Chemical Reactions and the Nature of Comets

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During the last decade, chemists have made significant contributions to astrophysical theory. Among the areas of research where chemists have been active are the analysis of meteoritic material and the construction of theories for the formation and condensation of compounds which compose our solar system, determining the chemical reactions responsible for the formation of molecules whose spectra are observed in interstellar space, creating models for the role of chemical processes in the distribution of energy in galaxies and in the formation of galaxies and stars, and using observations of interstellar molecular abundances and laboratory measurements of rate constants to determine quantities relevant to the question of the origin and destiny of the universe.

Experimental and theoretical chemists interact with astronomers studying the universe using radio, infrared, optical, ultraviolet, and even X-ray telescopes and thus have become central to the progress of astrophysics. Nowhere is this statement more true than in the study of comets. It may be said that the introduction of comprehensive and quantitative chemical reaction schemes into cometary research in the mid-1970s has transformed the subject, much as studies of the interstellar gas were transformed by the use of chemical reaction schemes a few years earlier.

In this Account, I shall discuss the role played by chemistry in the theory of comets and in elucidating the nature of these objects. First, I shall provide an introductory description of comets and explain their significance to astrophysical theory.

Comets appear in the heavens as elongated patches of light characterized by a leading bright knot called the head from which trails a much longer and more diffuse fan or pencil of light called the tail. For example, see Figure 1. The tail may have a complex appearance, including separate rays and various clumpy structures. The tail exhibits a solar reflection spectrum in the visible region and a blackbody spectrum in the infrared indicating that it is composed of micrometer-sized dust particles. Additional infrared emission features at 10 and 20 μm suggest that the particles are composed of silicates.[1] In addition, the tail frequently exhibits the emission spectra of molecular ions such as CO^+ and H_2O^+. The parts of the tail dominated by dust reflection and emission are spatially separated, and one or the other feature or both (referred to as the "dust tail" and the "ion tail") may be absent in a given comet. The head exhibits the emission spectra of numerous atoms, radicals, molecules, and molecular ions, as well as the same dust spectrum as the tail. Again, the rel-

Table I
Species Observed in Comets

C	C_2	OH^+	Na	Cr
C^+	C_3	H_2O^+	Al	Mn
N	CO	NH	Fe	Cu
O	CO^+	NH_2	Ni	Co
CH	CO_2^+	HCN	K	V
CH^+	CS	CH_3CN	Ca	S
CN	OH	N_2^+	Ca^+	

ative intensities and observed species vary from one comet to another. A list of all species observed in comets is given in Table I.

The general theory of comet spectral formation, called the "dirty iceball" model, is due to Whipple,[2] who expanded on earlier work by Wurm,[3] Bobrovnikoff,[4] Swings,[5] and others. The theory holds that the head surrounds a solid body or nucleus of about 1–10-km radius composed of ices of water and other volatile species, most of which are chemically saturated, in which are embedded dust grains in an approximate 1:1 mass ratio. As the nucleus approaches the sun in its elliptical orbit, the ices are volatilized into gases which drag along the dust into space. The visible head roughly corresponds to a spherically symmetric region of highest gas density (and highest brightness) called the coma. Stable molecules of the ices, called parents, stream radially from the nucleus and are ionized and dissociated by interaction with the solar radiation field and the solar wind. The emission spectra of the parents and their photofragments are observed on earth, by earth-orbiting satellites, and by high-flying rockets.

The formation of the tail from gas and dust streaming outward in the coma is controlled by a combination of solar photon pressure, solar gravity, and the solar wind acting on the matter. Ions are accelerated antisunward by coupling to the solar wind. Thus, the ion tail is apparent beyond 10^4 km from the nucleus, destroying the otherwise symmetric distribution of gas. Dust and other neutral particles are accelerated by radiation pressure, though less strongly than the ions, so that the ions and the dust follow different orbits behind the nucleus leading to the two distinct tails. The tails may extend more than one astronomical unit (1 au = 1.5 × 10^8 km) across the sky as the comet approaches the sun.

Most species do not extend into the tail due to their finite lifetime against photodestruction. These constituents are destroyed before their distributions about the nucleus are asymmetrized by the antisolar accelerations. Thus, the coma for most parent species is a spherically symmetric region whose extent is defined

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(1) E. P. Ney and K. M. Merrill, *Science*, **194**, 1051 (1976).
(2) F. L. Whipple, *Astrophys. J.*, **111**, 375 (1950); *Nature (London)*, **263**, 15 (1976).
(3) K. Wurm, *Mitt Hamburger Sternw.*, **8**, 51 (1943); *Ap. J.*, **89**, 312 (1939).
(4) N. T. Bobrovnikoff, *Rev. Mod. Phys.*, **14**, 164 (1942).
(5) P. Swings, *Ann. Astrophys.* **11**, 124 (1948).

Figure 1. Comet West (1976VI); direct photograph taken March 7, 1976, 11 days after perihelion. The comet tail points away from the sun, and both ion and dust tails are visible (Lick Observatory photograph).

by a scale length l_0. If parent molecules flow outward from the nucleus with a mean constant velocity v_0 and are removed with a time scale τ_0, then $l_0 \equiv v_0\tau_0$. The photoproducts of these removal processes are ions, radicals, and atoms which are also removed with a characteristic time scale τ_1. The shapes of the abundance distributions of these fragments are characterized by two scales: l_0, the production scale, and l_1 ($=v_1\tau_1$), the fragment photodestruction scale. Analytic solutions for the densities of parent and fragment species as a function of R, the distance from the nucleus, have been obtained in this model.[6] For parents, the effects of antisolar acceleration also can be accounted for analytically.[7,8]

Finally the density of a species may be integrated along a "line of sight" from the earth through the coma or tail. The resulting column abundance, N particles per centimeter squared, is proportional to the photon flux observed in emission lines. For an isotropic, monocinetic velocity distribution, N is a simple function of τ_0, τ_1, and ρ, the distance between the line of sight and the nucleus, projected onto the sky.[6] The expression for N becomes more complex when the effects of acceleration and distributed velocities are considered except for certain limiting cases.[9]

The goal of cometary research is to understand the composition and origin of comets and their place in the scheme of cosmic evolution. Comet orbits may be classified as short or long period, because the distribution of semimajor axes of the orbits of observed comets

is peaked in two places: one peak near the orbit of Jupiter, and the other near the very edges of the solar system, some 8×10^{17} cm from the sun. The short-period or "old" comets have traversed the inner solar system many times, while those long-period comets like Comet Kohoutek (1973f) with semimajor axes close to the distant peak of the distribution are believed to be new, first-time visitors. Presumably, occasional gravitational perturbations on a cloud of comets at the edge of the solar system eject these bodies into the inner regions.[10,11] Those captured into short-period orbits by encounter with planets may become "old" comets.

Thus new comets represent matter which has never been thermally processed by proximity to the Sun, matter which may closely resemble interstellar material, the stuff out of which the solar system was born. Comets with semimajor axes between the peaks like Comet Halley are relatively unprocessed and resemble new comets. The chemical composition of new comets may represent the thermodynamic state and the composition of matter at the boundaries, spatially and temporally, of the primitive cloud of presolar gas. Understanding their composition is central to understanding the process of star formation out of that presolar gaseous nebula.

The method of determining the composition of comets is to observe the spectrum of the coma and tail, as a function of heliocentric distance r, to obtain column abundances, $N(r,\rho)$, and to fit these abundances to a comet model to infer the parent molecules, and the nuclear composition. Candidate parents are chosen which are closely related to observed fragments. The problem with this method may be stated simply: in a century of comet observations ranging from ultraviolet to radio wavelengths, the identity of the major parent molecules has eluded investigators. It was originally believed that the appearance of certain fragments dictated the presence of specific parents which were fragmented by sequences of photodissociation and photoionization. Thus OH and H_2O^+ would indicate the presence of H_2O, CH^+ and CH the presence of CH_4, and so on.[2,3,5] The actual observational situation is more complex. Let us summarize the evidence.

It is generally believed that H_2O is the major component of the nucleus on the basis of several pieces of indirect evidence as discussed by Delsemme and Rud.[12] These include evidence that water controls the streaming of molecules and dust from the nuclei of some comets, that the production and brightness variations of H, OH, and O in some comets is consistent with photofragmentation of water, and that nongravitational effects in the orbits of short-period comets may be attributed to the sublimation of water. However, recent observations of carbon bearing species suggest in addition the presence of a substantial fraction of CO, CO_2, or some other molecule in the nucleus.[13]

Due to atmospheric absorption water is not easily observed from the earth, and, in fact, there is only a single unconfirmed identification of water in a comet spectrum.[14] However, observations of Comet Kohoutek

(6) L. Haser, *Bull. Acad. R. Belg. Cl. Sci.*, **43**, 740 (1957).
(7) L. Haser, *Mem. Soc. R. Sci. Liege, Ser. 5*, **12**, 223 (1966).
(8) L. B. Wallace and F. D. Miller, *Astrophys. J.*, **63**, 213 (1958).
(9) D. A. Mendis and W.-H. Ip, *Astrophys. Space Sci.*, **39**, 335 (1976).

(10) B. G. Marsden, *Annu. Rev. Astron. Astrophys.*, **12**, 1 (1974).
(11) A. H. Delsemme in "Comets, Asteroids and Meteorites", A. H. Delsemme, Ed., University of Toledo, Toledo, OH, 1977, p 453.
(12) A. H. Delsemme and D. A. Rud, *Astron. Astrophys.*, **28**, 1 (1973).
(13) P. D. Feldman, *Astron. Astrophys.*, **70**, 547 (1978).
(14) W. M. Jackson, T. Clarke, and B. Donn in "The Study of Comets", NASA, Washington, D.C., 1976, p 272.

Table II
Abundances of Major Elements in the Solar Neighborhood
Relative to Hydrogen[a]

O	6.7×10^{-4}	Mg	3.5×10^{-5}
C	3.7×10^{-4}	S	1.6×10^{-5}
N	1.2×10^{-4}	Ca	2.1×10^{-6}
Si	3.6×10^{-5}	Na	1.7×10^{-6}

[a] G. Withbroe, *NBS Spec. Publ. (U.S.)* No. 353 (1971).

(1973f) in the near infrared[15] allowed the determination of a reasonably firm upper limit on the water abundance, which was too low to explain some of the reported observations of H and OH abundances.[16,17] Other attempts to reconcile observed abundances of OH and H_2O^+ with models for production by fragmentation of water have also led to inconsistencies, as we shall show below.[18] Thus, no definite, direct observation of water as the dominant nuclear component exists, while limited evidence to the contrary has been uncovered. Conceivably, water is the dominant component of some comets, particularly short-period comets, but not of others.

A cursory study of Table I suggests that NH_3, CH_4, and CO_2 are other likely candidates for nuclear components on the basis of observed fragments.[2] These molecules are also favored from a theoretical standpoint as major carriers of N, C, O, and H in models of the presolar nebula. The expected relative abundances of these atoms in a comet, on the basis of their abundances in the sun, are listed in Table II. Note that hydrogen obtains a lower relative abundance in comets because those atoms bound into H_2 rather than H_2O or some other molecule will never condense into a comet nucleus. NH_3, CH_4, and CO_2 have never been observed in a comet spectrum, and severe constraints have been placed on their abundances, suggesting that they may not be major constituents of at least some comets.[9,18-21] In fact, only four chemically stable molecules have been observed in the spectra of comet comae: CO, CS, CH_3CN, and HCN.

CH_3CN and HCN were observed only in Comet Kohoutek over a small range of heliocentric distance and are not believed to be major nuclear components. CS may carry a substantial fraction of cometary sulfur, but sulfur is a minor component of both the interstellar and solar neighborhood gases, so, unless an unexpected differential accretion process is operating during comet formation, CS is not a major comet constituent. CO, which has been observed only in Comet West (1976V-I),[20] may indeed be the major parent of carbon atoms in that comet.[13] However, the observed CO abundance is far too small to account for the observed atomic oxygen abundance through some molecular dissociation process. Both oxygen and hydrogen atoms are far more abundant than carbon atoms in this comet. Finally CO itself may be formed through destruction of another molecule, such as CO_2. Obviously, CO is not the major

component of the only comet in which it has been observed.

In summary, the parents expected to be present on the basis of observed fragments and theoretical arguments are not observed while the stable molecules which are observed are not the major components of the nucleus. Furthermore, the shapes of the abundance profiles at a fixed r, $N(\rho)$, are often inconsistent with the scale lengths, l_0, of the proposed parents. For instance, the photodissociation lifetimes of proposed parents of C_2 and C_3, which dominate visible spectra of comets, are too large to be consistent with the observed C_2 and C_3 profile morphologies although recent improvements in the coma model may ameliorate this problem.

The Chemical Theory of Cometary Gas

The failure to identify the parent molecules in the context of the iceball model has led to major modifications in the theory of cometary gas. In 1974, I suggested that since proposed photoprocesses were insufficient to explain the observed distribution and identity of fragments in coma spectra, additional chemical reaction sources, particularly fast ion–molecule reactions, must be present.[22] At the same time, Aiken[23] published a quantitative study of reactions in a H_2O coma. The idea that chemical reactions might occur in the coma, leading to the production of some of the observed species, had been proposed earlier,[24-28] but not pursued extensively. This time, the implications of coma chemistry were explored vigorously for two reasons: first, ion–molecule reaction schemes had recently enabled astrophysicists to understand the origins of interstellar molecules and many of the significant rate constants had been measured in the laboratory; second, it was immediately clear that chemical reactions could, at least in theory, totally reshuffle the atoms in the coma, obscuring the information on the nuclear composition which is inferred from coma spectra.

The attention given chemical reactions provided renewed hope of understanding coma spectra and nuclear composition in two ways: first, it raised the number of possible parent molecules by introducing new pathways to a particular fragment; second, it provided a way to explain the peculiar shapes of those observed abundance profiles which were inconsistent with the scale lengths characterizing photoprocesses. Coma fragments might be the products of complex chains of photochemical reactions emanating from unrelated parent molecules which simply contained all necessary atoms. The observed stable species, such as CO, might themselves be products of chemical reactions rather than nuclear constituents. The process of deconvolving coma spectra to infer the parents became at once exciting and immensely complex. Detailed photochemical analyses of the coma involving extensive reaction networks were soon published.[29-32]

(15) W. A. Traub and N. P. Carleton, *Icarus*, **23**, 585 (1974).

(16) J. E. Blamont and M. Festou, *Icarus*, **23**, 538 (1974).

(17) G. R. Carruthers, C. B. Opal, T. L. Page, R. R. Meier, and D. K. Prinz, *Icarus*, **23**, 526 (1974).

(18) M. Oppenheimer, *Astrophys. J.*, **225**, 1083 (1978).

(19) E. Churchwell, T. Landecker, G. Winnewisser, R. Hills, and J. Rahe, "The Study of Comets", NASA, Washington, D.C., 1976.

(20) P. D. Feldman and W. H. Brune, *Astrophys. J. (Lett.)*, **209**, L45 (1976).

(21) S. A. Mango, K. J. Johnston, M. F. Chui, A. C. Cheung, and D. Matsakis, *Icarus*, **23**, 590 (1974).

(22) M. Oppenheimer, *Astrophys. J.*, **196**, 251 (1975); "The Study of Comets", NASA, Washington, D.C., 1976, p 753.

(23) A. C. Aiken, *Astrophys. J.*, **193**, 263 (1974).

(24) B. Donn and H. C. Urey, *Mem. Soc. R. Sci. Liege, Collect.* **4**, 18, 124 (1957).

(25) V. I. Cherednichenko, *Sov. Astron. J.*, **3**, 254 (1959/1960).

(26) L. Biermann and E. Trefftz, *Z. Astrophys.* **59**, 1 (1964).

(27) W. M. Jackson and B. Donn, *Mem. Soc. R. Sci. Liege, Ser. 5*, **12**, 133 (1966).

(28) A. H. Delsemme, *Mem. Soc. R. Sci. Liege, Ser. 5*, **12**, 77 (1966).

The role of chemistry can be appreciated best by writing the equations for transport of material outward from the nucleus. If R is the distance from the nucleus, v_i is the velocity of coma constituent i, q_{ik} is the production rate (cm^{-3} s^{-1}) of i from the kth source, and β_{ij} is the removal rate of i (s^{-1}) by the jth sink, then the steady-state density $n_i(R)$ is given by[9,18]

$$\frac{1}{R^2} \frac{d}{dR} [n_i(R)v_iR^2] = \sum_k q_{ik} - \sum_j \beta_{ij}n_i(R) \qquad (1)$$

When eq 1 is coupled with an equation for the velocity field, a complete description of the density distribution is obtained. In the simplest approximation, parent molecules stream from the nucleus with an isotropic, monocinetic distribution and experience negligible acceleration out to $R = 10^5$ km near $r = 1$ au. Ignoring collisional effects, the velocities of molecules streaming from a comet nucleus near 1 au from the sun are near 1 km s^{-1}.[9] Thus, the transport time to 10^5 km is on the order of a day. The only external sources of energy are solar in origin, and, except for very small heliocentric distances, they change with time scales on the order of several months because comet velocities are tens of km s^{-1}. Thus, the steady-state aproximation is valid well beyond $R = 10^5$ km near 1 au. If $q_{ik} = \beta_{ij} = 0$,

$$n_i(R) = \frac{n_0{}^i R_0{}^2}{R^2} \qquad (2)$$

where $n_0{}^i$ is the density of constituent i at the nuclear surface and R_0 is the nuclear radius, assumed to be 1–10 km. Neither $n_0{}^i$ nor R_0 can be directly measured, but Q_i, the production rate per second due to sublimation of a parent molecule, can be inferred from photon counts since the observed emission spectra are usually due to resonance fluorescence of solar radiation. Equation 2 can be written as

$$n_i(R) = \frac{Q_i}{4\pi R^2 v_i} \qquad (3)$$

by balancing fluxes near the nuclear surface.

If photoprocesses only are included in eq 1, $q_{ik} = \tau_{ik}{}^{-1} n_k(R)$ and $\beta_{ij} = \tau_{ij}{}^{-1}$, where τ_{ik} and τ_{ij} are time scales for production and removal processes, respectively. The solutions for the densities of both parent and fragment species are analytic.[6,7] For a parent molecule, eq 3 is modified by an exponential factor. Consideration of collisional hydrodynamic effects[9] and fragmentation exothermicities[33] alters the velocity field somewhat in the inner coma, but for our purpose, these corrections can be ignored, and we will use eq 3 to exhibit chemical effects. Table III illustrates some typical parent and fragment abundances, based on observed total atom production rates for a typical bright comet such as comet Bennett (1970II) or Comet Kohoutek (1973f), using model lifetimes for production of photodissociation fragments, and solutions to eq 1 given by Haser[6] in the isotropic, monocinetic approximation.

The importance of chemical reactions to the fragment abundances may now be illustrated.[22] Choose a comet

(29) W.-H. Ip and D. A. Mendis, *Icarus*, **28**, 289 (1976); **30**, 377 (1977).
(30) P. T. Giguere and W. F. Huebner, *Astrophys. J.*, **223**, 638 (1978).
(31) W. T. Huntress, Jr., M. J. McEwan, Z. Karpas, and V. G. Anicich, "Laboratory studies of some of the major ion-molecule reactions occuring in cometary comae", preprint (1980).
(32) M. Shimizu, *Astrophys. Space Sci.*, **36**, 353 (1975).
(33) M. R. Combi and A. H. Delsemme, *Astrophys. J.*, **237**, 633 (1980).

Table III
Model Abundances for Parent Molecule XY and Fragments X and Y at Distance R from the Nuclear Surface at Heliocentric Distance 1 au[a]
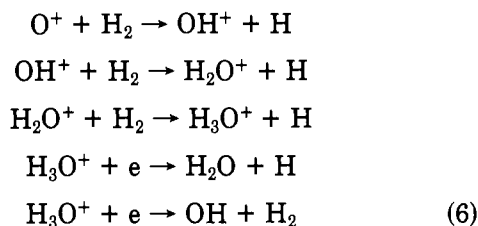
log R, km	XY, cm^{-3}	X, Y, cm^{-3}
$-\infty$	4.4×10^{13}	0
0	1.1×10^{13}	1.1×10^7
1	3.5×10^{11}	1.7×10^7
2	4.4×10^9	1.1×10^7
3	4.4×10^7	1.7×10^6
4	3.5×10^5	1.7×10^5

[a] Model produced following the methods of ref 22 on the basis on a photodissociation rate for XY of 1.2×10^{-5} s^{-1} and zero for X and Y, parent and fragment velocities of 0.9 km s^{-1}, a nuclear radius of 1 km, and a production rate for XY of 5×10^{29} s^{-1} at the nuclear surface. Chemical reactions are ignored.

whose major component is water with abundances given in Table III. H_2O^+ is formed by direct ionization by solar photons with $\lambda < 987$ Å

$$H_2O + h\nu \rightarrow H_2O^+ + e \qquad (4)$$
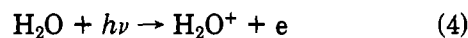
and removed by transport with a rate[18] $2v_{H_2O^+}/R \approx 2 \times 10^{-4}$ s^{-1} at $R = 10^4$ km. At $r = 1$ au, the photodestruction of H_2O^+ may be ignored. However, H_2O^+ also reacts rapidly with hydrides in the coma gas,[18,23] and with H_2O in particular by the rapid reaction

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (5)$$
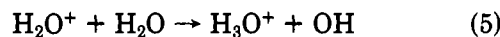
The rate constant of the reaction has been determined in the laboratory to be $k_5 = 2.05 \pm 0.10 \times 10^{-9}$ at thermal energies.[34] Using the model abundances in Table III, we note that the chemical removal rate for H_2O^+ by reaction 5 at 10^4 km is $k_5 n_{H_2O} = 7 \times 10^{-4}$ s^{-1}, much faster than the transport rate. Thus, the abundance distribution of H_2O^+ in comets may be controlled by chemistry, not transport or photoremoval, and an accurate interpretation of its spectral brightness profile as a function of ρ, which is proportional to $N(\rho)$, requires the addition of chemical sink terms on the right-hand side of eq 1. This effect is even more marked for $r < 1$ au where the gas production rate is larger since Q varies as r^{-2} in this region.

Similarly, the H_3O^+ ion cannot be produced by a gas-phase photoprocess in comets and must arise through chemical reactions. The chemical coma theory predicts, in fact, that H_3O^+ is more abundant than H_2O^+ in an H_2O-dominated comet in the inner coma.[23,29] Reaction 5 becomes progressively more dominant over transport as an H_2O^+ removal process at smaller R, due to the R^{-2} variation of H_2O abundance as compared to the R^{-1} variation of the transport rate. Most H_2O^+ ions are converted locally to H_3O^+ until $R \sim 10^5$ km. Thus, a description of the H_3O^+ abundances requires the addition of chemical source terms on the right side of eq 1. Various difficulties prevent the observation of H_3O^+ in comet spectra at present. Furthermore, interaction with the solar wind, which is ignored in the present model, may contract the region of validity of the steady-state approximation.

It is immediately apparent that chemical reactions may also be the source of stable molecules which may be mistaken for parents. For example, suppose the nucleus of a comet is composed of oxygen- and hydrogen-bearing molecules other than H_2O. Photodissoci-

(34) W. T. Huntress, *Astrophys. J. Suppl.*, **33**, 495 (1977).

ation and photoionization lead to the production of O^+. Photodissociation may lead to the production of H_2 from the hydride as in the case of CH_4. Subsequently, H_2O may be produced by the reaction sequence[22]

$$O^+ + H_2 \rightarrow OH^+ + H$$

$$OH^+ + H_2 \rightarrow H_2O^+ + H$$

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$

$$H_3O^+ + e \rightarrow H_2O + H$$

$$H_3O^+ + e \rightarrow OH + H_2 \qquad (6)$$

All reactions in sequence 6 are rapid.[34,35] Some of the intermediate steps may occur directly by hydrogen abstraction from the initial hydride. If H_2O or another stable molecule is identified in the coma, its brightness profile must be studied carefully in the context of eq 1 to differentiate between molecules sublimating from the nucleus and molecules created in the gas phase. In addition, we have identified in eq 6 chemical sources for OH and H_2O^+ which may operate in the absence of parent H_2O. However, as noted by Mendes and Ip,[9] reaction sequence 6 may only be significant in very bright comets with large atomic oxygen abundances since the initial production of O^+ by photoionization is slow. Calculations of abundances from this reaction sequence have been published previously for such comets.[22]

In summary, we have demonstrated the possibility that chemical reactions can (i) create fragments which cannot be produced by photoprocesses, (ii) create fragments in the absence of the expected parents, and (iii) create stable molecules which may be mistaken for parents.

Reaction Classes

Having demonstrated the importance of chemical considerations, we shall denumerate the classes of chemical reactions which have been found to be significant in the coma. The actual library of potentially important reactions runs into the thousands even if only a few candidate parents are considered.[29-31] Thus, we shall classify reactions into a few types and discuss the potential significance of each. The first type is ion-molecule reactions, of which eq 5 is a good example. The important point about these reactions is that they are often rapid, proceeding at gas-kinetic rates. Thus, they provide efficient pathways for the conversion of charge from one form to another. An ion created by photoionization in the inner coma has little chance of being transported to the outer coma without reacting with another molecule first.[22] Both atomic and molecular ions are generally reactive in this manner, as illustrated in eq 6. A compilation of laboratory measurements of the rate constants of many such reactions relevant to comets has been assembled by Huntress.[34] Although some ion-molecule pathways are slow or energetically forbidden, the number of possible neutral constituents in the coma creates a likelihood of reaction for most ions.

A second class of reactions is dissociative recombination, an example of which is also seen in eq 6. Again, these reactions are rapid in most cases studied in the laboratory, with rate constants between 10^{-6} and 10^{-7} cm^3 s^{-1}, the larger value obtaining for larger molecular ions. Due to the exoergicity of these reactions, many exit channels are generally available and the product distributions are highly uncertain. Because of their rapidity, these reactions, rather than transport, may limit the fractional ionization in some regions of the coma, which we now show with a crude calculation balancing ionization and recombination.

If the coma is primarily H_2O, then H_2O^+ is created at 1 au with a rate of about 4×10^{-7} s^{-1} per molecule. H_2O^+ is rapidly converted to H_3O^+ for $R \lesssim 10^4$ km, and H_3O^+ recombines with electrons as in eq 6, with a rate constant of about 1.3×10^{-6} cm^3 s^{-1}.[35] When transport of H_3O^+ is ignored, $(4 \times 10^{-7})n_{H_2O} = (1.3 \times 10^{-6})n_{H_3O^+}n_e$ or $n_e = n_{H_3O^+} \sim 0.6n_{H_2O}^{1/2}$. Using Table III for model H_2O densities, we find $n_e \sim 400$ cm^{-3} at $R = 10^4$ km, which is consistent with some comet observations. Thus, the recombination time scale is 2000 s, while the transport time scale is somewhat larger, assuming that the ion and neutral particle velocities are similar in this region.[36] The photoremoval of H_3O^+ is probably negligible at $r = 1$ au. So dissociative recombination must indeed be included in eq 1 when the charge balance is determined. Again, this effect is even more significant at $r < 1$ au. The charge balance, in turn, significantly affects the interaction of the coma and solar wind, an interaction which leads to formation of the ion tail and may be used as a probe of the solar wind.[37]

The final significant class of reactions is neutral-neutral processes. Molecules streaming from the nucleus must cross a region of density near 10^{13} cm^{-3}. Although the temperature is only near 300 K and thermal-energy neutral-neutral reaction rates are low for stable molecules, there may be a few reactions which will be rapid in that region. In particular, any photoproduct in the nuclear region will be transformed rapidly because even a small exoergicity in the photoprocess will enable a fast hot atom neutral-neutral reaction to occur. One expects at least the fragment distribution in the inner region near the nucleus to be totally dominated by these processes. At present, this region cannot be spectroscopically resolved, but a future comet fly-through mission will allow a detailed study of the deep inner coma. In any event, neutral-neutral particle exchange reactions involving radicals such as

$$OH + O \rightarrow O_2 + H \qquad (7)$$
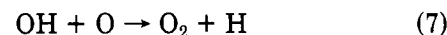
with a rate constant of 5×10^{-11} cm^3 s^{-1} at 300K[38] should play a significant role in rearranging species in the coma.[22,30]

Reaction Systems

I now present three specific examples of how chemistry has advanced our understanding of the composition of comets. I should emphasize at the outset that the parent molecule problem has not been solved and that the sources of cometary radicals and ions are not yet firmly established. But the introduction of chemical arguments has provided fertile new ground for exploration and provided plausible explanations of heretofore impenetrable theoretical difficulties.

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(36) A. H. Delsemme and M. R. Combi, *Astrophys. J.*, 228, 330 (1979).
(37) M. K. Wallis, *Astron. Astrophys.*, 29, 29 (1973).
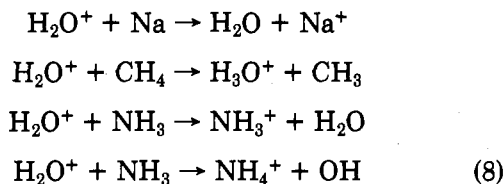(38) J. M. Campbell and B. A. Thrush, *Trans. Faraday Soc.*, 64, 1265 (1968).

**The $H_2O-H_2O^+$ System.** The first example involves Comet Bennett (1970II), a typical bright comet of intermediate aphelion distance characterized by a large gas production rate. Arguments on the composition of this comet should serve as a prototype for other bright comets which are new or strongly resemble new comets. Detailed observations of the $A^2\Sigma^+-X^2\Pi$ transition of OH[39] and the $8 \rightarrow 0$ band of the $\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$ transition of H_2O^+,[36] both excited by solar radiation, were made from satellite-borne and ground-based instrumentation, respectively. The OH observations fitted to solutions for eq 1 yielded scale lengths which were consistent with the known photolifetime of H_2O and the estimated lifetime of OH. Together with the H_2O^+ observation, these results could be interpreted as indicating that H_2O was a major nuclear constituent and the parent for both H_2O^+ and OH by photoionization and photodissociation.

However, analysis of the shape of one H_2O^+ profile in the sunward direction near $\rho = 10^4$ km showed that $N(\rho) \propto \rho^{-1}$ (see ref 36, Figure 5, spectrum B). This functional dependence is characteristic of solutions to eq 1 with $q_{ij}, \beta_{ik} = 0$. In other words, sources and sinks for H_2O are absent in this region and the H_2O^+ steady state is dominated by transport. But according to eq 5, H_2O^+ is rapidly removed by H_2O itself! By comparing the rate of process 5 in the coma with the transport rate, the removal process which should dominate if $N(\rho) \propto \rho^{-1}$, we were able to place an upper limit on $n(H_2O)$.[18] The resulting limit was much smaller than the value of $n(H_2O)$ inferred from the OH observations, a seeming contradiction unless H_2O is not the parent molecule for OH. Furthermore, the absence of a major source in the same region rules out photoionization of H_2O as the main source of H_2O^+ since the photoionization source would extend over all R. Thus, H_2O^+ must be produced inside $R = 10^4$ km by a chemical reaction sequence which becomes less important than transport as a source near 10^4 km, due to the particular distribution of other ions and neutrals.

Moreover, by comparing the transport rate with rates of atom exchange reactions such as reaction 6 as well as reactions with other possible coma species, such as in eq 8, which have measured rate constants,[34] one can

$$H_2O^+ + Na \rightarrow H_2O + Na^+$$

$$H_2O^+ + CH_4 \rightarrow H_3O^+ + CH_3$$

$$H_2O^+ + NH_3 \rightarrow NH_3^+ + H_2O$$

$$H_2O^+ + NH_3 \rightarrow NH_4^+ + OH \qquad (8)$$

place limits on the abundances of many candidate parent molecules. Finally, H_2O^+ can also be formed in charge exchange processes such as in eq 9.

$$H_2O + H^+ \rightarrow H_2O^+ + H$$

$$H_2O + O^+ \rightarrow H_2O^+ + O$$

$$H_2O + CO^+ \rightarrow H_2O^+ + CO \qquad (9)$$
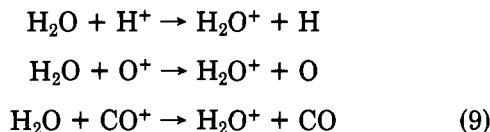
Using the measured rate constants for these and other similar processes, one can place limits on the abundances of many ions in the coma since the chemical production rate of H_2O^+ near 10^4 km must be slower

than the transport rate. If the observational data are to be taken seriously, the limits on the abundances of parent molecules and ions obtained from this chemical reasoning are extremely restrictive and place severe constraints on models for the coma gas in Comet Bennett (1970II). For instance, it is clear from this study that H_2O sublimating directly from the nucleus is not the source of OH in this comet and furthermore that H_2O is probably not the dominant nuclear component. Using this method, we can also show that ammonia and methane are also in relatively low fractional abundance. What is the major parent molecule? This question remains open, but chemistry has helped us narrow the focus of the search significantly.

We should note the following limitation on this analysis. There is some indication of a strong interaction between the solar wind and H_2O^+ ions in this comet.[36] Although this interaction does not appear to significantly affect the profile we have analyzed near 10^4 km, such an interaction, if present in this profile, would complicate the analysis and qualify our results.

The $C_2H^+-C_2$ System. A longstanding problem in the analysis of coma spectra involves the Swan bands of C_2 ($A^3\Pi_g \rightarrow X'^3\Pi_u$) which dominate the visible spectra of bright comets. It has been established that the ground state of C_2 is the $X^1\Sigma_g^+$ state rather than the $X'^3\Pi_u$ state. There is no definite observation of the bands originating on the $X^1\Sigma_g^+$ state, the Phillips system, in cometary spectra. Although the spectral atmospheric windows which permit observation may contain only weak transitions of the Phillips system, it is also possible that the absence of resonance fluorescence in the Phillips bands arises from selective population of the triplet Swan system during the C_2 formation process.[40] The formation of C_2 has troubled cometary theorists because its appearance at large heliocentric distances where the solar flux is weak presents difficulties in proposing reasonable candidates for the C_2 parent through photodissociation.[41] At present, there is no laboratory or theoretical evidence for selective population of the triplet states by photofragmentation of a parent molecule.[42,43]

My denumeration[22] of ion chemistry schemes for the formation of molecules in the coma included reaction sequence 10, in which C^+ and CH are observed coma

$$C^+ + CH \rightarrow C_2^+ + H$$

$$C_2^+ + XH \rightarrow C_2H^+ + X$$

$$C_2H^+ + e \rightarrow C_2 + H \qquad (10)$$
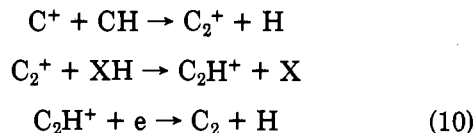
species and XH represents some hydride, such as H_2, for which reaction with C_2^+ is exothermic and rapid.[34] It is important to determine whether such reaction schemes can selectively populate the triplet system of C_2 and whether the reactions can produce C_2 in sufficient abundance to explain the observed C_2 abundances.

An answer to the first question can be obtained by either laboratory experimentation or by ab initio calculations of the molecular structure of candidate pro-

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genitor species. Recently, such calculations have been performed for several states of C_2H dissociating to C_2 + H and CH + C, as well as for the lowest $^3\Pi$ state of C_2H^+.[44] A cut along the CH–C axis of these potential energy surfaces shows a curve crossing between this C_2H^+ state in the Franck–Condon region of its ground vibrational state and the $2\_^4\Pi$ state of C_2H which dissociates to $C_2(X^3\Pi_g)$. Furthermore, no C_2H state dissociating to singlet C_2 crosses the C_2H^+ curve in the Franck–Condon region of its ground vibrational state. Thus, C_2H^+ must dissociatively recombine into a triplet state of C_2, and this sort of chemical formation "pumping" may provide the explanation for the selective appearance of the Swan bands in comets. The entire statistical equilibrium of C_2 in the solar radiation field, coupled with the chemical model for sources and sinks, is being reevaluated to determine the quantitative viability of this chemical source of C_2.[44]

The C–CO System. As a final example, we consider the observation in Comet West (1975VI) that a substantial fraction of atomic carbon is produced as $C(^1D)$.[20] This species cannot be produced by an allowed transition from the $C(^3P)$ ground state, and collisional excitation of $C(^3P)$ is probably slow in the coma. Photodissociation seems an unlikely source since the supposed carbon parent species CO or CO_2 do not produce $C(^1D)$ by the likely dissociation channels in the solar radiation field.[45] In order to preserve CO or CO_2 as carbon parents, one needs to find a fragmentation sequence with a high quantum yield of $C(^1D)$. Such a sequence was suggested by Feldman[13] on the basis, once again, of the dissociative recombination process. Although the branching ratios in the processes

$$CO^+ + e \rightarrow C(^3P) + O(^3P)$$
$$\rightarrow C(^1D) + O(^3P)$$
$$\rightarrow C(^3P) + O(^1D)$$

(11)
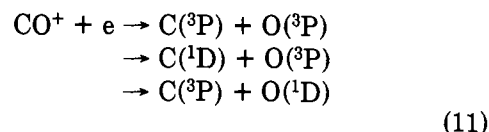
are unknown, Feldman has shown that under favorable but reasonable assumptions the observed $C(^1D)$ abundance can be fit to a coma model in which photoionization of CO is the source of CO^+ and reaction 11 leads to $C(^1D)$. CO is produced by photodissociation of parent CO_2 or is itself a parent molecule. Again, chemical arguments provide one more link in the chain of reasoning aimed at establishing the parent molecules.

Concluding Remarks

In summary, chemistry has brought to the astrophysical arena in general and comet science in particular new and fruitful avenues for interpreting observational data. These new paths are leading in the direction of a better understanding of the origin of the components of cometary gas and will play a significant role in specifying the composition of the comet nucleus. Future observations of comets, particularly such ventures as the proposed space mission to Comet Halley, will be planned with an eye toward obtaining data which can be interpreted from the chemical point of view, such as simultaneous density measurements of individual species. At the same time, the need for reaction rates, branching ratios, and product distributions by astrophysicists has prompted extensive laboratory and theoretical programs on reaction kinetics and molecular structure. The interaction between astrophysicist and chemist will continue to benefit both disciplines.

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