by millimeter wave astronomy) because of its symmetry, it has been detected in interstellar gas and in circumstellar shells by infrared absorption spectroscopy.[6] Dissociative recombination of $C_2H_2^+$ and $C_2H_3^+$ can also occur generating C_2H and C_2H_2.

Further carbon insertion reactions between C^+, CH_3^+, other hydrocarbon ions, and hydrocarbon neutral molecules are illustrated in Figure 2. The reaction of C^+ with C_2H_2 produces C_3H^+ which initiates a very interesting part of the hydrocarbon chemistry. Laboratory studies have shown[24] that the three-body reaction

$$C_3H^+ + H_2 + He \rightarrow 1\text{-}C_3H_3^+,\ c\text{-}C_3H_3^+ + He \tag{8}$$

produces both the linear and cyclic isomers of $C_3H_3^+$ as indicated. Hence it has been proposed[25] that the corresponding radiative association reaction in interstellar clouds

$$C_3H^+ + H_2 \rightarrow C_3H_3^+ + h\nu \tag{9}$$

will produce at least a fraction of the cyclic isomer c-$C_3H_3^+$, which in recombination with electrons could produce c-C_3H_2, the first cyclic molecule to be detected in interstellar clouds.[26] (Note however, that the cyclic molecule, c-SiC_2, had been previously detected in the circumstellar envelope of IRC+10216.[27]) Recently the two-body (radiative) association reaction 9 has been observed and the rate coefficient measured by Gerlich and colleagues[11] in their low-temperature, low-pressure ion-trap experiment.

Further lengthening of the hydrocarbon chains occurs via the reactions of C^+ with increasingly larger hydrocarbons as illustrated in Figure 2. A recent SIFT study of the reactions of ions in the series $C_nH_m^+$ (n = 4, 5, 6; m = 0–6) at both 300 K and 80 K[28] indicated that only the very unsaturated ions (i.e. $m \leq 1$) reacted at a significant rate with H_2 and CO and so ions with $m \geq 2$ are unreactive with these most abundant molecules in interstellar clouds and are therefore available for reactions with other species in the clouds including hydrocarbon molecules. (The very interesting reactions of $C_nH_m^+$ ions with CO are discussed below.) Thus the reactions of the unsaturated hydrocarbon ions with small (abundant) hydrocarbon molecules (e.g. CH_4, C_2H_2, CH_3CCH) can result in long-chain hydrocarbons as is illustrated in Figure 3 in which a possible route to the production of interstellar benzene is also indicated. It must be emphasized again that these chemical schemes are only qualitative and detailed quantitative modeling will be required to determine the relative importance of the various routes to particular interstellar molecules.

2. Cyano and Amino Molecules

The cyano and amino molecules given on the right side of Table I which are so numerous in interstellar clouds are most probably formed in the reactions between C^+ and small hydrocarbon ions and both nitrogen-bearing molecules and N atoms. The simplest species HCN and HNC can be formed in the reactions

$$C^+ + NH_3 \rightarrow H_2CN^+ + H \tag{10}$$

$$CH_3^+ + N \rightarrow H_2CN^+ + H \tag{11}$$

followed by

$$HCNH^+ + e \rightarrow (HCN,HCN) + H \tag{12}$$

The branching ratio into HCN and HNC in reaction 12 is not known, although the lower energy isomer HCN is usually the most abundant in interstellar clouds.[29]

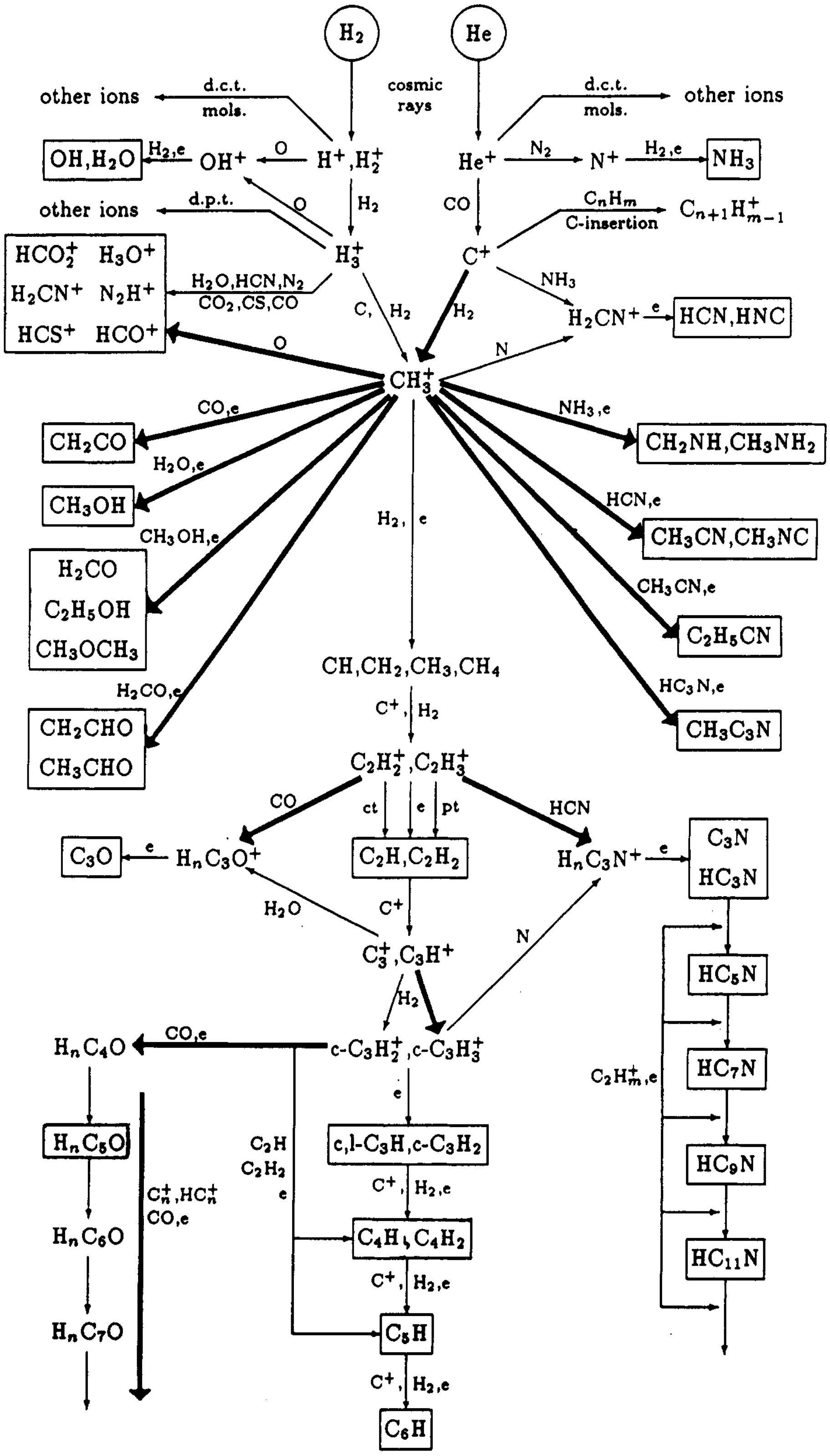


Figure 2. The ion chemistry of dense interstellar clouds. The molecules in boxes are known interstellar molecules. When both a neutral species (e.g. CO) and e are associated with an arrow, it implies that an ion–neutral reaction first occurs, and then the product ion of the reaction undergoes dissociative recombination with an electron to produce the neutrals indicated at the arrow head. The thick arrows indicate that radiative association occurs (see also Figure 3 for more details of the hydrocarbon chemistry). Radiative association reaction are also involved in the H_nC_mO column (bottom left) and the HC_nN column (bottom right) (see the text). The other symbols along the arrows indicate the following: ct, charge transfer; pt, proton transfer; dct, dissociative charge transfer; dpt, dissociative proton transfer.

Radiative association reactions of CH_3^+ with NH_3, HCN, and CH_3CN followed by dissociative recombination can produce (CH_2NH and CH_3NH_2), (CH_3CN, CH_3NC), and C_2H_5CN, respectively (see Figure 2).

The well-known interstellar cyanopolyynes HC_nH (n = 3, 5, 7, 9, 11) can be formed in the reactions of hydrocarbon ions with N atoms[30] and HCN.[31] Thus,the first in the series can be formed by

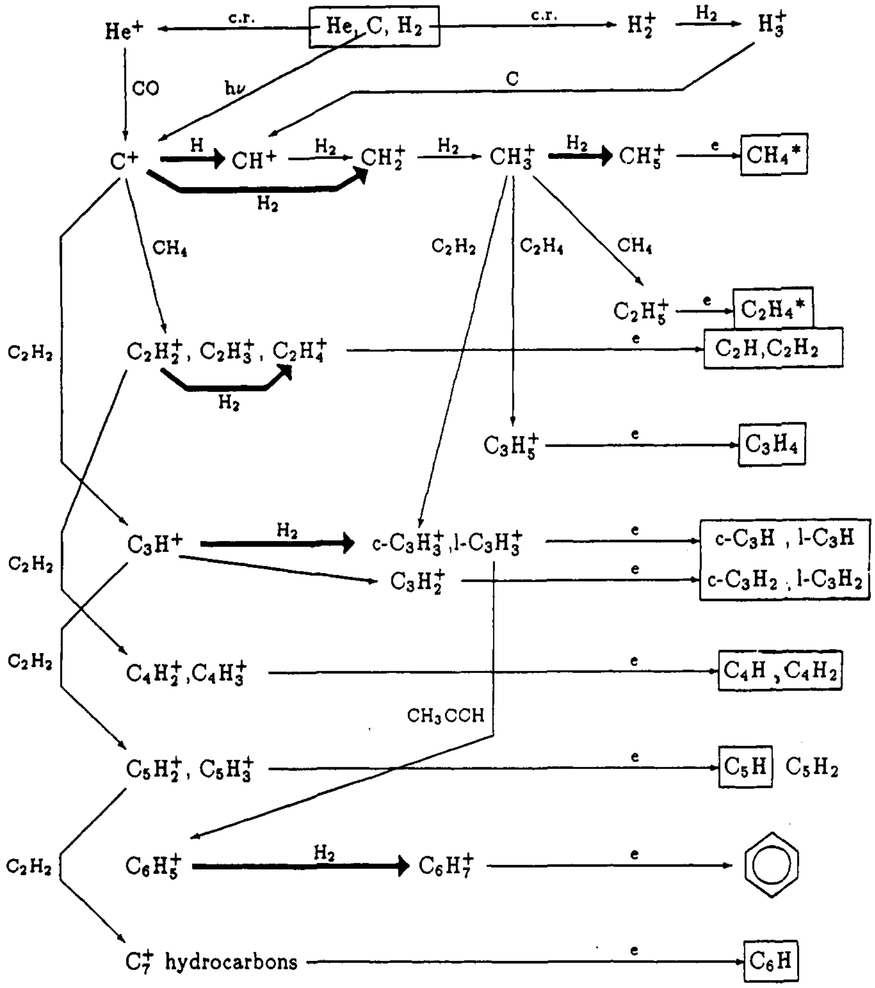


Figure 3. Some routes to the synthesis of hydrocarbons molecules in interstellar clouds. The molecules in boxes are known interstellar molecules. Those molecules marked with an asterisk have been detected only in circumstellar shells, but they must surely be interstellar also. The thick arrows indicate that radiative association occurs. Note the importance of C_2H_2 in the chemistry: cr indicates cosmic ray ionization; *e* indicates dissociative recombination.

$$C_2H_2^+ + HCN \rightarrow H_3C_3N^+ + h\nu \qquad (13)$$

$$C_3H_3^+ + N \rightarrow H_2C_3N^+ + H \qquad (14)$$

Dissociative recombination of the product ions can yield HC_3N. A detailed experimental study of the reactions of HC_3N has been carried out,[32] and the production and loss of these species in interstellar clouds has been considered.[33] A result worthy of note is that HC_3N rapidly associates with CH_3^+ in helium buffer gas at 300 K, and it seems very likely, therefore, that it will radiatively associate with CH_3^+ in interstellar clouds ultimately producing CH_3C_3N (see Figure 2). The growth of cyanopolyynes could perhaps occur in the reactions of $C_2H_2^+$ with the HC_nN molecules thus

$$C_2H_2^+ + HC_nN \rightarrow H_3C_{n+2}N^+ + h\nu \qquad (15)$$

followed by dissociative recombination of the product ion. Certainly the three-body analogue of reaction 15 involving HC_3N as the reactant neutral results in association,[32] and it is on this limited evidence that the cyanopolyyne chain is presumed to grow as is shown in Figure 2. Further laboratory work on this is inhibited because the higher-order cyanopolyynes are so unstable. Production of the HC_nN molecules via the reactions of higher-order hydrocarbon ions with N atoms is also possible as indicated above, but there is, as yet, no laboratory data to support this idea.

3. Carboxy Molecules

The oxygen-bearing (carboxy) molecules are shown on the left side of Table I, and the reactions producing them are indicated on the left side of Figure 2. The important neutral reactants are O, CO, and H_2O. H_3^+ and CH_3^+ react with O to produce OH^+ (and finally OH and H_2O) and HCO^+ (and finally CO), respectively. Radiative association reactions of CH_3^+ with CO and H_2O produce CH_2CO and CH_3OH respectively,[19] e.g.

$$CH_3^+ + CO \rightarrow CH_3CO^+ + h\nu$$

$$CH_3CO^+ + e \rightarrow CH_2CO + H \qquad (16)$$

Association of CH_3^+ with CH_3OH[19] could produce H_2CO and/or both of the isomers of C_2H_6O, i.e. C_2H_5OH and/or CH_3OCH_3 which are both known interstellar species. Higher-order hydrocarbons can react with O, CO, and H_2O generating larger oxygen-bearing molecules (carboxy molecules). It is known from laboratory studies that $C_2H_2^+$ and $C_2H_3^+$ undergo rapid collisional association with CO, and it has been shown[34] that the analogous radiative association reactions could be the route to the production of interstellar C_3O (see Figure 2):

$$C_2H_2^+ + CO \rightarrow H_2C_3O^+ + h\nu$$

$$H_2C_3O^+ + e \rightarrow C_3O + H_2 \qquad (17)$$

Similarly, 1-$C_3H_3^+$ rapidly collisionally associates with CO,[24] and the analogous radiative association reaction could generate HC_4O and C_4O in interstellar clouds.[35] It is exciting to report that very recently, Gerlich and his colleagues[11,36] have observed the two-body (radiative) association reactions 16 and 17 to occur in their low-pressure ion-trap experiment and measured the rate coefficients. The rate coefficients for reactions 16 and 17 are $\sim 10^{-14}$ cm^3 s^{-1} at 80 K and so both reactions will proceed at a significant rate at the low temperatures of dense interstellar clouds and so lead to the production of CH_2CO and C_3O. The recent study of the reactions of $C_4H_2^+$, C_5H^+, and C_6H^+ (which do not react with H_2) showed that they very rapidly collisionally associate with CO,[28] and it seems likely therefore that the analogous radiative association reactions could lead to C_5O (recently detected), HC_5O, C_6O, and C_7O in dense interstellar clouds. Such is illustrated in Figure 2. A point worthy of note here is that the reaction of C^+ with H_2O generates predominantly the isomer COH^+ (84%) as well as the more stable isomer HCO^+ (16%).[37] This is illustrated in Figure 1. There has been a tentative identification of COH^+ in interstellar clouds, but it must be in low concentration because it reacts rapidly with H_2 to produce both H_3^+ and the isomeric species HCO^+ which, of course, is a well-known interstellar ion.

4. Sulfur-Bearing Molecules

To avoid over-complication, the chemistry resulting in the formation of the several sulfur-bearing molecules that have been detected in interstellar clouds (see Table I) is not included in Figure 2, but this chemistry deserves some discussion. Most probably this chemistry begins with S atoms and S^+ ions, since S has a low ionization energy. Neither of these species reacts at a significant rate with H_2 in cold, quiescent clouds. Both of the H-atom abstraction reactions in the following sequence are endothermic:[38]

$$S^+ \xrightarrow{H_2} SH^+ \xrightarrow{H_2} SH_2^+ \xrightarrow{H_2} SH_3^+ \xrightarrow{e} H_2S, HS \qquad (18)$$

The dissociative recombination reaction indicated is of course exothermic and is rapid,[39] but this path to H_3S^+ is blocked. (Compare this with the similar sequence involving O^+ which rapidly leads to OH and H_2O; see Figure 1.) However, a possible route to H_2S is via the reaction sequences

$$H_3^+ \xrightarrow{S} HS^+ \xrightarrow{\text{metal}} HS; \quad H_3^+ \xrightarrow{HS} H_2S^+ \xrightarrow{\text{metal}} H_2S \qquad (19)$$

although it must be said that these exothermic reactions have not been observed, as yet, in laboratory experiments. Notice that the proposal is that HS^+ and H_2S^+ are neutralized by charge transfer with metal atoms (low ionization energies).

There are several interstellar molecules possessing C–S bonds (see Table I). Since S^+ does not react with H_2 it is available to react with other minority species, including hydrocarbons. Thus a SIFT study of the reactions of S^+ with several hydrocarbons has been carried out.[40] This study showed a propensity for C–S bond formation in these reactions, especially for small hydrocarbon reactants. Thus, in the reaction of S^+ with CH_4

$$S^+ + CH_4 \rightarrow H_3CS^+ + H \qquad (20)$$

the product ion H_3CS^+ on dissociative recombination can (energetically) form H_2CS and CS. The reaction of CH_3^+ with H_2S is also rapid and forms H_3CS^+ which could also contribute to the formation of H_2CS and CS. The reaction

$$S^+ + C_2H_2 \rightarrow HC_2S^+ + H \qquad (21)$$

could be the first stage in the formation of C_2S. Similarly, the reaction of S^+ with CH_3CCH could result in C_3S, but this molecule could also be formed in the reaction of S^+ with the ubiquitous interstellar species c-C_3H_2:

$$S^+ + \text{c-}C_3H_2 \rightarrow HC_3S^+ + H \qquad (22)$$

Unfortunately, reaction 22 cannot be studied in the laboratory because c-C_3H_2 is not stable under laboratory conditions. Other aspects of this organosulfur chemistry have also been discussed in some detail.[41] It is also worthy of note that organosulfur molecules may also be formed in the reactions of hydrocarbon ions with S atoms, e.g.

$$C_3H_3^+ + S \rightarrow H_2C_3S^+ + H \qquad (23)$$

but, again, such S-atom reactions have not been studied in the laboratory.

Because of the large proton affinity of CS molecules,[42] proton transfer occurs to them from many interstellar ions including HCO^+, N_2H^+, and, of course, H_3^+:

$$H_3^+ + CS \rightarrow HCS^+ + H_2 \qquad (24)$$

Thus, HCS^+ is relatively stable against proton loss and this is an important reason why it is readily detectable in interstellar clouds. Early calculations of the abundance ratio of HCS^+ to CS based on a canonical value of the rate coefficients for these proton transfer reactions of 10^{-9} cm^3 s^{-1} resulted in much smaller values of this abundance ratio than is observed. This problem was resolved when it was realized (following collaborative theoretical and experimental work[43]) that the rate coefficients for such reactions involving polar molecules proceed much more rapidly at the low temperatures of dense interstellar clouds than was previously thought. Because CS has a large permanent dipole moment (1.957 D), reactions such as 24 proceed more rapidly than previously assumed, and by using appropriately higher values of the rate coefficients, model predictions and observations of the HCS^+ to CS abundance ratios were reconciled.[44] It is interesting to note that an increase in the rate coefficients for fast ion–molecule reactions due to a permanent dipole on the reactant ion has recently been reported.[45]

5. Molecules with Other Elements

Two silicon-bearing molecules, SiO and SiS, have been detected in interstellar clouds and four other silicon-bearing molecules have been detected in circumstellar shells (i.e. SiC, c-SiC_2, SiC_4, and SiH_4). It is not clear which reactions form these molecules, although

Table II. Rare Isotopes in Interstellar Molecules

isotope	molecules in which isotope detected
D	H_2, H_2O, HCO^+, N_2H^+, C_2H, HCN, HNC, NH_3, H_2CO, c-C_3H_2, CH_3OH, CH_3CN, C_4H, HC_3N, HC_5N, CH_3CCH
^{13}C	CO, CS, HCN, HNC, HCO^+, OCS, H_2CO, HC_3N, 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

Bohme and his colleagues have made a major effort in this area.[46] One molecule possessing phosphorus, PN, has also been detected in the interstellar medium, and again it is not certain how this molecule is formed in quiescent interstellar clouds. (Note that CP has been detected in circumstellar shells.) Following detailed laboratory studies of the reactions of PH_n^+ ions (n = 0–4),[47] some indications have been given as to the gas-phase reactions which may be involved in the synthesis of PN and other phosphorus-bearing molecules in interstellar clouds.[48] Only one chlorine-bearing molecule, HCl, has been detected, and proposed routes to its production (and to other possible interstellar chlorine-containing molecules) based on laboratory studies have been discussed.[49]

The above discussions of diffuse and dense cloud chemistry are entirely qualitative. However, detailed quantitative models are required to substantiate the proposed routes to the observed interstellar molecules. Detailed models have been constructed (both steady-state and time-dependent models) involving large numbers of reactions,[50,51] which are upgraded when new molecules are detected and relevant laboratory data become available. Further references can be obtained from other reviews.[52,53]

IV. Fractionation of Rare Isotopes

As was mentioned in the Introduction, many interstellar molecules are seen to contain the rare, heavy isotopes of some elements and that these heavy isotopes appear to be enriched in the interstellar molecules. A list of the molecules in which the various rare isotopes have been detected is given in Table II. It is now understood, mostly as a result of detailed SIFT studies, that this enrichment is largely due to phenomenon of "isotope fractionation" in ion–neutral reactions. Much has been written recently about this very interesting phenomenon,[54,55,56] and so it is only necessary to allude to it here. It is best exemplified by the elementary reaction:

$$D^+ + H_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+ + HD \tag{25}$$

It is a simple matter to determine the forward (exothermic) and reverse (endothermic) rate coefficients, k_f and k_r, for such reactions using the SIFT technique, and when this is done it is observed that k_f exceeds k_r by a factor of 10 at 295 K and by a factor of 20 at 205 K.[57] This occurs because the reverse reaction is endothermic by 39.8 meV (3.84 kJ mol^{-1}) (by virtue of the zero-point-energy difference between H_2 and HD, and the ionization energies of H and D), and this is enough to greatly inhibit this reaction at and below room temperature. Indeed, in cold interstellar clouds the reverse reaction is effectively stopped and the forward reaction proceeds at the gas kinetic rate. Hence, this process effectively ensures that much of the deuterium in dense interstellar clouds is combined as HD.

The important role of H_3^+ and CH_3^+ in interstellar chemistry has been stressed throughout this paper, and so it is very significant that both these ions undergo H/D exchange reactions with HD:

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2 \tag{26}$$

$$CH_3^+ + HD \rightleftharpoons CH_2D^+ + H_2 \tag{27}$$

Again, the significant enthalpy changes in these reactions[58,59] ensures that D will be fractionated into H_2D^+ and CH_2D^+ in dense interstellar clouds, and thus the subsequent reactions of these ions (in common, of course, with H_3^+ and CH_3^+) will result in the enrichment of deuterium in many interstellar molecules. It is interesting to note that the enthalpy change in reaction 26 varies with temperature below 300 K because of the widely separated rotational energy states in the "small" reactants and products, and because of the "rotational" zero-point energy of H_3^+. A detailed experimental (SIFT) study of the reactions of H_3^+, H_2D^+, HD_2^+, and D_3^+ with H_2, HD, and D_2 has been carried out recently[60] which emphasises these interesting features of this reaction, and detailed calculations of the equilibrium constant for reaction 26 as a function of temperature have also been reported recently.[61] Such data are required if the magnitude of deuterium fractionation into H_2D^+ in interstellar clouds is to be assessed.

Similar SIFT studies of D/H exchange in the reactions of $C_2H_2^+$ with HD[62] and HCO^+ with D atoms[55] have been carried out. A very recent paper[63] describes a study of the reactions between CH_5^+ and CD_4, NH_4^+ and ND_3, and H_3O^+ and D_2O and discusses the "shuttling" of protons and deuterons within the proton (deuterium)-bound dimers. While these reactions are not involved in interstellar chemistry, they do provide insight into the phenomenon of isotope exchange in ion–molecule reactions.

Fractionation of the rare isotopes of heavier elements also occurs in ion–molecule reactions, although, because of the smaller mass differences, the enthalpy changes are much smaller than for H/D exchange. For example, in the reaction

$$^{13}C^+ + {}^{12}CO \rightleftharpoons {}^{12}C^+ + {}^{13}CO \tag{28}$$

the enthalpy change is only −3 meV (−0.29 kJ mol^{-1}).[64] However, it is sufficient to result in the fractionation of ^{13}C into CO, and the ^{13}CO to ^{12}CO abundance ratio in interstellar clouds is about a factor of 2 greater than would be expected (on the basis of the solar/terrestrial $^{13}C/^{12}C$ ratio). For the isotope exchange reaction of $H^{12}CO^+$ with ^{13}CO, the enthalpy change is only about −1 meV (about −0.1 kJ mol^{-1}), and this is too little to result in fractionation of ^{13}C into the ion at any interstellar cloud temperature. Further information on this very interesting topic can be obtained from several review papers.[54,56,65]

Table III. Production of Neutrals from Positive Ions in Interstellar Clouds

(1) Charge Transfer (e.g. with Metal Atoms) $X_2H^+ + \text{metal} \rightarrow X_2H + (\text{metal})^+$
(2) Proton Transfer (PA is the Proton Affinity) $X_2H^+ + M \rightarrow X_2 + MH^+ \{PA(M) > PA(X_2)\}$
(3) Neutralization on Grain Surfaces $X_2H^+ + \text{grain} \rightarrow X_2, XH, X, ...$
(4) Dissociative Recombination $X_2H^+ + e \rightarrow X_2, XH, X, H$ e.g. $H_3O^+ + e \rightarrow H_2O, OH, H, O?$
(5) Mutual Neutralization (with PAH^-) $X_2H^+ + PAH^- \rightarrow$ products (including X_2, etc.)

V. Production of Neutrals from Positive Ions

Implicit in most of what has been said is that interstellar molecules are primarily formed in the gas phase by positive ion–neutral reactions which produce increasingly complex positive ions which are then neutralized to form the observed neutral interstellar molecules. The accent has been placed on dissociative recombination as the most important neutralization process, but there are other processes which are listed in Table III. Since metal atoms have low ionization energies, they can transfer an electron to a positive ion to neutralize it. This process has already been invoked for the neutralization of H_2S^+ to produce H_2S (reaction 19). Since such charge-transfer reactions are not very exothermic, then concomitant fragmentation of the molecule is minimized. Proton transfer can also be effective in producing neutral molecules from ions, although, as for charge transfer, there is obviously no net loss of charge. Proton-acceptor molecules are those with large proton affinities (PA; see Table III) such as NH_3, but caution needs to be exercised here because such molecules are usually chemically reactive, and then other processes other than just proton transfer might occur, e.g.

$$CH_3^+ + NH_3 \rightarrow CH_2NH_2^+, NH_4^+ \qquad (29)$$

In this reaction, proton transfer is energetically allowed, and is indeed observed, but by far the major product is $CH_2NH_2^+$.[66] This forcibly illustrates that laboratory data should be used as far as possible in ion-chemical models and that generalizations should be used with great caution. In this regard, neutralization of ions on interstellar grain surfaces has been suggested as a possible mechanism, but little is known about this process and so it can only be a matter for speculation at this time.

1. Dissociative Recombination

What is quite certain is that the process of positive ion–electron dissociative recombination is a very efficient neutralization process in ionized gases and must be a major process for the neutralization of positive ions in interstellar clouds. From the earliest measurements of the coefficients for dissociative recombination, α_e, the process has been known to be efficient, even for diatomic ions at room temperature, the α_e then being $\sim 10^{-7}$ cm^3 s^{-1}.[67] For cluster ions such as $H_3O^+(H_2O)_n$, the α_e approaches 10^{-5} cm^3 s^{-1}.[68] Clearly, for the ion-chemical modeling of interstellar clouds, the α_e is needed for many positive ion species, preferably at low temperatures. Some such data are now available, obtained principally using the productive flowing afterglow Langmuir probe (FALP) technique (see section VI). From the available data, some generalizations concerning α_e can be made which are valuable when the α_e required for specific molecular ions are not available. For small (diatomic and triatomic) molecules, α_e at 300 K is typically (2–4) × 10^{-7} cm^3 s^{-1}, increasing with decreasing temperature (as $T^{-1/2} - T^{-1}$, in general accordance with theoretical predictions[67]). For polyatomic ions, the α_e are greater and depend on the complexity of the ion. They are typically within the range (5–12) × 10^{-7} cm^3 s^{-1} and increase only slowly (if at all) with reducing temperature.[69,70] One surprising result obtained using the FALP method was that the important interstellar ion H_3^+ did not appear to recombine rapidly with electrons,[70] contrary to the results obtained from previous experiments using other techniques. This particular FALP result is now being seriously questioned in the light of more recent results obtained using another flow apparatus[71] and using an IR spectroscopic technique.[72] Yet theory also predicts a small (insignificant) dissociative recombination coefficient for H_3^+.[73] Clearly, it is vital to determine the correct value of α_e for H_3^+, since this ion is so involved in interstellar ion chemistry.

Until quite recently, little was known about the product of dissociative recombination reactions, and in all models of interstellar chemistry, the neutral products of these reactions were literally guessed at (although the energetics of the reactions limit the number of neutral products that can be formed). The application of spectroscopic methods [vacuum ultraviolet (VUV) and laser-induced fluorescence (LIF)] to the FALP technique has now provided some much-needed information on the neutral products of dissociative recombination reactions of some interstellar positive ions. It was first used to identity the OH and H fragments produced in the recombination of HCO_2^+ ions at 300 K. The results of this study and the experimental technique have been reported in detail.[74] Subsequently, the products of recombination of H_3O^+ (and N_2OH^+) were determined and the implications to interstellar chemistry and to theoretical models of the reactions were discussed.[7] The recombination of H_3O^+ at 300 K was seen to proceed thus:

$$\begin{aligned} H_3O^+ + e &\rightarrow OH(v = 0) + H_2(2H) && 46\% \\ &\rightarrow OH(v > 0) + H_2(2H) && 19\% \\ &\rightarrow \text{other products} && 35\% \quad (30) \end{aligned}$$

Note that two H atoms could (energetically) be the products of the reaction, and note, also, that the experiment, as yet, provides no evidence that H_2O is a product of the reaction, as is usually assumed!

The FALP technique has also been used to determine the fraction of H atoms released per recombining ion "f_H" for the interstellar ions $C_2H_5^+$, NH_4^+, H_2CN^+, CH_3CNH^+, $OCSH^+$, H_3S^+, and CH_5^+. Such experiments are necessary, since in most interstellar chemical models it is assumed that during the recombination of such ions an H atom will be released, thus producing from the above ions, C_2H_4, NH_3, HCN, CH_3CN, OCS, H_2S, and CH_4. In all these recombination reactions, H atoms are indeed released, with f_H varying between about 0.2

for $OCSH^+$ and 1.2 for CH_5^+.[75] This implies that the $OCSH^+$ recombination reaction probably proceeds thus:

$$\begin{aligned} OCSH^+ + e &\rightarrow CO + SH \quad \sim 80\% \\ &\rightarrow OCS + H \quad \sim 20\% \qquad (31) \end{aligned}$$

For the CH_5^+ recombination, the products are not so certain, since, energetically, the reaction could proceed to produce CH_3 and 2 H (or H_2) and CH_4 + H. So it is not yet certain that the recombination of CH_5^+ produces CH_4! The detailed results of this collaborative work have now been reported,[76] and Bates[22] has considered which of the available channels in these recombination reactions are most probable. Very recently, the FALP method has been applied to the detection of NH_2 radicals (by LIF) from the recombination of NH_4^+ ions, although detailed results are not yet available (R. Johnson, private communication). Although these FALP studies are a good beginning of the quest to determine the neutral products of dissociative recombination reactions, it is clear that a good deal more effort is necessary to provide sufficient data to support comprehensive interstellar ion chemical models.

2. Mutual Neutralization

The process of mutual neutralization of positive ions by negative ions is included in Table III as a possible mechanism for the production of neutral molecules from positive ions in interstellar clouds. It is clear that when significant concentrations of negative ions are present in ionized gases or plasmas then this process is a potentially-important ionization loss process. Simple negative ions (e.g. H^-, O^-, Cl^-, CN^-, etc.) are not considered to be present in significant concentrations in interstellar clouds because there is no obvious mechanism by which they can form efficiently. However, it is now being seriously considered that large, negatively-charged molecules, specifically polycyclic aromatic hydrocarbons (PAH^-) may be present in dense clouds,[77,78,79] and if they are, then neutralization reactions such as

$$H_3^+ + PAH^- \rightarrow PAH + H_2 + H \qquad (32)$$

may be effective at removing the ionization from the clouds. Also, the reaction of PAH^- with polyatomic positive ions could result in large neutral molecules:

$$C_nH_m^+ + PAH^- \rightarrow \text{polyatomic hydrocarbons} \qquad (33)$$

Such neutralization reactions are less energetic than electron–ion recombination reactions, and the smaller amount of recombination energy can be dispersed within many vibrational modes of the products, so less fragmentation of the neutral products might be expected. Such processes could therefore be very important in building larger molecules. It is necessary, therefore, to know the rate coefficients for such mutual neutralization reactions (and ultimately the neutral products!). In this, again, the FALP technique has been most useful in determining the rate coefficients, α_i, for a large number of mutual neutralization reactions, some over an appreciable range of temperature.[80] Thus it was found that the α_i for such reactions, both the "simple" ion reactions (e.g. $NO^+ + NO_2^-$) and complex cluster ion reactions (e.g. $H_3O^+(H_2O)_3 + NO_3^-(HNO_3)_2$), vary within the limited range (3–8) × 10^{-8} cm^3 s^{-1} at 300 K. These α_i are equivalent to very large mean thermal cross sections exceeding 10^{-12} cm^2. The α_i are predicted theoretically to vary with temperature T, as $\alpha_i \sim T^{-1/2}$,[81] and the limited amount of FALP data available supports this prediction. Thus, at the temperature of dense interstellar clouds (say 20 K), α_i for PAH^- reactions would perhaps be within the range (2–4) × 10^{-7} cm^3 s^{-1}, which is about 1 order of magnitude smaller then a typical α_e at the same temperature. Clearly, however, the relative importance of dissociative recombination and mutual neutralization in neutralizing positive ions depends not only on α_e and α_i but also on the electron/negative ion number density ratio which is very difficult to assess.

VI. A Note on Laboratory Techniques

In order to validate the gas-phase ion–chemical models of interstellar chemistry mentioned in this paper, a great deal of laboratory data are needed. Thus the rate coefficients and product ions have been determined for some thousands of ion-molecule reactions, some over a wide temperature range, and some at the very low temperatures of dense interstellar clouds. Much of the early data were obtained by exploiting the ICR technique.[82] Subsequently, the SIFT technique was developed,[83] and then adopted in several laboratories to study ionic reactions of interstellar interest. Detailed references to the SIFT work and the major contributions are given in several reviews[65,84–86] and data compilations.[8] Also worthy of note is the CRESU (Cinétique de Reaction en Ecoulement Supersonic Uniformé) technique by which several ion–molecule reactions of interstellar interest have been studied at very low temperatures,[87] and the low-pressure guided-beam/ion-trap experiments from which the first reliable values of radiative association rate coefficients have been obtained.[11]

The first body of data on dissociative recombination coefficients was obtained using the stationary afterglow method.[67] Later the FALP technique was developed[88] and exploited to determine the recombination coefficients for a number of ions of interstellar importance, some over a wide temperature range.[69,70] The FALP technique has also been used to determine ion–ion mutual neutralization coefficients.[80,89] As has been discussed already, the latest use of the FALP technique is in the determination of the neutral products of dissociative recombination reactions.[74–76] A merged-beam technique has also been used extensively to determine the cross sections for dissociative recombination reactions over appreciable interaction energies, and the data are used to estimate the rate coefficients for recombination at low energies.[90]

VII. Concluding Remarks

Much has been learned about the processes involved in the production of interstellar molecules, due largely to the combined efforts of astronomers and spectroscopists, modelers, and laboratory experimentalists. However, many problems remain. The observed abundances of some interstellar molecules cannot be reconciled with the predictions of gas-phase ion-chemical models. The over-abundance of CH^+ in diffuse clouds has been referred to; is this due to kinetically-excited

C^+? Is the apparent over-abundance of NH_3 in some dense clouds due to NH_3 production on grain surfaces, or is it that the gas-phase routes to this molecule have not been properly identified? How is H_2S formed, and what really are the routes to the series of cyanopolyynes? The answers to some of these questions might be apparent if laboratory data were available on the reactions of ions with atomic and molecular radicals, such as C, N, S, NH_2, and CH_3. It seems very probable that N atoms are involved in the production of cyanopolyynes, but studies are needed of the reactions of N atoms with long-chain hydrocarbon ions. S atoms are probably involved in H_2S production, but no laboratory data are available to support such an hypothesis. Some O and N atom reactions with ions have been studied using SIFT methods,[30,91] but effort is now required to study more radical reactions using the SIFT and other techniques.

There seems little doubt that the phenomenon of ion–molecule radiative association is facile in interstellar clouds and that it results in the production of many interstellar molecules, but little is yet known about the rates of this process, especially for polyatomic reactants. An impressive start has been made to study such reactions,[11] but much more needs to be done. It would be particularly exciting if the radiation from such reactions could be detected.

Reference is not often made to the destruction of interstellar molecules in ion–molecule reactions, but this may be a significant process. A recent SIFT study of the reactions of H^+ ions with several interstellar molecules species[92] revealed that dissociative charge transfer is a common process which produces fragment ions and thus (following dissociative recombination) less complex neutral molecules. He^+ ions may be similarly effective. Also proton transfer from H_3^+ ions to many interstellar molecules is often sufficiently exothermic that dissociation of the resultant protonated molecule can occur as a recent SIFT study of this phenomenon has shown.[93] These processes which degrade some interstellar molecules are included in the overview of interstellar chemistry in Figure 2; their significance is currently being quantitatively assessed.[94]

A start has been made to determine the neutral products of dissociative recombination reactions using the FALP technique. FALP apparatuses are now being built in several laboratories and exploited in combination with spectroscopic techniques to obtain a body of data on the neutral products of dissociative recombination reactions, which are considered to be the most important neutralization process for ions in interstellar clouds. Ion–ion mutual neutralization may occur between PAH^- negative ions and some of the many positive ions referred to in this paper. It should be possible to study such neutralization reactions in the FALP, at least to determine the rate coefficients, but product determination is a problem of a much greater magnitude! So many challenging problems remain, but such is the excitement and appeal of interstellar chemistry that many of these problems will be tackled and eventually solved.

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