The phenomenon of excitability may be more important than oscillatory behavior per se. A steady state may be stable to infinitesimal fluctuations due to random molecular motion, but very minor external perturbations may still generate pulses of large chemical change. These pulses may then migrate to transmit signals.

These unusual events in purely chemical systems suggest obvious analogies to events in living organisms, and we believe the greatest significance of this work will be to suggest models useful for interpreting some of the basic processes of life itself.

Interstellar Chemistry

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The interstellar medium (ISM) of our galaxy lies mainly in the galactic disk and has a characteristic thickness of about 600 light years perpendicular to the galactic plane. Its mean density is roughly 1 H atom cm^{-3}, though large density variations occur. The ISM is composed of "clouds" of mainly neutral gas and an "intercloud" region of gas that is at least partly ionized. The latter type of gas is hot ($\simeq 10^3-10^5$ K) and of low density ($\lesssim 0.1$ particle cm^{-3}).

Clouds are cool ($\lesssim 100$ K) and dense ($\sim 10-10^6$ particles cm^{-3}) and contain the interstellar molecules. Characteristic dimensions for clouds are 30 light years. The lower density clouds ($\lesssim$ few hundred particles cm^{-3}) typically attenuate even ultraviolet starlight by less than an order of magnitude and can thus be observed with optical instruments. Other clouds (typically with $\gtrsim 10^4$ particles cm^{-3}) are completely opaque and can only be studied with radio telescopes.

For convenience, I will discuss interstellar molecule reactions in terms of these two extreme cases—the "diffuse" and the "dense" clouds. Their chemistry seems to be qualitatively different in that starlight is present in diffuse clouds, but not in dense clouds, to ionize atoms and dissociate molecules. Except for hydrogen, the gas is mainly atomic. The interstellar starlight spectrum is cut off at 13.6 eV due to absorption by hydrogen, so that the atoms with ionization potentials above that of hydrogen are mostly neutral and those with lower ionization potentials exist mainly in ionized form in diffuse clouds. Electron densities are about 10^{-4} of the gas density.

In the dense clouds which exclude starlight, dissociation is slow and collisions are more rapid so that most elements are bound into molecules. Ionization to initiate the proposed chemical reactions in the gas phase and to maintain at least a low-level electron density ($\lesssim 10^{-6}$ of the particle density) is presumably supplied by the higher energy ($\gtrsim 100$ MeV/nucleon) cosmic ray

protons. The intensity of these cosmic rays is measured directly for our neighborhood and indirectly throughout the galaxy from observation of γ rays produced in collisions between the cosmic rays and the interstellar gas.

Element abundances throughout the ISM are thought to be essentially the same as in young stars. Relative abundances by number are:[1] H, 1; He, 0.1; C, 4×10^{-4}; N, 9×10^{-5}; O, 6×10^{-4}; Ne, 5×10^{-5}; all other elements near or less than 10^{-5}.

Besides the gas of the ISM, there also exist dust grains. The presence of dust grains is indicated by the continuous attenuation of starlight as a function of wavelength, and their dimensions ($\simeq 10^{-5}$ cm) are determined from the wavelength dependence of this attenuation. Except close to bright stars, the temperatures of these grains are maintained by absorption of starlight from the galactic background and are $\simeq 10$ to 20 K. From cloud to cloud, the relative abundance of dust grains is approximately constant and expressed as a surface area per H atom in the gas is 5×10^{-22} cm^2. The mass of material in grains is roughly 0.01 of the gas and requires a considerable fraction (perhaps most) of the available "heavy" elements (C, N, O, etc.).

A major uncertainty in studying reactions in the ISM is the degree to which the heavy elements have been depleted in the gas by freezing onto the cold grains or by incorporation into the refractory grain material in the atmospheres of cool stars.

Observation of Molecules in the Interstellar Gas

In Table I we list the observed interstellar molecules along with the type cloud in which they are detected and a rough estimate of their abundance. Although H_2 and HD are not directly detectable in dense clouds, essentially all the hydrogen and deuterium is expected to be in this form. After H_2, carbon monoxide is the most abundant molecule in dense clouds and thus has special importance. The deuterated forms DCN (DCN/HCN $\simeq 1/200$) and DCO^+ ($DCO^+/HCO^+ \simeq 10^{-2}-1$) have been found in several dense clouds as well

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(1) C. W. Allen, "Astrophysical Quantities", 3rd ed, P. Athlone, London, 1973, p 30.

<div align="center">

Table I
Observed Interstellar Molecules[a]

</div>

H$_2$	hydrogen [−0.5]	CH$^+$	ionized methylidyne [−9]
CH	methylidyne (−8) [−8]	CO	carbon monoxide (−4) [−6]
CN	cyanogen (−8) [−9]	OH	hydroxyl (−7) [−8]
CS	carbon monosulfide (−7)	SiO	silicon monoxide (−7)
SO	sulfur monoxide (−7)	NS	nitrogen sulfide (−8)
SiS	silicon sulfide (−7)	H$_2$S	hydrogen sulfide (−8)
HDO	heavy water (10^{-8}?)	HNC	hydrogen isocyanide (−6)
HCN	hydrogen cyanide (−6)	SO$_2$	sulfur dioxide (−7)
OCS	carbonyl sulfide (−8)	HCO$^+$	protonated carbon monoxide (−7)
N$_2$H$^+$	protonated nitrogen (−7)	HCO	formyl (−8)
C$_2$H	ethynyl (−7)	H$_2$CO	formaldehyde (−8)
NH$_3$	ammonia (−6)	HNCO	isocyanic acid (−9)
H$_2$CS	thioformaldehyde (−10)	HC$_3$N	cyanoacetylene (−8)
HCOOH	formic acid (−10)	CH$_3$NH	methamine (−10)
NH$_2$CN	cyanamide (−9)	CH$_3$HCO	acetaldehyde (−10)
CH$_3$OH	methanol (−7)	HC$_5$N	cyanodiacetylene (−10)
NH$_2$HCO	formamide (−10)	HCOOCH$_3$	methyl formate (−10)
CH$_3$C$_2$H	methylacetylene (−9)	CH$_3$CH$_2$OH	ethanol (−10)
CH$_3$NH$_2$	methylamine (−10)	CH$_3$C$_3$N	methylcyanoacetylene (−10)
CH$_2$CHCN	vinyl cyanide (−10)	(CH$_3$)$_2$O	dimethyl ether (−10)

[a] An estimate of the fractional abundance by number is given for these molecules in dense clouds (x) and in diffuse clouds [x], where abundance = 10^x. Note that most molecules are detected only in the dense gas clouds. Although H$_2$ is not observed directly in these clouds, there is good evidence that the gas is mainly H$_2$.

as has HD (HD/H$_2$ $\simeq$ 10^{-6}) in diffuse clouds. Less abundant isotopes of C, N, O, and S have also been detected in molecules.

Introduction to Interstellar Molecule Formation

Historically, the first comprehensive study of interstellar molecule reactions seems to be that of Bates and Spitzer[2] directed toward CH and CH$^+$ in diffuse clouds. These authors recognized the importance of most processes that are considered at present which involve *atomic* reactants and concluded that serious difficulties arise. Despite considerable effort since 1951, the full solution to the CH/CH$^+$ problem is still unavailable.

A second phase of study concerning molecule formation began in the early 1960's in relation to H$_2$. Detection of H$_2$ did not occur until observations were possible from above the atmosphere for its ultraviolet, Lyman-band spectrum. This had not yet been achieved in 1960, and it was supposed that a large fraction of the galactic mass might be hidden as H$_2$. Radiative association and all other gas-phase processes make a negligible contribution to the formation of H$_2$ under normal conditions. Detailed investigations culminating with that of Hollenbach and Salpeter[3] concluded that essentially every H atom that hits a dust grain will stick and be converted to an H$_2$ molecule which is returned to the gas. The required rate for formation of H$_2$ deduced from observations[4] is in excellent agreement with that predicted for grains, and clearly excludes a major contribution from proposed gas-phase processes under normal conditions.

In response to the rapid expansion in molecule observations beginning in 1968–1969, re-investigations of gas and surface reactions were undertaken. This recent activity has generated ideas which are the primary topic for this Account—formation of molecules through gas-phase reaction schemes that depend heavily on positive ion–molecule reactions initiated mainly by

cosmic-ray ionization. Initial investigations of these reactions were performed independently by the author[5] and by Herbst and Klemperer.[6]

Under the low-temperature–low-density conditions of the ISM, chemical reactions must be exothermic and have no activation energy barrier in their ground electronic states in order to be important. Reactions of neutrals with H$_2$ and other chemically saturated molecules normally have at least an activation energy barrier which excludes them from importance in the ISM. Reactions between other neutrals often have such barriers so that it is difficult to predict which will be rapid at the low interstellar temperatures. For this reason reactions between positive ions and molecules, which normally have no activation-energy barrier when the reaction is exothermic, are now thought to be the dominant type of gas-phase reaction in the ISM. Since the reaction rates for these are typically independent of temperature, the available laboratory data, which are almost exclusively for 300 K, can be utilized with reasonable confidence in initial studies of the ISM.

In this Account, I discuss proposed reaction mechanisms that are in my opinion the most significant examples which indicate that gas-phase reactions can play a major role in the ISM. Numerical modeling to establish the quantitative importance of these processes is beyond the scope of the treatment here. The reader should consult the more detailed reviews[7,8] and the original papers that are cited.

Owing mainly to our poor knowledge of the physical parameters in gas clouds and the tendency for the observations to integrate over different regions in the gas, rigorous observational evidence that these mechanisms are in fact dominant does not exist in the laboratory sense. However, the extraordinary high abundance of HD in diffuse clouds seems unquestionably to be a result of the proposed reactions. Furthermore, the presence and abundance of HCO$^+$,

(2) D. Bates and L. Spitzer, *Astrophys. J.*, **113**, 441 (1951).

(3) D. Hollenbach and E. E. Salpeter, *Astrophys. J.*, **163**, 155 (1971); also D. Hollenbach, M. Werner, and E. E. Salpeter, *ibid.*, **163**, 165 (1971).

(4) E. J. O'Donnell and W. D. Watson, *Astrophys. J.*, **191**, 89 (1974).

(5) W. D. Watson, *Astrophys. J. Lett.*, **183**, L17 (1973); *Astrophys. J.*, **188**, 35 (1974).

(6) E. Herbst and W. Klemperer, *Astrophys. J.*, **185**, 505 (1973).

(7) J. Black and A. Dalgarno, *Rep. Prog. Phys.*, **39**, 573 (1976); E. Herbst and W. Klemperer, *Phys. Today*, **29**, 32 (1976).

(8) W. D. Watson, *Rev. Mod. Phys.*, **48**, 513 (1976).

N_2H^+, HNC as well as the strong isotope fractionation in DCO^+ and DCN in favor of deuterium strongly indicate that ion–molecule reactions are a major factor in the dense clouds.

The subsequent discussion treats "diffuse" and "dense" clouds separately since their differences in physical conditions also cause major differences in the reaction processes. Because diffuse clouds are nearby, optically transparent, and mainly in atomic form, the possible reaction mechanisms can be delineated and tested much more precisely than in the dense clouds. I will follow essentially all previous studies in ignoring time-dependent effects on molecular abundances, though the validity of doing so is open to some question for certain molecules in dense clouds.[9]

Proposed Formation Processes in Diffuse Interstellar Clouds

HD. Observations[10] typically yield $[HD]/[H_2] \simeq 10^{-6}$ in diffuse interstellar clouds with appreciable H_2, whereas the ratio by number for total deuterium to hydrogen is 2×10^{-5}. Unlike H_2 for which photodissociation in clouds is reduced by factors up to roughly 10^4, HD is not sufficiently abundant to benefit from such self-shielding. Hence the formation rate per deuterium atom for HD must exceed that per H atom for H_2 by a factor near 10^3.

If H_2 is produced at essentially every collision of an H atom with a grain as predicted and as indicated by observation, it is clearly necessary for HD to be produced mainly by some gas-phase process. This is generally accepted to be[11]

$$H^+ + D \rightarrow H + D^+ \tag{1}$$

followed by[11,12]

$$D^+ + H_2 \rightarrow HD + H^+ \tag{2}$$

The rate constant for reaction 2 has been measured down to 90 K and found to be temperature independent,[13] $k_2 = 1 \times 10^{-9}$ cm^3 s^{-1}. Since the photodissociation cross section for HD is accurately known, the abundance of HD can be predicted and utilized as a probe for the H^+ abundance. Neutralization of H^+ is chiefly a result of

$$H^+ + e \rightarrow H + h\nu \tag{3}$$

and

$$H^+ + O \rightarrow O^+ + H \tag{4}$$

followed by the sequence of reactions discussed in the following eq 5 for formation of OH.

With these reactions, the H^+ abundance can in turn be used to deduce a useful upper limit to the flux of low-energy cosmic rays which are probably the main cause for ionization of hydrogen. From such analysis, a cosmic ray ionization rate $\lesssim 10^{-16}$ (H atom sec)$^{-1}$ has been deduced[4] for most of the gas clouds in the solar neighborhood.

OH, H_2O. When appreciable H_2 is present, the O^+ produced in eq 4 immediately reacts to produce H_3O^+:

$$O^+ + H_2 \rightarrow OH^+ + H$$
$$OH^+ + H_2 \rightarrow H_2O^+ + H \tag{5}$$
$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$

Although laboratory data confirm that eq 5 are fast ($k \simeq 1 \times 10^{-9}$ cm^3 s^{-1} at 300 K), the charge exchange of eq 4 has been an outstanding uncertainty. Laboratory measurements at 300 K do find a large rate constant.[14] Extrapolation to lower temperature and pressure is not clear, however, especially since reaction 4 is endothermic by $\Delta E/k = 227$ K and excited fine-structure states are well populated under the laboratory conditions though not always in the ISM.

The H_3O^+ is converted into OH and H_2O

$$H_3O^+ + e \rightarrow H_2O + H$$
$$\rightarrow OH + H_2 \tag{6}$$

followed by

$$H_2O + h\nu \rightarrow OH + H \tag{7}$$

though at higher densities eq 8 competes with reaction

$$C^+ + H_2O \rightarrow HCO^+ + H \tag{8}$$

7. Uncertainty about the relative importance of the two possible branches in eq 6 makes it unclear how much H_2O should be produced. Except at rather high densities, reaction 7 dominates, and essentially all H_3O^+ does lead to OH. The predictions for the OH abundance based on the above reaction sequence with $k_4 \simeq 10^{-9} \exp(-227/T)$ made prior to the recent detection of OH in diffuse clouds[15a] are in excellent agreement with the observed abundances. That is, astrophysical uncertainties allow less than roughly a factor of ten flexibility. Water has not been detected, and the low upper limit that is suggested is somewhat surprising if the above reactions dominate for OH.[15b] The oscillator strength for the transition under observation has not actually been measured.

NH. Although the OH abundance is in excellent agreement with that predicted from gas-phase processes, there is sufficient uncertainty in the physical conditions and the surface area of grains per H atom $(n_g\sigma_g/n)$ that it is also consistent with formation of OH mainly on grains. This is the case for the CH abundance as well. Grain surfaces in diffuse clouds are most likely to be inert so that they catalyze reactions only by holding the atoms with binding energies near that of physical adsorption and by acting as a third body to absorb reaction energy. Except for differences in the abundance of nitrogen and oxygen, the production rate for NH, NH_2, and NH_3 are expected to be the same as that for OH and H_2O.[16a] Observationally, $([NH]/[OH])/([N]/[O] \lesssim 1/15)$ if the $[N]/[O]$ ratio is the "cosmic" value. Although there are differences between OH and NH, especially if the chief products of surface

(9) W. D. Langer and A. E. Glassgold, *Astron. Astrophys.*, **48**, 395 (1976).

(10) L. Spitzer, J. F. Drake, E. B. Jenkins, D. C. Morton, J. B. Rogerson, and D. G. York, *Astrophys. J. Lett.*, **181**, L116 (1973).

(11) W. D. Watson, *Astrophys. J. Lett.*, **182**, L69 (1973).

(12) A. Dalgarno, J. Black, and J. Weisheit, *Astrophys. Lett.*, **14**, 77 (1973).

(13) F. C. Fehsenfeld, D. B. Dunkin, E. E. Ferguson, and D. L. Albritton, *Astrophys. J. Lett.*, **183**, L25 (1973).
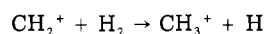
(14) F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **56**, 3066 (1972).

(15) (a) R. M. Crutcher and W. D. Watson, *Astrophys. J. Lett.*, **203**, L123 (1976); T. P. Snow, *ibid.*, **204**, L127 (1976); (b) W. H. Smith and E. G. Zweibel, *Astrophys. J.*, **207**, 758 (1976).

(16) (a) W. D. Watson and E. E. Salpeter, *Astrophys. J.*, **174**, 321 (1972); **175**, 659 (1972); (b) R. M. Crutcher and W. D. Watson, *ibid.*, **209**, 778 (1976).

reactions are H_2O and NH_3, detailed analysis indicates that the differences are unlikely to compensate for this factor of one-fifteenth.[16b] The absence of NH thus tends to support formation of OH in the gas phase.

CH, CH^+. Since the earliest studies of molecule reactions in the ISM, understanding the abundance of CH and CH^+ has probably been the most outstanding and extensively investigated problem. Until reactions 9, followed by reactions 10 and 11, were recently rec-

$$CH^+ + H_2 \rightarrow CH_2^+ + H \tag{9}$$

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H$$

$$CH_3^+ + e \rightarrow CH + H_2 \tag{10}$$
$$\rightarrow CH_2 + H$$

$$CH_2 + h\nu \rightarrow CH + H \tag{11}$$

ognized to be an efficient conversion mechanism from CH^+ and CH_2^+ to CH,[17] formation of CH on grains was thought to be necessary. Reasonable rate coefficients for radiative association to produce CH^+ and CH_2^+ lead to the observed CH abundance.

At present a knotty problem is CH^+. Its rapid destruction due either to reactions 9 or to reaction 12

$$CH^+ + e \rightarrow C + H \tag{12}$$
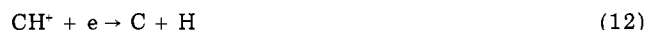
places severe requirements on the formation process. The rate constant for reactions 9, though not for reaction 12, has been measured[18] in the laboratory. Except for one or two cases, all known rate constants for dissociative electron recombination are $\gtrsim 10^{-7}$ cm^3 s^{-1} and calculations by some investigators indicate that excited states of CH cross the potential-energy curve for CH^+ in a manner that is favorable for a rapid dissociative recombination.[19a] However, very recent calculations[19b] disagree with the earlier work and suggest a much slower dissociation rate.

CH^+ is produced directly by

$$C^+ + H \rightarrow CH^+ + h\nu \tag{13}$$

where the best, calculated value for the rate constant seems to be $k_{13} = 1.3 \times 10^{-17}$ cm^3 s^{-1} at 100 K.[20] CH^+ will also be produced through eq 14, followed by re-

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \tag{14}$$

actions 9 and 10 after which photoionization and photodissociation can produce the CH^+.

$$CH_3^+ + h\nu \rightarrow CH_2^+ + H \tag{15}$$
$$\rightarrow CH^+ + H_2$$

$$CH_2 + h\nu \rightarrow CH_2^+ + e \tag{16}$$

$$CH_2^+ + h\nu \rightarrow CH^+ + H \tag{17}$$

$$CH + h\nu \rightarrow CH^+ + e \tag{18}$$

Most of the rate constants and cross sections for photoprocesses in this scheme have not been measured or calculated. Nevertheless, if k_{12} is small ($\lesssim 10^{-9}$ cm^3

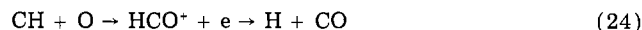s^{-1}) there appears to be no serious problem in producing adequate abundances of CH^+ with reasonable estimates for uncertain quantities. If $k_{12} \simeq 10^{-7}$ cm^3 s^{-1} as has seemed more likely, it is extremely difficult if not impossible for currently proposed reactions to yield enough CH^+ within acceptable constraints.[21]

Attention has been focused on reaction 14 to assess whether the required, large rate constant, $k_{14} \simeq 10^{-14}$ cm^3 s^{-1}, is likely.[22,23] Very recent work[24] does indicate $k_{14} = 10^{-14\pm1.5}$ cm^3 s^{-1}. However, calculations[25] show that the photodissociation (eq 15) is slow so that the conversion from CH_3^+ to CH^+ must go through eq 10 and 16–18 with good efficiency. To avoid producing excessive CH, it seems to be necessary that the recombination (eq 10) and photoabsorption by CH_2 produce CH in only a small fraction of the events.

Other Diatomics (CO, CN, C_2, N_2, NO, O_2). Although the dominant reactions producing the diatomic hydrides in the initial step for converting atoms to molecules might be either surface or gas phase, the diatomics with two "heavy" atoms are almost certainly produced by exchange reactions in the gas phase,[26] e.g.
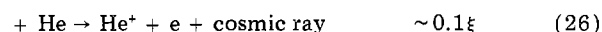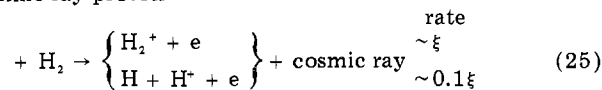
$$CH^+ + O \rightarrow CO + H^+ \tag{19}$$
$$+ N \rightarrow CN + H^+ \tag{20}$$
$$OH + C^+ \rightarrow CO + H^+ \tag{21}$$
$$+ N \rightarrow NO + H \tag{22}$$
$$+ O \rightarrow O_2 + H \tag{23}$$

though

$$CH + O \rightarrow HCO^+ + e \rightarrow H + CO \tag{24}$$

At the higher densities reaction of C^+, N, and O with H_2O, CH_2, CH_3, CH_4, and NH_3 can also contribute.

Proposed Formation Processes in Dense Interstellar Clouds

We now discuss selected aspects of the proposed gas-phase chemistry based primarily on ion–molecule reactions.[5,6] Although the lack of detailed information about dense clouds makes most quantitative tests unrealistic, qualitative support for the general ideas is derived from the presence and abundance of certain key molecular species (e.g., HCO^+, DCO^+, N_2H^+, HNC, CCH) for which formation processes are outlined here. A cornerstone of the "ion–molecule" scheme is the efficient transfer of ionization by cosmic rays from hydrogen and helium to the less abundant "heavy" elements.

Initial Ionization. The beginning step is

cosmic ray proton

$$+ H_2 \rightarrow \begin{cases} H_2^+ + e \\ H + H^+ + e \end{cases} + \text{cosmic ray} \quad \begin{matrix} \text{rate} \\ \sim \xi \\ \sim 0.1\xi \end{matrix} \tag{25}$$

$$+ He \rightarrow He^+ + e + \text{cosmic ray} \quad \sim 0.1\xi \tag{26}$$

where $\xi \simeq 10^{-17}$–10^{-18} ionizations per gas particle per

(17) J. Black and A. Dalgarno, *Astrophys. Lett.*, **15**, 79 (1973); W. D. Watson, *Astrophys. J.*, **189**, 221 (1974).

(18) J. K. Kim, L. P. Theard, and W. T. Huntress, *J. Chem. Phys.*, **62**, 45, (1975).

(19) (a) J. N. Bardsley and B. R. Junker, *Astrophys. J. Lett.*, **183**, L135 (1973); M. Krauss and P. Julienne, *ibid.*, **183**, L139 (1973); (b) A. Giusti-Suzor and H. Lefebvre-Brion, "Comments on the Dissociative Recombination of CH^+ Ions", to be published (1977).

(20) A. Giusti-Suzor, E. Roueff, and H. van Regemorter, *J. Phys. B*, **9**, 1021 (1976).

(21) A. Dalgarno in "Atomic Processes and Applications", P. G. Burke and B. L. Moiseiwitsch, Ed., North-Holland Publishing Co., Amsterdam, 1977.

(22) F. C. Fehsenfeld, D. B. Dunkin, and E. E. Fergusen, *Astrophys. J.*, **188**, 43 (1975).

(23) P. Pearsen and E. Roueff, *J. Chem. Phys.*, **64**, 1240 (1976).

(24) E. Herbst, J. G. Schubert, and P. R. Certain, "The Radiative Association of CH_2^+", to be published (1977).

(25) R. J. Blint, R. F. Marshall, and W. D. Watson, *Astrophys. J.*, **206**, 627 (1976).

(26) P. Solomon and W. Klemperer, *Astrophys. J.*, **178**, 389 (1972).

second. Reaction 25 is followed directly by eq 27. This

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{27}$$

H_3^+ is destroyed mainly by eq 28 or by eq 29 and 30,

$$H_3^+ + e \rightarrow H_2 + H \tag{28}$$
$$\rightarrow 3H$$
$$H_3^+ + CO \rightarrow HCO^+ + H_2 \tag{29}$$
$$+ N_2 \rightarrow N_2H^+ + H_2 \tag{30}$$

or possibly by reaction with C, N, and O atoms if they are abundant. Since CO is observed to be present in sufficiently high abundance that reaction 29 accounts for an appreciable fraction of the H_3^+ destructions, HCO^+ is clearly an indicator for the cosmic rays that are the basis the "ion–molecule" scheme. Identification of one of the strongest microwave lines from the ISM (89, 189 MHz) with HCO^+ [27,28] as advocated earlier for other reasons[29] has been the critical development in support of the proposed processes based on ion–molecule reactions.

Though they seem less likely to be important, other reactions that are not initiated by cosmic-ray ionization can produce HCO^+. Thus detection[30] and identification[31] of N_2H^+, which has a parallel role to HCO^+ but is less susceptible to alternative production mechanisms, are valuable supporting evidence. N_2H^+ was not necessarily expected in advance as the abundance of N_2 is unknown. Except at the highest densities, both N_2H^+ and HCO^+ are expected to be destroyed mainly by dissociative electron recombination with approximately the same rate constant. Their rate constants for formation via reactions 29 and 30 are equal, so that $[N_2H^+]/[HCO^+]$ should reflect the $[N_2]/[CO]$ ratio. However, at the highest gas densities, the $[CO]/[e]$ ratio is likely to be large enough that destruction of N_2H^+ is chiefly a result of reaction 31.

$$N_2H^+ + CO \rightarrow HCO^+ + N_2 \tag{31}$$

The expected decrease in the N_2H^+/HCO^+ ratio which then results with increasing density has apparently been observed in one gas cloud.[32]

Generation of Free Atoms. Although ionization of H_2 leads to HCO^+ and N_2H^+ which are valuable indicators for the "ion–molecule" scheme, these pathways usually are dead ends and are relatively unimportant for formation of other molecules. Ionization of helium produces the free, reactive C, N, and O atoms that are utilized in molecule formation and is thus much more effective. That the loss of the He^+ in collisions with hydrogen is negligible due to the small rate constants for reaction with H and H_2 ($k \lesssim 10^{-13}$ cm^3 s^{-1}) is another key aspect of the proposed "ion–molecule" scheme. Most ionization of He thus contribute to breaking up CO, N_2, and possibly O_2.

$$He^+ + CO \rightarrow He + C^+ + O \tag{32}$$
$$+ N_2 \rightarrow He + N^+ + N \tag{33}$$
$$+ O_2 \rightarrow He + O^+ + O \tag{34}$$

Formation of Hydrides. Both the O^+ and N^+ produced in reactions 33 and 34 react immediately with H_2 in the same manner as for O^+ in diffuse clouds (eq 5). The C^+ attaches hydrogen by radiative association (eq 14) and then reacts with H_2 (eq 9). These exchange reactions with H_2 terminate with H_3O^+, NH_3^+, and CH_3^+. Reaction of NH_3^+ with H_2 is negligibly slow,[33] and further reactions of H_3O^+ and CH_3^+ with H_2 are endothermic. Thus H_2O and OH are readily produced in the subsequent electron recombination (eq 6), though other processes must occur to produce NH_3 and CH_4 (if the latter is abundant). One possibility (eq 35) is

$$NH_3^+ + M \rightarrow NH_3 + M^+ \tag{35}$$

charge exchange with an atom M of low ionization energy (e.g., Mg, Si, Ca) if these are sufficiently abundant in the gas. Another is further radiative association with H_2, e.g., eq 36, for which large rate

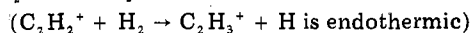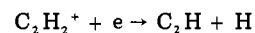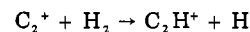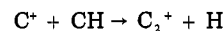$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \tag{36}$$

constants have been estimated,[34] followed by electron recombination (eq 37). The electron density can be low

$$CH_5^+ + e \rightarrow CH_4 \rightarrow H \tag{37}$$

enough that reaction with H_3^+ contributes significantly to the formation of hydrides, e.g., eq 38.

$$H_3^+ + O \rightarrow OH^+ + H_2 \tag{38}$$

CCH. This molecule is the natural product of the presence of C^+ and any of the CH, CH_2, CH_3, CH_4 group, both of which should be produced efficiently according to the foregoing discussion. One reaction chain is

$$C^+ + CH \rightarrow C_2^+ + H$$
$$C_2^+ + H_2 \rightarrow C_2H^+ + H$$
$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H \tag{39}$$
$$C_2H_2^+ + e \rightarrow C_2H + H$$
$$(C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H \text{ is endothermic})$$

CCH has now been widely observed and is almost as basic to a gas-phase chemistry as HCO^+ and N_2H^+. Quantitative predictions[5] for the abundance of CCH were in agreement with the subsequent measurement.

HCN, HNC. With the presence of an appreciable abundance of NH_3 established by observation and C^+ a direct product of reaction 32, the reactions that are expected to dominate for the formation of HCN and HNC are eq 40 and 41. Reaction with C^+ also destroys

$$C^+ + NH_3 \rightarrow H_2CN^+ + H \tag{40}$$
$$H_2CN^+ + e \rightarrow HCN + H \tag{41}$$

HCN (eq 42). Under the time-independent conditions

$$C^+ + HCN \rightarrow C_2N^+ + H \tag{42}$$

that are assumed to prevail, a constraint then exists on the abundance ratio

$$[HCN]/[NH_3] < k_{40}/k_{42} \simeq 0.6 \tag{43}$$

according to measured rate constants.[35] Equation 43 is in agreement with the observations, though the uncertainties in the observed HCN and NH_3 abun-

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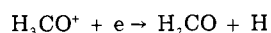(34) E. Herbst, *Astrophys. J.*, **205**, 94 (1976).
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dances are large. Another strong interstellar emission line at millimeter wavelengths has recently been identified as due to the isomer HNC.[36] Its abundance is frequently comparable with that of HCN which seems especially suggestive of formation through the dissociative recombination of H_2CN^+ (reaction 41). More generally, the occurrence of this unstable isomer is also strong evidence for gas-phase formation processes.

H_2CO. Formaldehyde is widely observed throughout the galaxy. It occurs in both high and relatively low density interstellar clouds. Thus the reactions that produce formaldehyde must be operative under a range of physical conditions. Also, formaldehyde is perhaps the most complex interstellar molecule for which specific gas-phase reaction sequences have been proposed. It thus becomes a test case for whether the more complex molecules are likely to be generated in gas-phase reactions or whether reactions on surfaces are necessary.

The chief proposals are[6,40a,b] reactions 44 or 45 or 46.

$$HCO^+ + H_2 \rightarrow H_3CO^+ + H$$
$$H_3CO^+ + e \rightarrow H_2CO + H$$
(44)

$$CH_3 + O \rightarrow H_2CO + H$$
(45)

$$CH_3^+ + O \rightarrow H_2CO^+ + H$$
(46)

Indirect laboratory studies[22] are not encouraging for reactions 44, nor are observations that indicate a much larger ratio of DCO^+/HCO^+ than of $HDCO/H_2CO$.[37] For reactions 45 and 46 the difficulties are qualitatively similar—a molecular ion (CH_3^+ or H_2CO^+) must be neutralized efficiently. The rate constant for reaction of H_2CO^+ with H_2 apparently is negligible,[38] and the fraction of reactions 46 that produce H_2CO^+ instead of HCO^+ is small.[39] Observational evidence against formation through reactions 45 and 46 also exists.[40b] In summary, formation of formaldehyde in the gas phase is an open question.

Isotope Fractionation (Mainly of Interest in Dense Clouds)

Zero-point energy differences between various isotopic forms of a molecule can cause significant fractionation at the temperatures of ISM clouds if isotope exchange reactions approach thermodynamic equilibrium. In the case of (deuterium/hydrogen), observations of (DCN/HCN)[41] and (DCO^+/HCO^+)[42] indicate

that enhancement occurs by factors of approximately 10^2 and up to roughly 10^4, respectively, over the actual (D/H) ratio for the ISM. Reactions of the form

$$XH^+ + HD \rightleftarrows XD^+ + H_2 + \Delta E$$
(47)

are thought to be responsible,[8] where $\Delta E/k \simeq 200$ to 500 K. Reaction 47 with X = H_2 probably causes the enhancement of DCO^+. For this, $k = 3 \times 10^{-10}$ cm^3 s^{-1} (see ref 35), and I have estimated $\Delta E/k$ to be near 180 K. The low proton affinity of H_2 and CO allows a high abundance of H_2D^+ and DCO^+ to affect essentially all other molecules through reactions of the form

$$H_2D^+ + AH \rightarrow H_2 + AHD^+$$
$$AHD^+ + e \rightarrow AD \rightarrow H$$
(48)
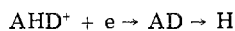
and the analogous reaction involving DCO^+. Abundances predicted from the above considerations are consistent with the observed enhancement.[8]

Of the other elements, an isotope fractionation process has been proposed in detail only for carbon. Here, the key reaction is the exchange

$$^{13}C^+ + {}^{12}CO \rightarrow {}^{12}C^+ + {}^{13}CO + \Delta E$$
(49)
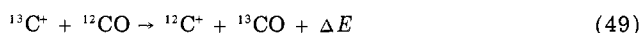
where $\Delta E/k = 35$ K and the rate constant has been measured[43] at 300 K to be 2×10^{-10} cm^3 s^{-1}. Under ISM conditions, reaction 49 may indirectly cause fractionation of carbon isotopes in all molecules relative to the actual value in the ISM.[43] Observational evidence exists in support of at least some fractionation.[44]

Conclusions

Studies of reaction mechanisms and their comparison with observation indicate that gas-phase processes in which ion–molecule reactions are utilized heavily are likely to dominate the chemistry of small, interstellar molecules other than H_2. The present challenge in such investigations is to develop unambiguous observational tests of proposals and to determine whether the more complex molecules (i.e., larger than formaldehyde) can be produced in the gas phase. Reactions on the surfaces of dust grains may be critical, though studies of surface reactions are not yet so quantitative and precise as studies of gas-phase reactions. Uncertainties about the surface chemistry are formidable. Surface reactions have been reviewed elsewhere[8] and are beyond the scope of this Account.

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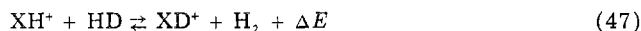(37) Compare ref 40b and 42.
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