Ion–Molecule Reactions in the Evolution of Simple Organic Molecules in Interstellar Clouds and Planetary Atmospheres

By W. T. Huntress, Jr.
JET PROPULSION LABORATORY, PASADENA, CALIFORNIA 91103, U.S.A.

1 Introduction

There is a general appreciation among scientists for the fundamental physics involved in the structure of the universe as we perceive it through the media of astronomy. The word astrophysics has been coined by this appreciation, and the subject is fostered by the application of the newest developments in modern physics to the science of astronomy. Neutron stars, black holes, and quasars are just a few examples of the marriage of modern physics and astronomy. The new understanding of the universe as a dynamic and evolving entity, alive with the exotic fires of an only dimly understood relativistic particle physics, is a perception which was made possible by modern physics and which in turn provides impetus to the progress of both physics and astronomy. The ancient and revered science of astronomy has undergone a rebirth in recent decades in the wake of these advances.

The science of chemistry is now beginning to make its mark upon astronomy and space science in the same way that physics has done in the past 20 years. Chemistry, in the sense of nuclear reactions in stars and of the spectroscopic detection of atomic and molecular species in the atmospheres of stars and the planets, has been a part of astronomy for almost the entire century. It is only since the advent of the space programme, of radio astronomy, and of air pollution, that chemistry has been considered in astrophysics and space science in the sense of chemical reactions in these environments. Through the technique of radio astronomy, organic molecules have been discovered in the depths of interstellar clouds. The work being done to explain the origin of these molecules[1] is providing a new science of astrochemistry. The space programme has opened new spectroscopic eyes on the atmospheres of the other planets in our solar system and has been communicating back new data on the chemical constituents of the atmospheres of Mercury, Venus, Mars, and Jupiter. Work is now needed on the chemistry of these atmospheres in order to explain their composition.[2] In turn, recent concern over chemical pollution of our own atmosphere has stimulated much new effort into photochemical reactions in the Earth's atmosphere.[3]

[1] Reviewed by W. D. Watson in 'Atomic and Molecular Physics and the Interstellar Matter', North-Holland, Amsterdam, 1975, and by A. Dalgarno and J. H. Black, *Reports Progr. Phys.*, 1976, **39**, 573.

[2] J. S. Lewis, *Ann. Rev. Phys. Chem.*, 1973, **24**, 339.

[3] Department of the Environment, Central Unit on Environmental Pollution, 'Chlorofluorocarbons and their Effect on Stratospheric Ozone' (Pollution Paper No. 5 H.M. Stationery Office, 1976).

Ionic processes play a very significant part in the chemistry of interstellar clouds and planetary atmospheres. In this review we will examine the role of ion–molecule reactions in the chemical processes which result in the evolution of organic molecules in extraterrestrial environments. The approach will be to start with the ion chemistry of the most tenuous of astrophysical environments and work up to the most dense. The most tenuous are the thin interstellar clouds dispersed throughout the galaxy. The densities in these clouds range from 10 to 10^9 molecules cm^{-3} depending on their mass and evolutionary history. Working up through astronomical condensations of increasing density, we will follow the important contribution made by ion chemistry to the chemical evolution of both inorganic and organic compounds in these clouds from atomic to diatomic to polyatomic species. These chemical compounds eventually find their way as frozen volatiles in comets and are present as the gaseous envelopes around planetary objects when the interstellar cloud collapses through the stellar nebula stage to form a sun and a planetary system. From this point we will examine the importance of ion–molecule reactions for the synthesis of organic molecules in planetary atmospheres of reducing composition. Jupiter is an example of such a planet in our own solar system, and the primitive atmosphere of the Earth was most likely reducing in nature also.[4] These same ionic reactions may also be responsible for the formation of some of the intermediate organic compounds which have been observed in laboratory studies of the prebiotic, abiogenic synthesis of complex organic molecules, those compounds required to initiate and sustain chemical life on our own and other planets in the universe.[5]

2 Ion–Molecule Reactions

Ion–molecule reactions are defined as the formation of new product species as the result of a collision between an ion and a neutral atom or molecule. Ions are formed in extraterrestrial environments by the impact of energetic particles or photons on neutral species. In interstellar clouds, atoms and molecules can be ionized by both the galactic ultraviolet (u.v.) flux from starlight and by cosmic rays and *X*-rays.[1] In planetary atmospheres, solar photoionization in the tenuous part of the upper atmosphere forms an ionosphere about the planet.[6] In more dense regions of planetary atmospheres, where clouds can form from condensable species and where precipitation can occur, ions are formed in electrical discharges in thunderstorms.[7] Cosmic rays can also produce a low level of ionization in planetary atmospheres above the heights at which the pressure is of the order of several atmospheres.[8]

[4] W. T. Huntress, Jr., *J. Chem. Educ.*, 1976, **53**, 204.

[5] C. Ponnamperuma and N. W. Gabel, *Space Life Sci.*, 1968, **1**, 64.

[6] M. J. McEwan and L. F. Phillips, 'Chemistry of the Atmosphere', Arnold, London, 1975.

[7] A. Bar-Nun and A. Shaviv, *Icarus*, 1975, **24**, 192.

[8] L. A. Capone, R. C. Whitten, S. S. Prasad, and J. Dubach, *Astrophys. J.*, 1977, **33**, 495. L. A. Capone, R. C. Whitten, J. Dubach, S. S. Prasad, and W. T. Huntress, Jr., *Icarus*, 1976, **28**, 367.

The types of ion–molecule reaction which will be important are a function of the density. For pressures much below 1 atmosphere, bimolecular ion–molecule reactions are generally the most important. Reaction (1) is a very simple example

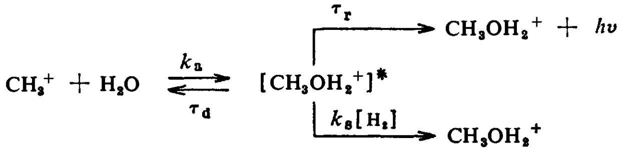
$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (1)$$

of a bimolecular ion–molecule reaction important in dense interstellar clouds and in the atmospheres of the Jovian planets where H_2 is the dominant molecular species. At the very low densities ($\sim$10—10^6 molecules cm^{-3}) of interstellar clouds, the time between collisions is very long, from 3 years to 20 minutes, and

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \qquad (2)$$

radiative association reactions become important. Reaction (2) is a prime example of a radiative association reaction important in interstellar clouds.[1] In this process, a photon ($h\nu$) is emitted rather than a heavy neutral particle as in reaction (1). The C^+ ion is otherwise unreactive towards molecular hydrogen. Bimolecular reactions can and most often do occur at nearly every collision between an ion and a molecule when the process is thermodynamically allowed. On the other hand, the probability for emission of a photon to stabilize the collision complex is very small during the short time the ion and neutral species are in close contact. Radiative association reactions are therefore very much slower than bimolecular reactions.

Radiative association reactions have not yet been confirmed in laboratory experiments, and the existence of the radiative association process is based primarily on theory. These reactions are very much akin to collisional association reactions. An appropriate example is the reaction between methyl cations and water [reaction (3)], where the excited intermediate complex formed during the



$$CH_3^+ + H_2O \underset{\tau_d}{\overset{k_a}{\rightleftharpoons}} [CH_3OH_2^+]^* \xrightarrow{\tau_r} CH_3OH_2^+ + h\nu \qquad (3a)$$

$$[CH_3OH_2^+]^* \xrightarrow{k_s[H_2]} CH_3OH_2^+ \qquad (3b)$$

collision between CH_3^+ and H_2O can either dissociate back into the reactants (no reaction) or can emit an infrared photon to produce protonated methanol (radiative association), or where before dissociation the complex can undergo another collision with a third spectator species, H_2 in this case, which stabilizes the complex to form protonated methanol. The collisional association reaction (3b) becomes important only at high pressures (greater than about 10^{-3} atm) because of the requirement for a third-body collision, but collisional association reactions are also clearly related to the radiative association reaction because the rates for both processes depend on the lifetime τ_d of the intermediate complex. Collisional association reactions are commonly observed at high pressures in the laboratory,[9] from which the dissociative lifetime τ_d can be deduced. From τ_d and from τ_r, the radiative lifetime of the excited intermediate ion, the rate for the radiative process can be estimated. The lifetime of the complex towards dissociation, τ_d, is temperature dependent since at lower encounter velocities the excitation energy in the complex is smaller and therefore the lifetime is longer. The larger τ_d at low temperatures in interstellar clouds may allow radiative association reactions to become important even in competition with bimolecular reaction channels for the complex. Smith and Adams[9] have observed the collisional association reaction (3b) and have proposed that the radiative analogue (3a) may be important for methanol synthesis in interstellar clouds ($\rho \approx 10^6$ molecules cm^{-3}, $T = 10$—30 K). Likewise, the collisional process (3b) may be important for methanol synthesis in the lower atmosphere of Jupiter ($\rho \approx 10^{20}$ molecules cm^{-3}, $T = 300$ K). Both of these reactions become important because the bimolecular reaction between CH_3^+ ions and H_2O, reaction (4), to produce

$$CH_3^+ + H_2O \rightarrow [CH_3OH_2^+]^* \rightarrow CH_2OH^+ + H_2 \qquad (4)$$

protonated formaldehyde does not occur.[10]

Reaction (4) is one of the few thermodynamically allowed biomolecular ion–molecule reactions which do not occur at the collision rate. More often, thermodynamically allowed ion–molecule reactions occur with nearly unit efficiency: almost every collision results in a chemical reaction. Even condensation reactions requiring rearrangement in an intermediate complex are often observed to occur at the collision rate.[10] Collisions between ions and molecules are in general 100—1000 times more rapid than collisions between neutral collision partners. Consequently, this results in much larger rate constants for ion–molecule reactions than for reactions between neutral species. Both the larger collision frequencies and the large chemical reaction efficiency in ion–molecule collisions are the result of the charge on the ion.[11] The ion induces a dipolar field in the polarizable neutral collision partner. This field forms a potential between ion and neutral which is much more attractive than the simple van der Waals attraction between neutral species. The ion and neutral are attracted over very much larger distances than are neutral species. The collision cross-section for ions with neutrals is therefore much larger than the hard-sphere cross-section of molecular dimensions ($\sim$ few Å^2) appropriate for neutral–neutral collisions. Ion–molecule collision cross-sections are of the order of a few hundred Å^2. Because of the form of the ion-induced dipole potential, the collisional rate constant is also independent of ion velocity, and consequently of kinetic temperature.[11]

The reason that reaction efficiency in ion–molecule collisions is high is also due to the ion-induced dipole field. From infinite separation, the energy gained in bringing ion and neutral together at molecular dimensions along this

---

[9] D. Smith and N. Adams, *Astrophys. J.*, 1977, in press.

[10] W. T. Huntress, Jr., *Astrophys. J.*, *Supp. Ser.*, 1977, in press.

[11] E. W. McDaniel, 'Collision Phenomena in Ionized Gases', Wiley, New York, 1964.

potential is of the order of tens of kcal mol^{-1}.[11] This is sufficient energy to overcome most kinetic barriers to reaction, so that most ion–molecule reactions have little if any activation energy. Their rate constants can therefore be essentially independent of temperature. This fact is extremely important in astrophysical applications.[1] The temperature in the interior of interstellar clouds can be as low as 3—10 K, at which temperature most chemical reactions among neutral reactants are infinitely slow, excepting a few radical–radical reactions. Ion–molecule reactions can be extremely fast even at these low temperatures. Another feature of the ion-induced dipole potential is that it allows for spiralling and multiple impact encounters,[11] so that the time the ion and molecule remain in intimate contact can be much longer than in neutral–neutral collisions. This longer time facilitates the formation of longer-lived intermediate complexes, which are important for bimolecular as well as associative ion-molecule reactions.

3 Diffuse Interstellar Clouds

The conditions in diffuse interstellar clouds have been reviewed recently both by Watson and by Dalgarno and Black.[1] These are regions in interstellar space where the density of gas increases above the normal ~0.1 molecules cm^{-3} pervading the distances between stars. Diffuse interstellar clouds have densities of the order 10—10^3 molecules cm^{-3} and are optically thin. Stars are visible through them, and some of the species which are present in these clouds are identified by their absorptions in the spectra of background stars. In many cases these regions are illuminated by radiation from nearby stars, which resonantly excites the atoms present in them. The luminous regions of the Great Nebula in Orion pictured in Plate 1* are examples of diffuse interstellar clouds. The temperatures in diffuse clouds can be as high as several hundred degrees (see Table 1). The majority of the material in diffuse clouds is atomic, and they contain only a very small proportion of molecular species other than H_2. In diffuse clouds $n(H_2) < n(H)$ in general.

Table 2 gives the cosmic abundances of elements as they are found in the universe. The composition given in Table 2 represents the average composition of interstellar and stellar material as it has been compiled from spectral observations of the sun and the stars, from particles in the solar wind, and from meteoritic abundances.[12] Hydrogen and helium dominate the composition of the universe. In diffuse clouds, atoms are ionized by cosmic rays, by *X*-rays, and by the u.v. flux from the collective starlight in the galaxy. The galactic u.v. flux has a cut-off above 13.6 eV. Hydrogen atoms in the space near stars are ionized by u.v. light with energies above 13.6 eV so that the light which reaches interstellar clouds only contains photons with energies of less than 13.6 eV. The galactic u.v. flux through diffuse interstellar clouds therefore is not capable of ionizing atoms with ionization potentials greater than 13.6 eV, such as H, He, O, N, Ne, or Ar atoms. These latter atoms are ionized by cosmic rays and *X*-rays. The atoms with ionization potentials less than 13.6 eV, such as C, S, Cl, Si, and metal atoms, are

---

* Plates 1—3 are between pp. 306 and 307.

[12] A. G. W. Cameron, *Space Sci. Rev.*, 1973, **14**, 383; *ibid.*, 1973, **15**, 121.

Table 1 *Typical conditions in interstellar clouds*

	Diffuse	*Dense*
Density	$10—10^3$ cm^{-3}	$10^3—10^6$ cm^{-3}
Ion mean free time	3 years—10 days	10 days—20 min
Temperature	100—30 K	20—10 K*
$n(H_2)/n(H)$	$0.05—10^2$	$10^2—10^6$
Major ion	C^+	S^+, Mg^+, metal ions
Fractional ionization	$10^{-4}—10^{-5}$	$10^{-5}—10^{-7}$
Chemical equilibration time	150—10 My	10—0.1 My

*For clouds with embedded proto-stars, or with hot stars nearby, the temperature can be much higher. The Orion molecular cloud with $\rho \approx 10^5—10^6$ molecules cm^{-3} has a temperature $T \approx 70—90$ K.

Table 2 *Cosmic elemental abundances and ionization potentials*

Element	*Relative abundance*	*Ionization potential*/eV
H	1.00	13.6
He	0.063	24.6
O	5.9×10^{-4}	13.6
C	3.5×10^{-4}	11.3
N	8.5×10^{-5}	14.6
Ne	7.6×10^{-5}	21.6
Si	3.5×10^{-5}	8.2
Mg	3.0×10^{-5}	7.7
S	1.6×10^{-5}	10.4
Ar	5.5×10^{-6}	15.8
Fe	3.2×10^{-6}	7.9
Al	2.5×10^{-6}	6.0
Ca	2.1×10^{-6}	6.1
Cl	2.0×10^{-6}	13.0
Na	1.5×10^{-6}	5.2
F	1.1×10^{-6}	17.4

ionized by the galactic u.v. flux and by cosmic rays and *X*-rays. The ionizing galactic u.v. flux is of the order of $10^6—10^7$ times higher than the ionizing cosmic ray and *X*-ray flux, so that in diffuse clouds u.v. ionization of C atoms is the most important ionization mechanism. The recombination of C^+ ions with electrons is a radiative process, and is consequently very slow. Practically all of the carbon atoms are ionized in diffuse clouds and $n(C^+) \approx n(e^-) \approx n_0(C)$ where $n_0(C)$ is the cosmic abundance of carbon. All S, Cl, Si, and metal atoms are ionized by the galactic u.v. as well. H^+ and He^+ ions are produced by cosmic and *X*-ray ionization of H and He, but these atoms remain mostly neutral and the number of H^+ and He^+ ions is of the order of, or less than, the number of C^+ ions.

In diffuse clouds, where the species are mostly atomic, the only processes which can occur in gas-phase collisions between atomic ions and atoms, other than simple scattering, are charge transfer and radiative association. Among the more abundant atoms H, He, C, N, and O and their ions, the only charge-transfer reaction which occurs at thermal energies is the reaction

$$H^+ + O \rightleftarrows O^+ + H \tag{5}$$

Reaction (5) is an accidentally resonant charge-transfer reaction. The ionization potentials of H and O atoms are almost exactly the same: IP(O) = 13.62 and IP(H) = 13.60 eV. Charge-transfer reactions are unusual among ion–molecule reactions in the sense that they involve transfer of a very light particle, the electron, at potentially very large distances (>100 Å) so that they therefore exhibit strong quantum mechanical effects.[13] Charge-transfer reactions among the first row of atoms are generally not observed even though thermodynamically allowed. For example, the IP of He is greater than that of O, but the He^+–O charge-transfer reaction does not occur. Charge-transfer reactions require that there be a state available in the product ion which is resonant in energy with the recombination energy of the reactant ion, and furthermore that the probability be large for the transition from the ground state of the neutral reactant to the resonant state of the product ion.[13] This condition is met by the ground states of H, O^+, and O in the forward and reverse reactions (5). The forward reaction (5) only is very slightly endothermic ($\Delta H = +0.5$ kcal mol^{-1}, corresponding to about 250 K) and therefore probably has a strong temperature dependence.

The charge-transfer reaction (5) does not contribute in any large way to the synthesis of diatomic ions or molecules in diffuse clouds other than to enhance the O^+ ion density.[14] The important step required to start the fires of chemistry burning is the synthesis of diatomic species. Once this is accomplished, fast bimolecular ion–molecule reactions become possible and new species can be synthesized. In order to synthesize diatomic species, however, radiative processes and heterogeneous reactions at interstellar grain surfaces must be invoked. Heterogeneous recombination of H atoms on grain surfaces is the generally accepted mechanism for synthesis of interstellar H_2:[1]

$$H + H \xrightarrow{\text{grain}} H_2 \tag{6}$$

Molecular hydrogen is non-polar and has a very low boiling point. It is easily evaporated from grain surfaces even at low interstellar temperatures. Any other molecular species, such as CH, even if formed on a grain surface, is difficult to evaporate back into the gas phase at interstellar temperatures. Reaction (6) is required in order to explain the presence of interstellar H_2; gas-phase processes do not work. Gas-phase reactions are probably responsible, however, for the synthesis of most of the other molecules observed in interstellar clouds.

---

[13] J. B. Laudenslager, W. T. Huntress, Jr., and M. T. Bowers, *J. Chem. Phys.*, 1974, **61**, 4600.
[14] S. S. Prasad and W. T. Huntress, Jr., submitted to *Astrophys. J.*

The gas-phase mechanisms acting to produce diatomic species in diffuse clouds are formation of CH^+ by the radiative association of C^+ and H and formation of OH by associative detachment of O^- to H or H^- to O,

$$C^+ + H \rightarrow CH^+ + h\nu \tag{7}$$

$$O^- + H \rightarrow OH + e^- \tag{8}$$

$$H^- + O \rightarrow OH + e^- \tag{9}$$

Reactions (8) and (9) owe their origin to the formation of O^- and H^- by the radiative association of electrons with O and H atoms:

$$e^- + O \rightarrow O^- + h\nu \tag{10}$$

$$e^- + H \rightarrow H^- + h\nu \tag{11}$$

There are no laboratory data on any of the reactions (7)—(11), but there are theoretical calculations for the rate constants of the rate-determining radiative association steps (7), (10), and (11).[15,16] If either or both of the detachment reactions (8) and (9) are fast, then OH formation can be just as important as CH^+ formation *via* (7) in diffuse clouds.[14] Generally, reactions of negative ions are not important in interstellar clouds because the abundance of negative ions is far less than the abundance of positive ions.[16] Negative ions are formed only by pair processes ($AB \rightarrow A^+ + B^-$) in ionization events, or by electron attachment reactions. The cross-sections for these processes are very small compared with positive-ion formation and scattering.[11] Reactions (8) and (9) are important as an initiating process only in diffuse clouds.[14]

Radiative association as in reaction (7) occurs by a transition between energy levels during a collision which leaves the diatomic molecule or ion in a state below the asymptotic dissociation limit along which the reactants have approached each other. This situation is illustrated in Figure 1. The probability for this transition, and the consequent emission of a photon during collision, is largest for transitions between electronic energy levels where the lifetime of the excited state towards radiation is the shortest ($\tau_r \approx 10^{-6}$—10^{-8} s). If the lifetime of the collision complex is of the order of several vibrations ($\tau_d \approx 10^{-13}$ s) then the probability for emission per collision is of the order of $P = \tau_d/\tau_r \approx 10^{-7}$—$10^{-5}$. Vibrational transitions from the dissociation limit to lower states take too long ($\tau_r \approx 10^{-3}$—10 s) for these processes to be important for synthesis of diatomic species. For more complex intermediates such as in reaction (3), τ_d can be quite long owing to the number of available modes into which the collisional excitation can be channeled. Vibrational transitions can become effective under these circumstances and radiative rate constants relatively large. For diatomic species, however, the only potential candidates for radiative association are those which have low-lying electronic states correlated with the reactants in their ground states, as in Figure

---

[15] E. Herbst, J. G. Schubert, and P. R. Certain, *Astrophys. J.*, 1977, in press.

[16] A. Dalgarno and R. A. McCray, *Astrophys. J.*, 1973, **181**, 95.

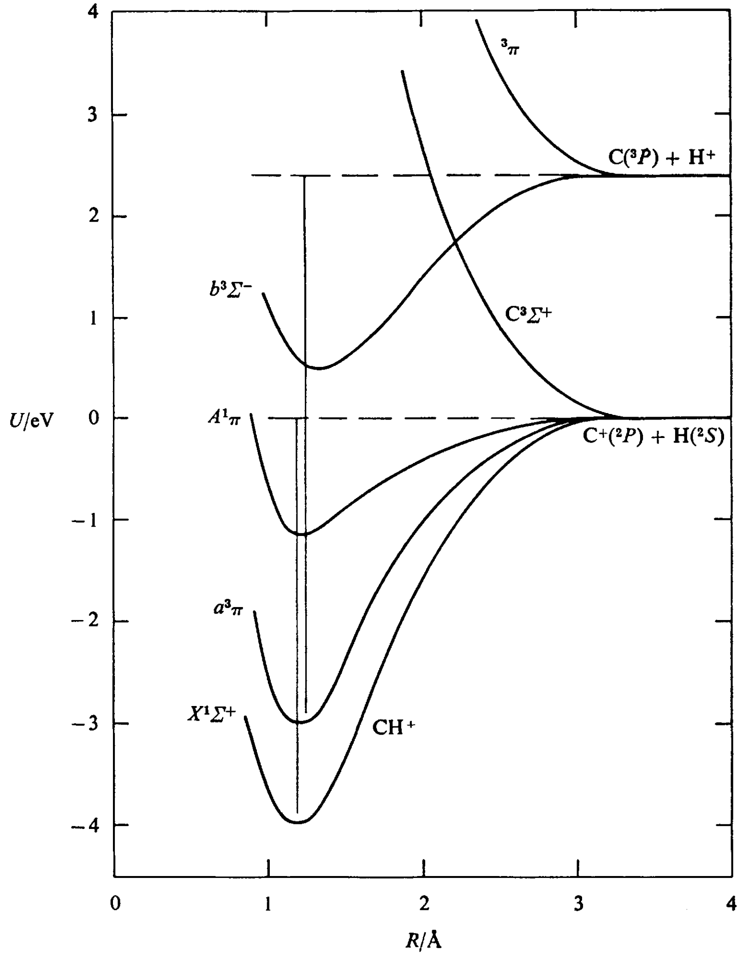


Figure 1 *Illustration of radiative processes forming* CH^+ *during collisions of* C^+ *and* H, *or* H^+ *and* C. *The former is more important because of the large* C^+/C *ratio in diffuse interstellar clouds. An allowed radiative transition from the low-lying* $A'\pi$ *state to the* $X'\Sigma^+$ *state can result in* CH^+ *formation in a small fraction of* C^+–H *collisions*

1. Only reactants in their ground states need be considered in interstellar clouds, since there is sufficient time available between collisions for even the longest lived of excited states to decay radiatively to the ground state. The temperature is also so low in interstellar clouds that any repulsive character in the potential curve for the low-lying excited state will prevent the reactants from approaching to internuclear distances sufficiently close for a radiative transition to take place. Given these restrictions and the relative abundances of atoms and atomic ions in diffuse clouds, the ionic radiative association reaction

$$C^+ + H \rightarrow CH^+ + h\nu \tag{12}$$

appears to be the most important in these regions.[1]

Having now available three diatomic species, H_2, CH^+, and OH, we can proceed to examine what bimolecular ion–molecule reactions will occur involving these species and what new molecules or ions will be formed. The rate of formation of H_2 is by far the greatest among these three so that much more H_2 will be available than CH^+ or OH. Beginning with H_2, and examining all of the potential reactions of H^+, He^+, C^+, N^+, and O^+ ions with H_2, we find that H^+, He^+, and C^+ do not react rapidly with H_2. Both O^+ and N^+ react rapidly with H_2 to initiate a chain of reactions by successive hydrogen-atom abstractions from H_2 to form H_3O^+ and NH_3^+ ions [reactions (13—(18)]. Aside from H and He, the H_2 molecule is generally the next most abundant species in diffuse clouds. Even for densities as low as 10 molecules cm^{-3}, the fractional abundance of H_2 is greater than that of O or N atoms[14] (carbon is mainly ionic). The OH^+, NH^+, H_2O^+, and NH_2^+ ions do not react with H or He, so that reactions with H_2 are the most important. The reaction

$$O^+ + H_2 \rightarrow OH^+ + H \tag{13}$$

$$\xrightarrow{H_2} H_2O^+ + H \tag{14}$$

$$\xrightarrow{H_2} H_3O^+ + H \tag{15}$$

$$N^+ + H_2 \rightarrow NH^+ + H \tag{16}$$

$$\xrightarrow{H_2} NH_2^+ + H \tag{17}$$

$$\xrightarrow{H_2} NH_3^+ + H \tag{18}$$

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \tag{19}$$

is thermodynamically allowed, but experiments have shown it to be inordinately slow.[17] The abstraction chain (16)—(18) therefore does not proceed to complete H atom saturation as it does in the oxygen analogue, reactions (13)—(15).

The OH radicals formed by reactions (8) and (9) probably react with the most abundant ion, C^+, to produce CO^+. The CO^+ ion reacts further with H_2 to produce HCO^+, the ion which has been identified as the source of the 'X-ogen' line observed in interstellar clouds [reactions (20) and (21)].[18] The CO^+ ion may also react with H atoms by charge transfer to form neutral CO:

$$C^+ + OH \rightarrow CO^+ + H \tag{20}$$

$$\xrightarrow{H_2} HCO^+ + H \tag{21}$$

---

[17] W. T. Huntress, Jr. and V. G. Anicich, *Astrophys. J.*, 1976, **208**, 237.

[18] R. C. Woods, T. A. Dixon, R. J. Saykalley, and P. G. Szanto, *Phys. Rev. Letters*, 1975, **35**, 1269.

$$\mathrm{CO^+ + H \rightarrow H^+ + CO} \qquad (22)$$

Carbon monoxide has been observed in abundance in diffuse interstellar clouds (Table 3).

Table 3 *Atomic and molecular abundances in ζ-Ophiuchii*

	Abundances	
Atom/molecule	*Observed*	*Black and Dalgarno model*
H	(1.00)	(1[illegible]
H_2	0.79	0.79
O	5.6×10^{-4}	4.6×10^{-4}
C^+	2.7×10^{-4}	2.3×10^{-4}
N	9.5×10^{-5}	5.8×10^{-5}
C	6.9×10^{-6}	7.6×10^{-6}
CO	2.0×10^{-6}	2.0×10^{-6}
OH	9.8×10^{-8}	9.3×10^{-8}
CH	6.5×10^{-8}	7.1×10^{-8}
CH^+	1.8×10^{-8}	4.0×10^{-10}
CN	1.7×10^{-8}	1.1×10^{-8}
H_2O	$<4.5 \times 10^{-9}$	2.0×10^{-9}
C_2	$<1.0 \times 10^{-8}$	2.6×10^{-8}
NH	$<1.4 \times 10^{-7}$	2.6×10^{-11}
CH_2		1.8×10^{-7}
CH_2^+		1.4×10^{-9}
CH_3^+		7.2×10^{-9}
C_2H		1.8×10^{-8}
HCO^+		9.3×10^{-11}
H_2CO		1.0×10^{-10}
HCN		8.0×10^{-10}
NH_2		3.5×10^{-14}
NH_3		1.1×10^{-14}

The CH^+ ion formed by reaction (7) does not react rapidly with H or He, but does react with H_2 [reactions (23) and (24)]. The reaction to form CH_4^+ from CH_3^+ and H_2 is endothermic, so that the chain terminates at the CH_3^+ ion. An alternative mechanism to forming hydrocarbon ions is *via* radiative association of C^+ with H_2:[1]

$$\mathrm{CH^+ + H_2 \rightarrow CH_2^+ + H} \qquad (23)$$

$$\mathrm{\xrightarrow{H_2} CH_3^+ + H} \qquad (24)$$

$$\mathrm{C^+ + H_2 \rightarrow CH_2^+ +} h\nu \qquad (25)$$

A large rate constant has been theoretically predicted[15] for reaction (25), but has not yet been confirmed in the laboratory.[9,19] If as large a fraction as 10^{-6} of the collisions between C^+ and H_2 result in CH_2^+ formation, then reaction (25) rather than (7) is the more important mechanism for initiating hydrocarbon ion formation. A large rate constant for reaction (25) may also help to explain the large CH^+/CH ratio observed in clouds where $n(H_2) > n(H)$[20]: for large fractional abundances of H_2, CH^+ is rapidly destroyed by reaction (23), and CH is produced from CH^+ by reactions (23) and (24) followed by dissociative recombination of CH_2^+ and CH_3^+ ions with electrons as in reaction (26b) below. The additional quantities of CH^+ required to match the observed CH^+/CH ratio might be formed by reaction (25) followed by u.v. photodissociation of CH_2^+ ions [or CH_3^+ ions formed *via* reactions (25) and (24)] to give CH^+. The present status of the interstellar CH^+/CH ratio problem has been reviewed recently by Dalgarno.[21]

The major loss mechanism for ions, and the major mechanism for forming neutral species from ions in diffuse clouds, is dissociative recombination with electrons [reactions (26)—(29)]. Once the density is sufficiently high for the

$$CH_3^+ + e^- \rightarrow CH_2 + H \tag{26a}$$

$$\rightarrow CH + 2H \tag{26b}$$

$$NH_3^+ + e^- \rightarrow CH_2 + H \tag{27a}$$

$$\rightarrow NH + 2H \tag{27b}$$

$$H_3O^+ + e^- \rightarrow H_2O + H \tag{28a}$$

$$\rightarrow OH + H \tag{28b}$$

$$HCO^+ + e^- \rightarrow CO + H \tag{29}$$

formation of diatomic species initiated by reactions (6)—(9), the successive processes of ionization, reaction, and recombination proceed rapidly to synthesize new polyatomic species. Dalgarno and Black[1] have reviewed more extensively the chemistry of diffuse interstellar clouds and have constructed a model of a typical diffuse cloud, ζ-Ophiuchii, based on this chemistry.[22] Table 3 shows the molecules which have been observed in ζ-Ophiuchii and the results of Dalgarno and Black's model. The agreement is very good for those molecules which have been observed and for those for which observational upper limits are available. The model also predicts densities for molecular species for which observations have not yet been made. The fractional density of molecular species is very small in diffuse clouds because of the presence of the strong u.v. radiation field, which dissociates neutral as well as ionic molecular species. In more dense clouds, where the interior of the cloud is shielded from the galactic

---

[19] F. C. Fehsenfeld, D. B. Dunkin, and E. E. Ferguson, *Astrophys. J.*, 1974, **188**, 43.

[20] J. H. Black, A. Dalgarno, and M. Oppenheimer, *Astrophys. J.*, 1975, **199**, 633.

[21] A. Dalgarno, in 'Atomic Processes and Applications', ed. Burke and Moiseiwitsch, North Holland, Amsterdam, 1976.

[22] J. H. Black and A. Dalgarno, *Astrophys. J. Suppl. Ser.*, 1977, **34**, in press.

Plate 1 *Great Nebula in Orion. Luminous regions are thin, high-temperature regions. Darker condensations of denser material are visible against the luminous background*
(Copyright by the California Institute of Technology and Carnegie Institution of Washington. Reproduced by permission from the Hale Observatories)

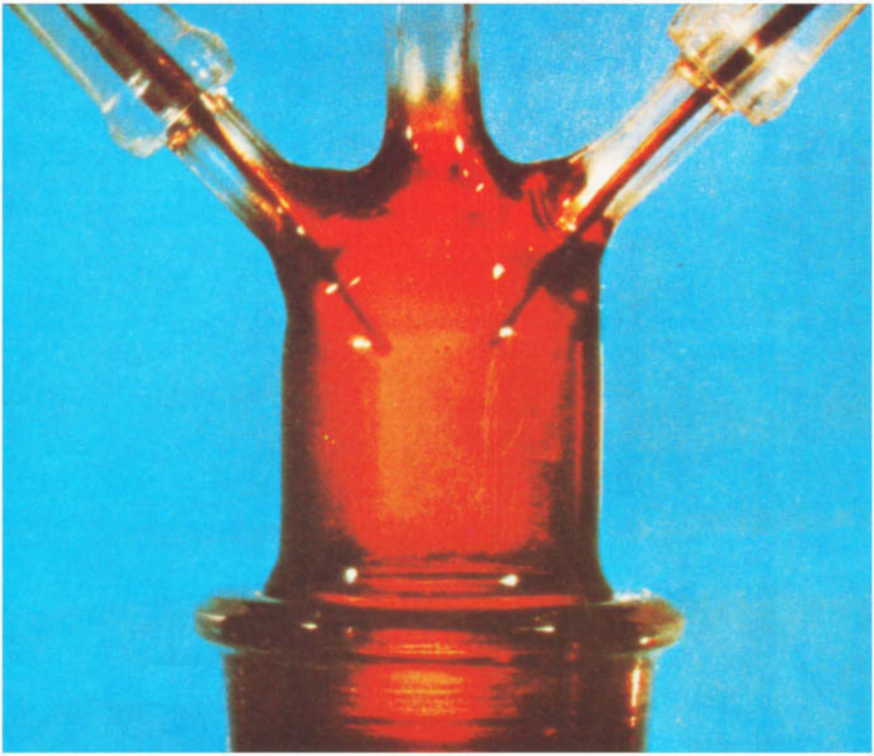


Plate 2 *Results of an electrical discharge in a methane–ammonia gas mixture*
(Reproduced by permission from *Icarus*, 1969, **10**, 386)

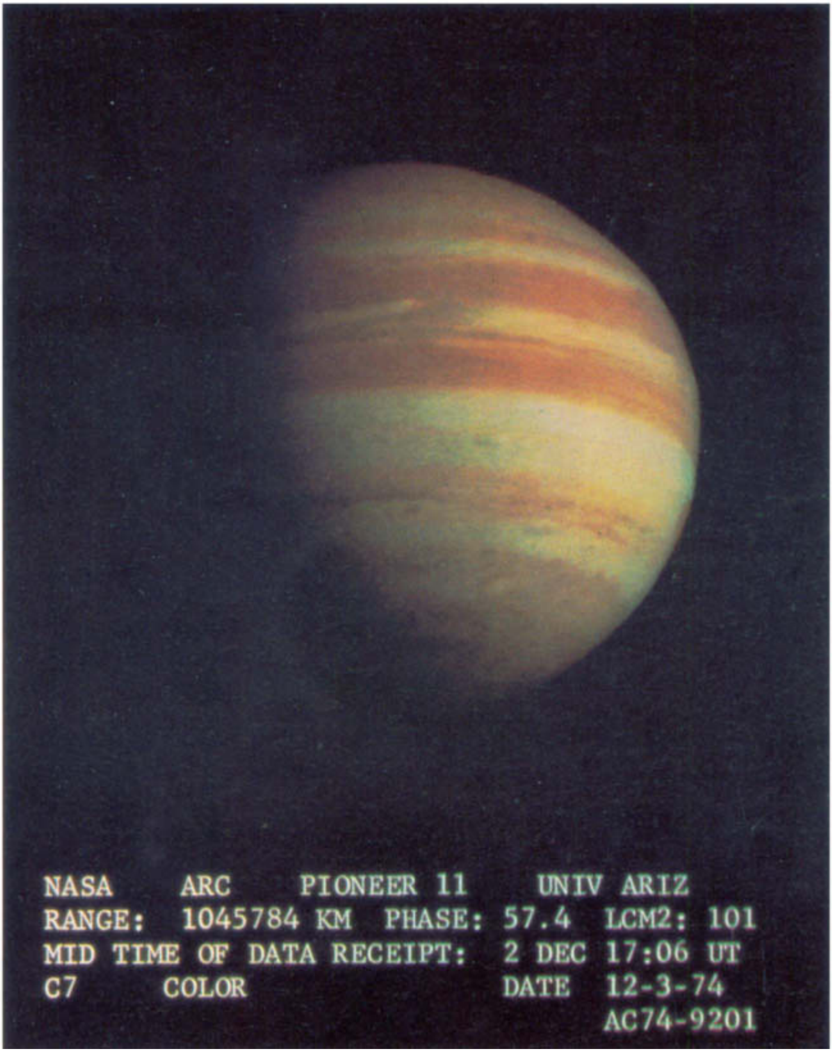


Plate 3 *Imaging photopolarimeter colour photograph of Jupiter taken by the Pioneer II spacecraft from a distance of* 10^6 km *on* 2 *December* 1974

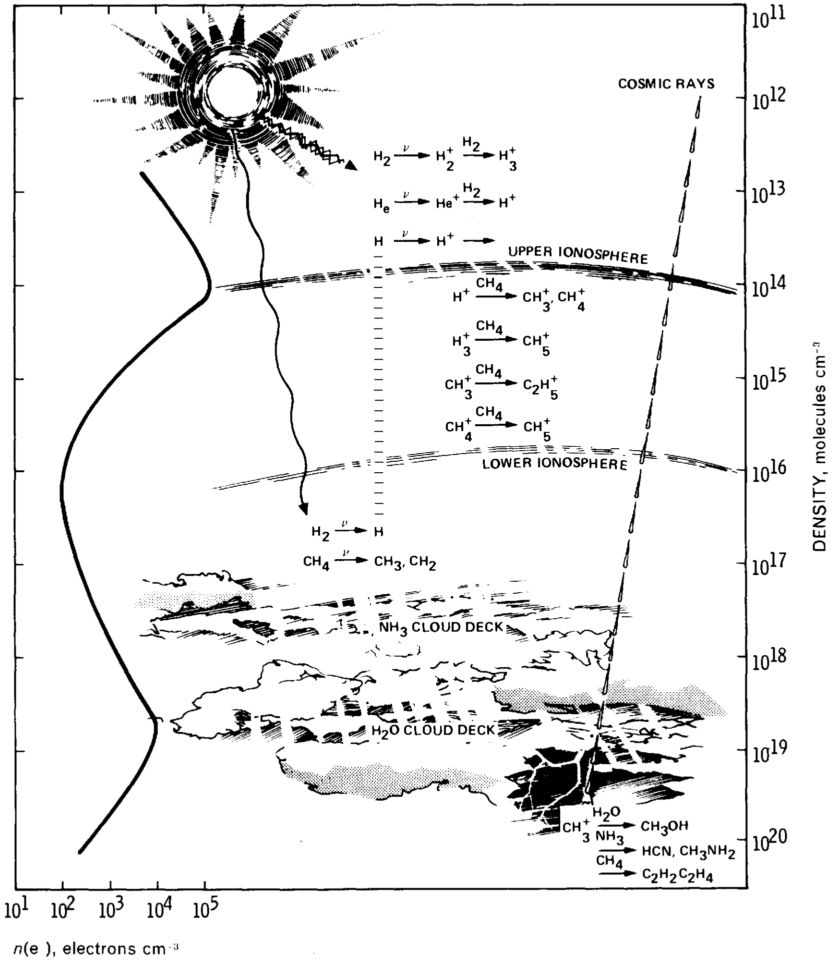


Figure 4 *Simplified representation of the ionic processes occurring at various altitudes in the atmosphere of Jupiter or Saturn. Solar photoionization and photodissociation occur in the upper atmosphere. Cosmic ray and electrical discharge ionization cause a second ionization peak at lower altitudes*

u.v. radiation, the fractional concentration of molecular species increases considerably.

4 Dense Interstellar Clouds

For densities much larger than several hundred molecules cm^{-3}, most of the hydrogen in interstellar clouds is in molecular form and the cloud becomes increasingly shelf-shielded from the galactic u.v. flux. Cosmic ray ionization becomes the most important ionization mechanism. In the course of condensation through the diffuse stage a significant fraction of C^+ has been converted into CO *via* reactions such as (20)—(22) and (29) so that $n(CO) \approx 10^{-5}$—10^{-4} $n(H_2)$. Carbon monoxide is the next most abundant molecular species after H_2. Other molecules are present in quantities of about 10^{-6}—$10^{-10}n(H_2)$. Table 4 lists some of the molecules which have been observed by radio astronomers in clouds with densities of 10^3—10^6 molecules cm^{-3}. New molecules are being added to the list constantly as observations proceed. Complex organic molecules are observed, some containing as many as nine atoms, and no doubt even more complex organic molecules will be discovered. Just over a decade ago it was beyond suggestion that such highly evolved organic molecules could ever exist in such cold, thin, isolated regions of interstellar space. It is becoming increasingly

Table 4 *Molecular species observed in dense clouds. Estimated fractional abundances given by* $(x) = 10^x$

Diatomic		*Tetra-atomic*		*Octa-atomic*	
H_2	(0)	NH_3	(−6)	$CH_3C{\equiv}CCN$	(−10)
OH	(−7)	H_2CO	(−8)	$HCOOCH_3$	(−10)
CH	(−8)	H_2CS	(−10)		
CO	(−4)	HNCO	(−9)	*Nona-atomic*	
CN	(−8)			CH_3CH_2OH	(−10)
CS	(−7)	*Penta-atomic*		CH_3OCH_3	(−10)
NS	(−8)	CH_2NH	(−10)		
SO	(−7)	HCOOH	(−10)		
SiO	(−7)	$HC{\equiv}CCN$	(−8)		
SiS	(−7)				
		Hexa-atomic			
Triatomic		CH_3OH	(−7)		
HCO	(−8)	NH_2CHO	(−10)		
HCO^+	(−7)				
HCN	(−6)	*Hepta-atomic*			
HNC	(−6)	CH_3CHO	(−10)		
N_2H^+	(−7)	CH_3NH_2	(−10)		
C_2H	(−7)	$H_2C{=}CHCN$	(−10)		
H_2S	(−8)	$CH_3C{\equiv}CH$	(−9)		
SO_2	(−7)	$HC{\equiv}C{-}C{\equiv}CCN$	(−10)		
OCS	(−8)				

obvious that ion–molecule reactions are responsible for the synthesis of a large number of them.

The C^+ ion remains a cornerstone in the formation of organic species in dense clouds, even though they are present in much smaller fractional abundance than in diffuse clouds.[1] The ionization rate is lower in dense clouds owing to the lack of u.v. ionization. Carbon is mainly in the form of atomic carbon and CO in dense clouds. However, the C^+ ion is still one of the most abundant ionic species present. It is produced by the reaction

$$He^+ + CO \rightarrow C^+ + O + He \qquad (30)$$

The He^+ ions are produced by cosmic ray ionization of He. Since $n(He)/n(H_2) \approx 0.15$, reaction (30) represents a large fraction of the total ionization rate. The importance of reaction (30) results from the fact that the He^+ ion does not react rapidly with H_2. The reaction

$$He^+ + H_2 \rightarrow H^+ + H + He \qquad (31)$$

occurs in less than 0.01% of the collisions with H_2 at 300 K,[23] and is even slower at interstellar temperatures.[17]

Ionization of H_2 by cosmic rays accounts for the major proportion of the ionization in dense clouds. For every H_2 molecule ionized, an H_3^+ ion is produced *via* reaction (1). H_3^+ ions are rapidly lost *via* dissociative recombination with electrons, whereas C^+ ions are lost only very slowly by radiative recombination. For this reason C^+ ions are an important ionic species in dense as well as diffuse clouds. The function of H_3^+ ions in dense clouds is to produce protonated species *via* reactions of the type (32).[1,10] For O atoms this reaction initiates the abstraction chain to produce OH and H_2O. For C atoms this reaction initiates the abstraction chain to produce the CH_3^+ ion and CH and CH_2 *via* reaction (26). For N atoms, reaction (32) is not thermodynamically allowed, and an alternative reaction channel (33) may initiate the abstraction chain terminating in NH_3^+ *via* reaction (18).

$$H_3^+ + X \rightarrow XH^+ + H_2 \qquad (32)$$

$$H_3^+ + N \rightarrow NH_2^+ + H \qquad (33)$$

The NH_3^+ ion does not abstract an H atom rapidly from H_2 at low temperatures. Abstraction is possible, however, from OH and H_2O:[10,17]

$$NH_3^+ + OH \rightarrow NH_4^+ + O \qquad (34)$$

$$NH_3^+ + H_2O \rightarrow NH_4^+ + OH \qquad (35)$$

Ammonia can then be synthesized by the dissociative recombination of NH_4^+ ions with electrons:

$$NH_4^+ + e^- \rightarrow NH_3 + H \qquad (36)$$

[23] R. Johnsen and M. A. Biondi, *Icarus*, 1974, **23**, 139.

Alternatively, NH_3 may be synthesized directly from NH_3^+ by charge transfer to a metal atom such as Mg, Si, Na, Al, or Fe:

$$NH_3^+ + Mg \rightarrow Mg^+ + NH_3 \qquad (37)$$

Because OH, H_2O, and the metals are so much less abundant than H_2, the NH_3/H_2O ratio is expected to be small, of the order of 10^{-3}, even though the cosmic N/O ratio is about 0.5. This low NH_3/H_2O ratio has been confirmed in the Orion nebula,[24] which provides support for the gas-phase ion–molecule reaction theory for interstellar molecular synthesis. The temperature must be of the order of 200 K or more in order for reaction (19) to be sufficiently fast for the NH_3/H_2O ratio to approach the cosmic N/O value.

Hydrogen cyanide is another commonly observed molecule in dense clouds. One method of synthesis is shown in reactions (38) and (39). However, in the absence of effective NH_3 synthesis, more likely reactions are[14]

$$C^+ + NH_3 \rightarrow H_2CN^+ + H \qquad (38)$$

$$H_2CN^+ + e^- \rightarrow HCN + H \text{ (or CNH + H)} \qquad (39a)$$

$$\rightarrow CN + 2H \qquad (39b)$$

$$C^+ + NH_2 \rightarrow HCN^+ + H \qquad (40)$$

and

$$CH_3^+ + N \rightarrow HCN^+ + H_2 \qquad (41)$$

followed by

$$HCN^+ + H_2 \rightarrow H_2CN^+ + H_2 \qquad (42)$$

and reaction (39). The H_2CN^+ ion most likely has the structure $HCNH^+$ so that the observation of both HCN and HNC in interstellar clouds with near equal densities fits nicely with the theory of production by ion–molecule reactions.

The HCO^+ ion is isoelectronic to HCN and is produced by a number of reactions (43)—(46)[1,14] in addition to reactions (20) and (21). Reaction (46) is a chemi-ionization reaction between neutral radicals, and may be fast even at interstellar temperatures. The carbon–oxygen family of observed interstellar molecules includes CO, CH_2O, and CH_3OH. Carbon monoxide is synthesized *via* dissociative recombination of HCO^+ ions with electrons [reaction (29)]. Methanol is most likely synthesized *via* radiative association of CH_3^+ ions with H_2O [reaction (3a)],[9] followed by dissociative recombination. Ion–molecule

$$C^+ + H_2O \rightarrow HCO^+ + H \qquad (43)$$

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \qquad (44)$$

$$CH_3^+ + O \rightarrow HCO^+ + H_2 \qquad (45)$$

$$CH + O \rightarrow HCO^+ + e^- \qquad (46)$$

---

[24] J. W. Waters, J. J. Gustincic, J. J. Kakar, T. B. H. Kuiper, H. K. Roscoe, P. N. Swanson, A. R. Kerr, and P. Thaddeus, *Astrophys. J.*, 1977, in press.

schemes to produce formaldehyde have been difficult to formulate, and present theory[25] favours the neutral reaction

$$CH_3 + O \rightarrow CH_2O + H \tag{47}$$

Neutral radical–radical recombination reactions can have very small activation energies and may possibly occur at interstellar temperatures. The difficulty with reaction (47) is the problem of synthesizing CH_3 by a low-probability process, *i.e*, radiative recombination of CH_3^+ with electrons in competition with reaction (26). A more likely process would seem to be the radical–radical reaction (48) where

$$CH_2 + OH \rightarrow CH_2O + H \tag{48}$$

CH_2 is derived from reaction (26a) and OH from reaction (28b). A possible scheme for formaldehyde production involving ion–molecule reactions is

$$CH_3^+ + OH \rightarrow CH_2O^+ + H_2 \tag{49}$$

$$CH_2O^+ + Mg \rightarrow Mg^+ + CH_2O \tag{50}$$

A variant of this scheme suggested by Dalgarno *et al.*[25] uses reaction (51)

$$CH_3^+ + O \rightarrow CH_2O^+ + H \tag{51}$$

but recent laboratory work[26,10] indicates that the product of the CH_3^+–O reaction is most likely $HCO^+ + H_2$ and not $CH_2O^+ + H$. Radiative association of HCO^+ and H_2 has also been suggested [reactions (52) and (53)],[27] but

$$HCO^+ + H_2 \rightarrow CH_2OH^+ + h\nu \tag{52}$$

$$\xrightarrow{e^-} CH_2O + H \tag{53}$$

laboratory work[19] indicates that the structure of intermediate complex, in collisional association reactions at least, is probably a cluster ion $HCO^+ \cdot H_2$ and not protonated formaldehyde.

The ethynyl radical observed in dense clouds is readily explained from ion chemistry in the hydrocarbon family. C—C bonds are synthesized by the reactions[14]

$$C^+ + CH \rightarrow C_2^+ + H \tag{54}$$

$$C^+ + CH_2 \rightarrow C_2H^+ + H \tag{55}$$

$$CH_3^+ + C \rightarrow C_2H^+ + H_2 \tag{56}$$

followed by

$$C_2^+ + H_2 \rightarrow C_2H^+ + H \tag{57}$$

$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H \tag{58}$$

[25] A. Dalgarno, M. Oppenheimer, and J. H. Black, *Nature Phys. Sci.*, 1973, **245**, 100.
[26] F. C. Fehsenfeld, *Astrophys. J.*, 1976, **209**, 638.
[27] E. Herbst and W. Klemperer, *Astrophys. J.*, 1973, **185**, 505.

The abstraction chain from H_2 stops at $C_2H_2^+$. Dissociative recombination with electrons produces C_2 and C_2H from $C_2H_2^+$:

$$C_2H_2^+ + e^- \rightarrow C_2H + H \qquad (59a)$$

$$\rightarrow C_2 + 2H \qquad (59b)$$

Gas-phase chemical reaction schemes have been proposed[1,25,28] for the synthesis of a few of the other species listed in Table 4, such as SO, SN, CS, OCS, H_2O, H_2CS, N_2H^+, SiO, and SiS, but no schemes have yet been put forward for the synthesis of most of the other more complex species listed in Table 4. Smith and Adams[9] have suggested that radiative association of CH_3^+ ions with H_2O, NH_3, CH_2O, CH_3OH, and CH_3NH_2 can lead to production of the protonated ions of methanol, methylamine, acetaldehyde, ethanol (or dimethyl ether), and dimethylamine, respectively. The parent neutrals could then be formed from the protonated ions by dissociative recombination with electrons. Except for the reaction with H_2O, fast bimolecular reactions occur between CH_3^+ and the other neutrals listed by Smith and Adams. The importance of radiative association *versus* bimolecular reaction depends on the temperature dependence of the lifetime of the intermediate complex. Methyl cations do not undergo bimolecular reactions with CO or HCN, and radiative association in these collisions can lead to synthesis of ketene and acetonitrile as in reactions (60)—(63). A number of

$$CH_3^+ + CO \rightarrow CH_3CO^+ + h\nu \qquad (60)$$

$$\xrightarrow{e^-} CH_2CO + H \qquad (61)$$

$$CH_3^+ + HCN \rightarrow CH_3CNH^+ + h\nu \qquad (62)$$

$$\xrightarrow{e^-} CH_3CN + H \qquad (63)$$

such reactions can be envisioned to synthesize many of the species given in Table 4. For an astrochemist, the prospect of constructing mechanisms for the synthesis of interstellar molecules and testing them both in the laboratory and against observations is an exciting one. An interdisciplinary approach is required since hints can sometimes be gleaned from observations, and in the course of constructing synthetic mechanisms from laboratory work or theoretical work the astrochemist can often suggest confirming observations to the radio astronomer.

5 Planetary Atmospheres

A. Origin and Evolution of Planetary Atmospheres.—As the more massive of dense interstellar clouds proceed on a course of self-gravitating collapse, both observation and theory suggest that the central densities and temperature can get sufficiently high to initiate nuclear reaction, resulting in star formation. There do appear to be infrared-emitting objects located at the central point of some dense

---

[28] J. L. Turner and A. Dalgarno, *Astrophys. J.*, 1977, **213**, 386.

clouds, such as Orion A. These objects may be proto-stars. At densities $n > 10^6$ molecules cm^{-3}, and at elevated temperatures of the order of several hundred degrees, reactions among neutral species become ever more important. Gradually, as the proto-star becomes a new sun and the initiating nebula builds planets around the central sun, all of the gaseous material in the nebula is converted into stable, reduced forms. Because of the overwhelming relative abundance of hydrogen, carbon is converted almost entirely into CH_4, nitrogen into NH_3, and oxygen into H_2O. It is curious to note that in the highly reducing environment of dense interstellar clouds a large percentage of the carbon is in an oxidized form, CO, but that at the higher temperatures and densities of proto-stellar nebulae, CH_4 is probably the major reservoir of carbon. This difference may be due to the lower temperature and much higher fractional ionization in interstellar clouds compared with proto-solar nebulae and planetary atmospheres.

In the above scenario, large massive planets will develop atmospheres containing molecular hydrogen with about 15% helium and very much smaller percentages of CH_4, NH_3, and H_2O according to the cosmic abundances of C, N, and O. Jupiter is a primary example of such a body in our own solar system. Jupiter is a gas giant composed mostly of H_2 and He.[29] Methane and ammonia have been detected in Jupiter's atmosphere in roughly their equivalent cosmic abundances. Whatever rocky core Jupiter may possess is small compared with its own deep atmosphere. The planet is almost entirely gaseous because of the very low cosmic abundance of the refractory, solid-forming elements such as Fe, Mg, Al, and Si. The radius of a Jovian rocky core could be no more than one-fifth of the total radius of the planet. The pressure at the bottom of the Jovian atmosphere is of the order of 10^8 atmospheres, and the temperature is of the order of 20 000 K. Under these conditions, hydrogen is completely dissociated and probably exists in metallic form. Saturn is very similar to Jupiter, and Uranus and Neptune are both somewhat smaller examples of the same class of gas giant. Together, these four planets are referred to as the Jovian family of planets. The relative sizes of the planets of our solar system are shown in Figure 2, and Table 5 gives what is known of their atmospheric composition.

Table 5 *Atmospheric Compositions*

	Venus	*Earth*	*Mars*	*Jupiter*
Major species	CO_2	N_2	CO_2	H_2
		O_2		He
Minor species	H_2O	Ar	N_2	CH_4
	O_2	CO_2	Ar	NH_3
	CO	H_2O	H_2O	H_2O
	O_3	O_3	O_2	C_2H_2
	HCl	CO	CO	C_2H_6
	HF	N_2O	O_3	CO
				PH_3

---

[29] A source book on Jupiter, the major member of the Jovian family of planets, is edited by T. Gehrels: 'Jupiter', University of Arizona Press, Tucson, 1976.

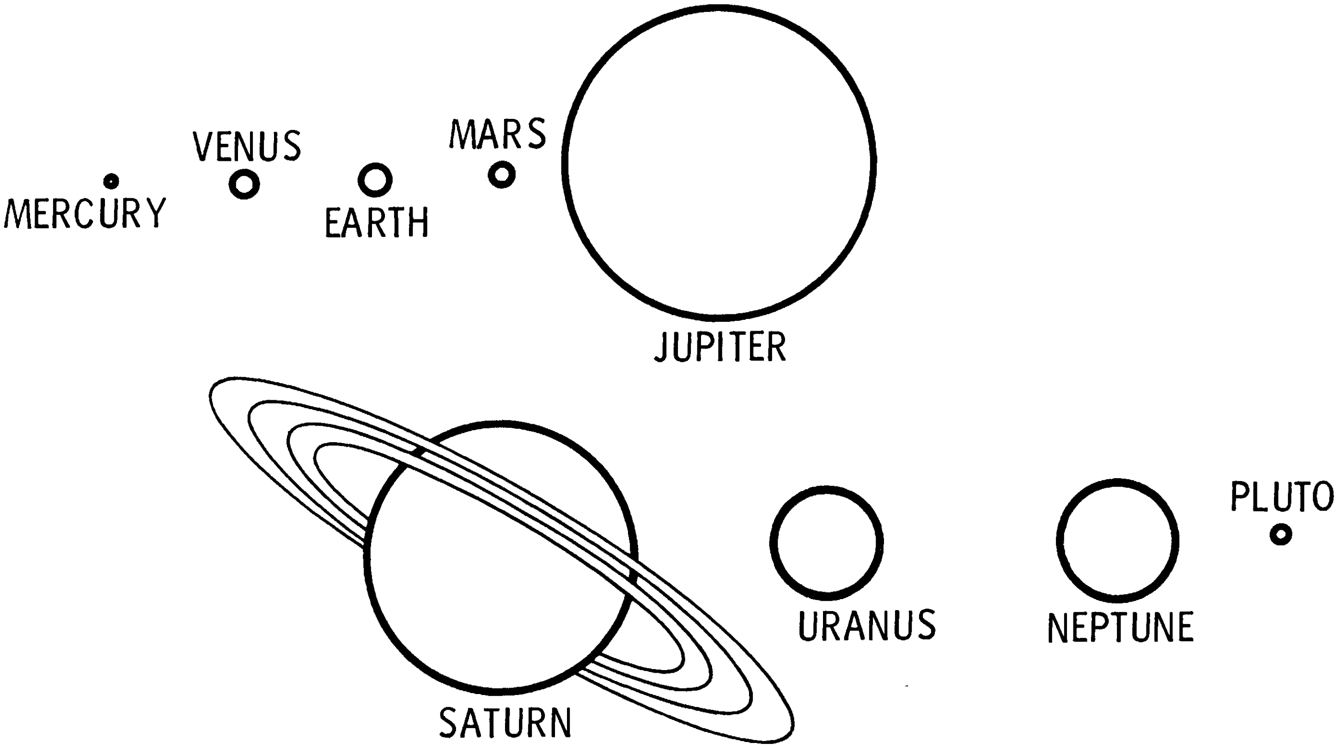


Figure 2 *Relative sizes of the planets of the solar system*

The smaller terrestrial planets, Mercury, Venus, Earth, and Mars, are examples of planets which were too small in their formative stages to accrete massive atmospheres from the surrounding solar nebula. The dividing line between gas giant and terrestrial-type planet is defined by whether or not hydrogen atoms can escape from the upper atmosphere by thermal excitation. The gas giants are so massive that H atoms cannot escape from their atmospheres in times approaching that of the age of the solar system. The gas giants are also distant from the sun and their atmospheres are cold. The terrestrial planets are closer to the sun, and their atmospheres can get much warmer. The terrestrial planets are also quite small. Hydrogen atoms take only several times 10^4 years to escape from the upper atmosphere of the Earth. Thus, through the continuing process of loss of hydrogen to space, the atmospheres of the terrestrial planets have become more oxidizing in nature.[30–33] Furthermore, any original atmospheres the terrestrial planets may have accreted in their formative stages must have subsequently been completely lost very early in their history. The present atmospheres of the terrestrial planets can only be of secondary origin; that is they can only have been formed by outgassing of the interior.

The evidence for loss of the primordial atmosphere of the Earth comes from the observation that the so-called ‘rare’ gases, Ne, Ar, Kr, and Xe, are in fact rare in the Earth’s atmosphere.[30] The same situation holds true for Mars’s atmosphere. Neon and the natural isotopes of Ar, Kr, and Xe are simply not present in the atmospheres of Earth and Mars in their cosmic proportions; they are depleted by factors of the order of 10^7. Helium readily escapes from the atmosphere of Earth, but not the heavier noble gases. Where did all these gases go? The geological record shows that the Earth’s interior is strongly degassed owing to tectonic activity. Therefore, the missing quantities cannot be trapped in the interior. The only remaining explanation is that the entire primordial atmospheres of Earth and Mars (Venus and Mercury probably as well), if indeed there were any primordial atmospheres, must have been entirely lost at some early catastrophic epoch in their formative stages. Jupiter, on the other hand, has clearly retained all of its initial atmosphere since hydrogen and helium are present in roughly their cosmic proportions. Jupiter at least among the gas giants is a fossil relic of the nebula which condensed to form the sun. Jupiter’s atmospheric composition has probably not changed since the time of formation of the planets.

Some clues as to the composition of the primordial atmosphere outgassed from the primitive terrestrial planets can be gained from theoretical studies and by examining the composition of the gases evolved by heating meteorites.[31] Certain classes of meteorite, such as the chondrites, are believed to be relics left over from a swarm of particles out of which the solid bodies of the terrestrial planets were formed. Table 6 shows the composition of the gas released from a

[30] F. P. Fanale, *Chem. Geol.*, 1971, **8**, 79.
[31] F. P. Fanale, *Icarus*, 1971, **15**, 279.
[32] A. J. Meadows, *Planet. Space Sci.*, 1973, **21**, 1467.
[33] L. Margolis and J. E. Lovelock, *Icarus*, 1974, **21**, 471.

Table 6 *Primordial Rock Gas Composition Released above* 1050 K

	Normal chondrite	*Earth basalt*	*Equilibrium theory*
CO_2	64	50	55
H_2	26	40	36
CO	4	3	6
N_2	2	2	3
CH_4	4	2	—
H_2O	—	1000	1500

normal chondritic meteorite and from a primitive Earth basalt (primitive unmodified volcanic rock) when heated to melting. The third column in Table 6 shows what would be expected on the basis of chemical equilibrium between rock melt and gas at 1050 K. A large quantity of hydrogen is present in addition to CO_2 and H_2O, and on release of this hot gas from the interior of the Earth to the surface the gas cools rapidly where the chemical equilibrium (64) shifts

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O\downarrow \tag{64}$$

strongly to methane formation, especially with the condensation of H_2O to form oceans. The initial, secondary atmosphere of the Earth was therefore probably reducing in nature and contained carbon largely as CH_4. Methane would then have been slowly oxidized back to CO_2 in the Earth's primitive atmosphere by thermal processes, by solar photolysis, and by other energetic mechanisms as the equilibrium is shifted back to CO_2 by the rapid escape of H_2 from the atmosphere:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2\uparrow \tag{65}$$

The difference between Mars and Earth is that Mars, being a much smaller planet, lost its reducing atmosphere much more rapidly than did the Earth[31] and did not (probably because of the loss of a reducing atmosphere) develop life on its surface. The present O_2/N_2 atmosphere is due to the action of biology on the Earth's surface and in the oceans,[32,33] and the Earth's primitive CO_2 atmosphere has been completely dissolved and deposited by the Earth's oceans. The difference between Earth and Venus is that Venus, being much closer to the sun, accreted out of higher-temperature material that contained very little water of crystallization.[2] Hence, very little H_2O was outgassed from Venus's interior. Therefore, ocean formation was not possible and the atmosphere remained forever as CO_2. If all of the CO_2 presently dissolved in the Earth's oceans and deposited in the Earth's sedimentary formations (carbonates) were to be released into the atmosphere, the Earth would have almost the exact equivalent of Venus's atmosphere; almost pure CO_2 at a surface pressure of 90 atm![30,31]

For the abiogenic synthesis of organic compounds, a reducing environment is required.[5] The oxidizing atmospheres of the present-day terrestrial planets are incapable of such synthesis. The primitive methane atmosphere of the Earth probably was, and the present-day atmospheres of the gas giants almost certainly are, sites where the abiological synthesis of organic compounds from simple hydrides can and did take place. The classic experiment was conducted by Stanley

Miller[34] in the early 1950's. Miller showed that simple amino-acids were produced in electrical discharges through mixtures of gaseous CH_4, NH_3, and H_2O. These are exactly the same starting materials available in the atmospheres of the gas giants, and probably in the Earth's primitive atmosphere as well. Plate 2 shows the results of an electrical discharge in a mixture of methane and ammonia. A red tarry substance condenses on the wall of the reaction vessel, which on hydrolysis yields amino-acids. The intermediate products have been identified as HCN, α-aminonitriles, CH_2O, and other aldehydes.[5,34] Curiously enough, similar molecules are also observed in dense interstellar clouds! The coloration of the material in Plate 2 is tantalizingly close to the coloration of the cloud bands in the Jovian atmosphere shown in Plate 3. It is tempting to ascribe the Jovian colorations to the same processes which produce the colours in the experiments illustrated in Plate 2.

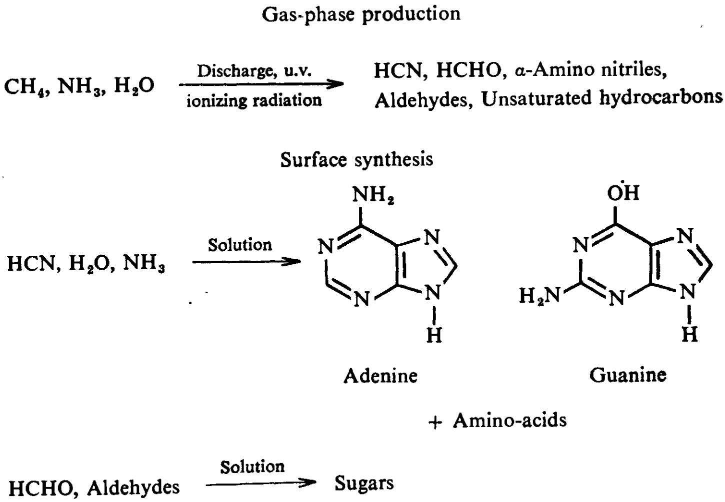


Figure 3 *Generalized scheme for the abiogenic synthesis of biologically important compounds, starting with the simple hydrides in the gas phase*

The general scheme of prebiotic, or abiogenic, synthesis of organic compounds is illustrated in Figure 3. From simple hydrides in the gas phase, energetic processes such as solar u.v., cosmic rays (ionizing radiation) and discharges produce simple organic precursors such as HCN, CH_2O, α-aminonitriles, aldehydes, and unsaturated hydrocarbons. These species are captured in aqueous solutions (oceans in the case of the primitive Earth, water droplets in a massive planet-wide cloud deck in the case of Jupiter) where they undergo hydrolysis and condensation to form amino-acids, purines, and pyrimidine bases and sugars.

---

[34] S. L. Miller, *Science*, 1953, **117**, 528.

These latter are the basic building blocks for formation of peptides, nucleosides, nucleotides, and various other complex organic material required for the initiation and sustenance of organic chemical life. The theory of chemical evolution leading towards the origin of life has been discussed in detail in a number of review books[35] and articles.[5] In the following sections, an examination is made of what is presently known about the potential contributions that ionic processes make to the overall scheme of gas-phase organic synthesis in both the prebiotic synthesis experiments and in their natural counterpart in the atmospheres of the Jovian planets.

B. Ionospheric Chemistry.—The ionosphere is that upper region of the atmosphere where the density is very low ($\lesssim 10^{14}$ molecules cm^{-3} or $\lesssim 10^{-5}$ atm) and the species present are ionized by the solar u.v. flux. In general, photochemical products are present also, formed by solar photodissociation of atmospheric species below the ionosphere and having diffused up to more tenuous ionospheric heights. In the case of the gas giants,[2,29] atomic hydrogen is the most abundant photochemical product present in the ionosphere. Some methane is also present in the lower part of the ionospheres of the gas giants, but no NH_3 or H_2O. These latter gases are condensed out of the atmosphere into cloud decks at much lower altitudes. Figure 4* provides a simplified representation of the processes occurring at various levels in the Jovian atmosphere. The chemistry of the ionospheres of the Jovian planets is then the ion chemistry in a mixture principally of H, H_2, and He with a small percentage of methane near the lower boundary.[36]

Without NH_3 or H_2O, the ionospheric chemistry is not effective in producing organic species except for minor amounts of hydrocarbons. The ionospheres of the outer planets are warmer ($\sim$ 80—150 K) and denser than interstellar clouds so that the reaction of He^+ ions with H_2 [reaction (31)], albeit slow, is an efficient He^+ ion loss mechanism. Solar ionization of H, He, and H_2 then results in H^+ and H_3^+ being the most important ions, and H_3^+ is rapidly lost by recombination with electrons to produce H atoms. At lower altitudes where CH_4 is present, reactions (66) and (67) convert hydrogenic ions into hydrocarbon ions,

$$H^+ + CH_4 \rightarrow CH_3^+ + H_2 \qquad (66a)$$

$$\rightarrow CH_4^+ + H \qquad (66b)$$

$$H_3^+ + CH_4 \rightarrow CH_5^+ + H_2 \qquad (67)$$

followed by reactions (68) and (69). Most of the ionization of CH_4 is accomplished

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (68)$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad (69)$$

---

* Opposite p. 307

[35] A source book on these processes is edited by S. L. Fox: 'The Origin of Prebiological Systems', Academic Press, New York, 1965.

[36] W. T. Huntress, Jr., *Adv. Atom. Mol. Phys.*, 1974, **10**, 295.

by reactions (66) and (67) since hydrogen is so abundant, but solar photoionization of CH_4 and its photochemical products does contribute. Neither CH_5^+ nor $C_2H_5^+$ reacts with H_2 or CH_4, but at the lowest altitudes, where the pressures are highest, three-body collisional association reactions, *e.g.* (70)—(74), can become

$$CH_3^+ + H_2 \xrightarrow{H_2} CH_5^+ \tag{70}$$

$$CH_5^+ + CH_4 \xrightarrow{H_2} C_2H_9^+ \tag{71}$$

$$C_2H_5^+ + H_2 \xrightarrow{H_2} C_2H_7^+ \tag{72}$$

$$+ CH_4 \xrightarrow{H_2} C_3H_9^+ \tag{73}$$

$$C_2H_7^+ + CH_4 \xrightarrow{H_2} C_3H_{11}^+ \tag{74}$$

important. These and higher-order clustering reactions have been used in model calculations of the chemistry in the ionospheres of the Jovian planets.[8] These reactions serve to produce hydrocarbons by subsequent dissociative recombination with electrons, such as reactions (75) and (76). Ethane and acetylene have

$$C_2H_5^+ + e^- \rightarrow C_2H_4 + H \tag{75a}$$

$$\rightarrow C_2H_2 + H + H \tag{75b}$$

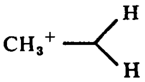
$$C_2H_7^+ + e^- \rightarrow C_2H_6 + H \tag{76}$$

been identified with the atmosphere of Jupiter.[29]

At lower altitudes the atmosphere is shielded from solar ionizing photons. Ionization can still occur at these lower levels owing to the penetration of cosmic rays. Model calculations of the atmospheres of Saturn, Uranus, and Neptune show that ionization by cosmic rays peaks near the 1 atm level and can produce number densities of ions and electrons ($\sim 10^4$ cm^{-3}) nearly equal to that produced by solar photoionization hundreds of kilometres higher in the ionosphere.[8] The base of the water cloud in the atmosphere of Jupiter is near the 1 atm level. Thus, cosmic ray ionization can provide the activation energy necessary to initiate ionic reactions leading to the synthesis of new organic species in the regions of the atmosphere within and below the cloud layers in the Jovian planets where NH_3 and H_2O exist.

C. Ion Chemistry in the Lower Atmosphere of the Jovian Planets.—In addition to cosmic ray ionization, discharges in the turbulent cloudy regions in the lower atmospheres of the Jovian planets during thunderstorms can also contribute to primary ionization. An electrical discharge was the energy source used in the classic Miller experiment,[34] and electrical discharges remain one of the primary energy sources advocated for the prebiotic synthesis of organic compounds in the atmosphere of the primitive Earth.[5,35] Earth-based and spacecraft photographs of Jupiter's cloud bands show the atmosphere to be extremely turbulent.[29] Swirling vortices are clearly evident, and convection occurs on a large scale with giant plumes reaching high into the atmosphere. Under these conditions there is every reason to believe that thunderstorm activity can be prevalent.[37] Laboratory experiments clearly show the formation of the organic compounds necessary to begin and sustain life during electrical discharges under the conditions present at these levels in the Jovian atmosphere.[5,35] Since ion formation is a necessary part of electrical discharges, ion chemistry in discharges may play an important role in the synthesis of organic compounds both in the laboratory experiments and in the present atmospheres of the Jovian planets.

At pressures appropriate to the cloudy regions in the Jovian atmosphere, 0.1 atm and above, three-body collisional association reactions become very important. Even if a bimolecular ion–molecule reaction is possible, the collisional association reaction can often dominate. Methyl cations are among the most important of ionic species produced by ionization of H_2, CH_4, NH_3, and H_2O since they are formed in almost half of the methane ionization events, and since they are a very good condensation reagent.[10] There are no bimolecular reactions between CH_3^+ ions and H_2, so that the ion is stable in H_2 and can react with the trace species present. At high pressures, collisional association of CH_3^+ ions with H_2 can form CH_5^+ in a hydrogen atmosphere. However, the rate constant of the CH_3^+–H_2 association reaction is a hundred times smaller than, for example, the rate constant for the CH_3^+–H_2O reaction.[9] This relationship probably also holds true for association of CH_3^+ ions with any polar molecule in relation to H_2, so that even in a hydrogen-dominated atmosphere association reactions of CH_3^+ ions can still be important. Also, the structure of the CH_5^+ ion involves a three-centre bond so that the ion looks very much like a CH_3^+–H_2 complex (1). It is possible, therefore, that in collisional association reactions the CH_5^+ ion may react very much like a CH_3^+ ion *via* attendant H_2 elimination, although this premise remains to be examined in the laboratory. In the discussion to follow we will emphasize the importance of association reactions at atmospheric pressures for organic synthesis. Attention was first called to this point by Hiraoka and Kebarle[38] with regard to alcohol and organic acid formation. Here we expand on this notion to illustrate further the utility of the mechanism for abiogenic synthesis of organic species by ionic reactions at high pressures. It is important to emphasize that at this point most of the mechanisms suggested are speculative.



(1)

---

[37] A. Bar-Nun, *Icarus*, 1975, **24**, 86.

[38] K. Hiraoka and P. Kebarle, *J. Amer. Chem. Soc.*, 1977, **99**, 360, 366.

An excellent example of competition between bimolecular reaction and association reaction is found in the case of CH_3^+ ions reacting with NH_3 [reaction (76)]. At low pressures ($< 10^{-5}$ atm) only the $CH_2NH_2^+$ ion product is observed

$$CH_3^+ + NH_3 \longrightarrow [CH_3NH_3^+]^* \begin{cases} \longrightarrow CH_2NH_2^+ + H_2 & (76a) \\ \xrightarrow{H_2} CH_3NH_3^+ & (76b) \end{cases}$$

from this reaction[10] (another reaction channel forming NH_4^+ ion is also observed but is unimportant for the discussion). Recombination of $CH_2NH_2^+$ ions with electrons can then lead to methanimine or HCN formation:

$$\begin{tikzcd} CH_2NH_2^+ + e^- \arrow[r] & CH_2NH + H \arrow[d, squiggly] & (77) \\ \arrow[r] & HCN + H_2 + H & (78) \end{tikzcd}$$

Methanimine is not a particularly stable species and can decompose readily to HCN. [At low interstellar temperatures, however, methanimine is clearly stable since the molecule has been observed in these regions by radio astronomers. The reaction sequence (76a)—(77) may account for its presence.] The reaction sequence (76a)—(78) could be responsible for HCN formation in the Jovian lower atmosphere, but at these high pressures the collisional association reaction (76b) can also become important. The atmospheric pressure at which reaction (76b) competes effectively with (76a) can be calculated by equating the bimolecular and three-body rates, or $[H_2] \gtrsim K_{76a}/K_{76b}$. Using $K_{76a} \approx 10^{-9}$ cm³ s⁻¹, $K_{76b} \approx 10^{-26}$ cm⁶ s⁻¹, and Loschmidt's number (at 300 K), we find $[H_2] \gtrsim 0.003$ atm. so that the collisional association reaction can compete even at fairly low pressures on the atmospheric scale. Reaction (76b) has been observed at pressures as low as 0.2 Torr in helium by Smith and Adams.[9] Dissociative recombination of the product ion with electrons can then yield methylamine:

$$CH_3NH_3^+ + e^- \rightarrow CH_3NH_2 + H \quad (79)$$

Methanol can likewise be produced by the collisional association of CH_3^+ and H_2O followed by recombination with electrons:

$$\begin{tikzcd} CH_3^+ + H_2O \arrow[r, "H_2"] & CH_3OH_2^+ \arrow[d, "e^-"] & (3b) \\ & CH_3OH + H & (80a) \end{tikzcd}$$

The proton affinity of ammonia is very high and, since ammonia is abundant in the Jovian atmosphere, proton transfer to NH^3 is a viable alternative to recombination for formation of neutral from protonated species. For example,

$$CH_3OH_2^+ + NH_3 \rightarrow NH_4^+ + CH_3OH \qquad (81)$$

Collisional association in the Jovian atmosphere leads to synthesis of the same products as radiative association in interstellar clouds.

Like HCN, formaldehyde is an important precursor for synthesis of higher-order organic compounds in prebiotic synthesis schemes. Formaldehyde may be synthesized in discharges by (3a) followed by dissociative recombination of $CH_3OH_2^+$ with electrons,

$$CH_3OH_2^+ + e^- \rightarrow CH_2O + H_2 + H \qquad (80b)$$

by the sequence of reactions (82), (53), (83),[10]

$$CH_3^+ + CH_3OH \rightarrow CH_2OH^+ + CH_4 \qquad (82)$$

$$CH_2OH^+ + e^- \rightarrow CH_2O + e^- \qquad (53)$$

$$+ NH_3 \rightarrow CH_2O + NH_4^+ \qquad (83)$$

or by the neutral reactions (47) and (48). Carbon monoxide could likewise be produced from formaldehyde by the series of neutral reactions

$$H + CH_2O \rightarrow HCO + H_2 \qquad (84)$$

$$H + HCO \rightarrow CO + H_2 \qquad (85)$$

Carbon monoxide has been detected in the Jovian atmosphere[39] at a mixing ratio $CO/H_2 \approx 10^{-9}$. The CO molecule cannot exist in equilibrium at low temperatures (< 1100 K) in the highly reducing environment of the Jovian atmosphere, and must be produced by non-equilibrium processes such as those just described.

In addition to HCN, CH_2O, CH_3NH_2, and CH_3OH, other more complex organic species can be synthesized by methyl cation association reactions in the lower atmospheres of the Jovian planets. Nitriles can be synthesized by condensation with HCN [reactions (86)—(88)]. Aldehydes can be synthesized by condensation with CO [reactions (89)—(92)] or by condensation with CH_2O

$$CH_3^+ + HCN \xrightarrow{H_2} CH_3CNH^+ \qquad (86)$$

$$\xrightarrow{e^-} CH_3CN + H \qquad (87)$$

$$\xrightarrow{NH_3} CH_3CN + NH_4^+ \qquad (88)$$

$$CH_3^+ + CO \xrightarrow{H_2} CH_3CO^+ \qquad (89)$$

---

[39] R. Beer, *Astrophys. J.*, 1975, **200**, L167.

$$CH_3CO^+ + H_2 \xrightarrow{H_2} CH_3CH{=}OH^+ \tag{90}$$

$$\xrightarrow{e^-} CH_3CHO + H \tag{91}$$

$$\xrightarrow{NH_3} CH_3CHO + NH_4^+ \tag{92}$$

[reaction (93)], followed by reaction (97) or (92). The methyl cation does not

$$CH_3^+ + CH_2O \xrightarrow{H_2} CH_3CH{=}OH^+ \tag{93}$$

exhibit bimolecular reactions with HCN or CO so that the high-pressure association reactions are the only available pathways for these reactions in the Jovian atmosphere. Likewise in interstellar clouds, radiative association of CH_3^+ with HCN and CO is possible to yield nitriles and aldehydes. There is a bimolecular reaction between CH_3^+ and CH_2O,

$$CH_3^+ + CH_2O \rightarrow HCO^+ + CH_4 \tag{94}$$

but at high pressures in the Jovian atmosphere reaction (93) might possibly contribute. Aldehyde formation *via* radiative association of CH_3^+ and CH_2O in interstellar clouds may be hindered because of the existence of the bimolecular reaction channel.

Other alkyl cations besides CH_3^+ should react in a similar manner to produce more complex alcohols, amines, nitriles, and aldehydes. Hiraoka and Kebarle[38] have demonstrated the equivalent of reaction (3b) for $C_2H_5^+$, i-$C_3H_7^+$, and t-$C_4H_9^+$ ions. The $C_2H_5^+$ ions can be produced in the Jovian atmosphere by reaction (68). These workers have also demonstrated gas-phase carbonylation *via* the equivalent of the solution-phase Koch–Haaf synthesis for organic acids using $C_2H_5^+$ and i-$C_3H_7^+$ ions. The equivalent for CH_3^+ ions produces acetic acid [reactions (89) and (95)—(97)]. Hiraoka and Kebarle[38] also demonstrated the

$$CH_3^+ + CO \xrightarrow{H_2} CH_3CO^+ \tag{89}$$

$$CH_3CO^+ + H_2O \xrightarrow{H_2} CH_3COOH_2^+ \tag{95}$$

$$\xrightarrow{e^-} CH_3COOH + H \tag{96}$$

$$\xrightarrow{NH_3} CH_3COOH + NH_4^+ \tag{97}$$

formation of protonated formic acid by a similar condensation of HCO^+ ions with H_2O. The HCO^+ ions could be formed in the Jovian atmosphere by reactions (44) and (94).

The α-aminonitriles have been identified as important precursors along with HCN and the aldehydes in prebiotic synthesis experiments using electrical discharges.[5] These compounds may possibly be produced by ionic association reactions such as (98) and (99), where $CH_2NH_2^+$ ions are produced by reaction

(76a). Subsequent hydrolysis in the liquid phase then yields amino-acids, glycine

$$\mathrm{CH_2NH_2^+ + HCN \rightarrow NH_2CH_2CNH^+} \tag{98}$$

$$\xrightarrow{e^-} \mathrm{NH_2CH_2CN} \tag{99}$$

in the above case. It seems likely that ion–molecule association reactions could be responsible for the formation of a large number of the simple organic compounds produced in experiments on prebiotic organic synthesis, and that these processes are now taking place in the atmospheres of Jupiter and the other gas giant members of the solar family of planets.

6 Conclusion

Ion chemistry is ubiquitous in the universe, and permeates the environment in regions as tenuous as the thin wisps of matter that make up interstellar clouds and in regions as dense as the deep, turbulent atmosphere of the Jovian planets. Gas-phase ion–molecule reactions are probably responsible for the synthesis of most of the molecules observed by radio astronomers in interstellar clouds, and probably contribute greatly to the synthesis of simple organic compounds in the atmospheres of the Jovian planets. Ion–molecule reactions may also have participated in the initial stages of chemical evolution, leading from the simplest hydrides in the gas phase to large organic molecules in solution, and thence possibly to chemical life itself.