

WHAT SPECIES REMAIN TO BE SEEN?

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ABSTRACT. We review what species remain to be seen for several types of astrochemistry: Thermochemical Equilibrium (TE) in circumstellar envelopes (CSEs); photo- and ion-molecule chemistry in CSEs; ion-molecule chemistry in cold interstellar clouds; grain chemistry (passive, catalytic, disruptive); and shock chemistry. In CSEs, a rich Si gas-phase chemistry is now recognized, and two predicted species (SiN, SiH₂) have been seen. Others are predicted. In the ISM, a global picture of refractory-element chemistry predicts that compounds of Mg, Na, Fe, and possibly Al occur with detectable gas-phase abundance. Predicted species require laboratory synthesis and spectroscopy. Reactions of hydrocarbon ions with neutral species dominate the formation of the families C_nH, HC_nN, H₂C_n, and C_nO in both interstellar (TMC-1) and circumstellar (IRC10216) cases, and readily explain the favored values of n in each case as well as predicting which higher-n species remain to be seen. Confirmation of H₃O⁺ (interstellar) is discussed.

1. Circumstellar Molecules

1.1 TE CHEMISTRY

In their innermost regions, temperatures and densities of CSEs are high enough to insure TE, the products of which are assumed to flow outward in the expanding shell rapidly enough to minimize further reaction by the time they reach the outer envelope. Such simple models agree quite well with observations, even for refractory elements, which also condense into solids. In O-rich objects the most abundant molecular species involving second and third row elements are predicted (Tsuji 1973) to be SiO*, SiS*, SiH₄, FeO, FeS, Fe(OH)₂, MgOH*, AlOH*, AlF, AlCl, CaOH*, NaCl, PS, KCl, TiO. Here, * denotes a dominant species with detectable predicted abundance. In C-rich envelopes, existing predictions (Tsuji 1987; Turner et al 1990; Tsuji 1991) are SiS*, SiO*, Si₂C, SiH₄, NaCN*, NaCl, HCP, TiO. The elements Mg, Na, and Fe are predicted to remain almost entirely atomic. Predicted condensates (Tarafdar 1987) are FeS, Fe₂SiO₄, SiO, SiS, MgSiO₃, Mg₂SiO₄, Al₂O₃, AlCl for O-rich envelopes, and Fe₃C, SiC, AlN, TiC, TiN for C-rich objects.

Observationally, SiO and SiS dominate the Si species, as predicted. SiH₄ is also seen in IRC10216, at surprisingly high abundance. The metallic compounds AlF, AlCl, NaCl, KCl are seen in IRC10216 at 10 times or so smaller abundances than predicted in O-rich envelopes. CP is observed, presumably as a photodissociation product of the predicted HCP. CaOH is not seen at levels roughly predicted in both O- and C-rich objects, while TiO is undetected at levels now somewhat below those predicted. Species which should provide important tests when measured frequencies become available are MgOH, AlOH, and possibly Fe(OH)₂ (O-rich envelopes), and NaCN (C-rich envelopes). As of now, TE models for Si, Al, K, Na appear quite satisfactory for IRC10216, when (uncertain) allowance is made for loss of these elements to condensation or subsequent adsorption of their gas-phase molecules onto grains. The predictions for Mg, Fe, Ca, Ti are not yet tested.

1.2. PHOTO- AND ION-MOLECULE CHEMISTRY OF THE OUTER ENVELOPE

A rich gaseous Si chemistry of the outer envelope of IRC10216 is indicated by the recent detection of SiN (Turner 1991b) and possible detection of SiH₂ (Turner and Steimle 1991). These detections substantiate the Si ion-molecule chemistry proposed by Glassgold et al (1986) and Herbst et al (1989) in which Si⁺ reacts rapidly with NH₃ to produce SiN (and HNSi), and with C₂H₂ to produce SiC₂. If SiN and SiC₂ are destroyed at the same rate, and if NH₃/C₂H₂ is the same in the outer and inner (TE) envelopes, then we expect SiN/SiC₂ ~ 1/8, and we observe ~ 1/30, in reasonable agreement. HNSi (iminosilicon) is also expected, though the SiN/HNSi ratio is uncertain. The source of Si⁺ is taken to be SiH₄, which can be shown from its IR observation in the inner envelope (SiH₄/Si ~ 10⁻³) to have a column density in the outer envelope comparable with that of SiO + SiS (2 × 10¹⁵ cm⁻²) if the same SiH₄/Si ratio persists. SiH₄ photodissociates more readily than SiO or SiS, first to SiH₂ (with 75% efficiency), then to Si⁺ or Si with unknown efficiency. The possible detection of SiH₂ (2 transitions; N ~ 10¹⁵ cm⁻²) provides a suitable source of Si⁺ to drive the outer envelope chemistry, and also means that the fraction of Si lost to the ISM in gas phase (SiS + SiO + SiC₂ + SiN + SiH₄) is ~ 7 × 10⁻³, so that the traditional picture of the gas/dust ratio of ~ 150 representing condensation of *all* refractories needs no modification. No other Si compounds of significant abundance are expected.

The ions Mg⁺, Na⁺, and possibly Al⁺ are expected with abundances comparable with that of Si⁺ in the outer envelope, and their reactions with C₂H₂, if exothermic, should produce MgC₂, NaCCH (sodium acetylide), and :AlCCH. MgC₂ and NaCCH are known to be stable. No microwave spectra exist. Reaction of the ions with NH₃ to produce MgN (MgNH), NaN (NaNH) are possible also. Detection of such species would be important in establishing whether gas-phase chemistry is similar among the refractory-element ions.

Turning to first-row elements, the recent detections of H₂C₄ and HC₂N in IRC10216 have drawn attention to the patterns observed in the C_nH, HC_nN, and H₂C_n families. The dominance of even values of n in the C_nH sequence stems from the dominance of reactions of C₂H₂⁺ and C₂H₂, both highly abundant. For example, C₄H is produced from C₂H₂⁺ + C₂H₂ → C₄H₃⁺, and C₆H from C₄H₃⁺ + C₂H₂. Species with n = 8, 10, ... are expected. Odd-n species occur by various, relatively inefficient branching routes, and n ≥ 7 is doubtful, based on current observations. The HC_nN family favors odd n, because these species start with C₂H₂⁺ + HCN → HC₃N, and successive reactions of HC_nN (n ≥ 3) with C₂H₂⁺ lead to higher-n members. Even-n members require reaction of a hydrocarbon ion other than C₂H₂⁺ with N, neither of which have significant abundance. For the cumulene family, we predict that even-n members of H₂C_n dominate (C₂H₂ + C₂H₂⁺ → C₄H₃⁺ → C₂C₄, and successive reactions with C₂H₂⁺ add two C atoms each). Finally, the C_nO family is not expected in IRC10216, even though it forms from reactions of the form C_nH_m⁺ + CO → C_{n+1}OH_m⁺ + hν, because the required radiative association reactions (Adams et al 1989) have negligible rates in the warm gas of the outer envelope.

2. Interstellar Ion-Molecule Chemistry in Cold Clouds

2.1. HYDROCARBON SPECIES AND THEIR DERIVATIVES

Predictions for these species are much more difficult in the interstellar context. We refer to a diagram of hydrocarbon reaction pathways given by Turner (1989), and based on mostly measured reactions existing in the literature. The preference for even-n in C_nH and odd-n in HC_nN and C_nO results from the details of this reaction scheme, not from a dominance of a certain reactant (e.g. C₂H₂ in the case of IRC10216). The observations clearly imply large amounts of C₃H₃⁺ in the interstellar case, which means small amounts of C₃H₂⁺ (competing pathway) and hence C₃H. There are several paths to C₄H from

$C_3H_3^+$, but after C_4H only one path leads to C_5H (not seen in TMC-1) while several lead to C_6H (detected in TMC-1). Predictions to higher n depend on as yet unknown pathways. Similarly, HC_3N forms from $C_3H_3^+ + N$, and several pathways via $C_2H_2^+$ or C_2H_2 lead to HC_5N etc. HC_2N (recently identified in IRC10216) is not seen in TMC-1, signalling a low abundance of $C_2H_3^+$. HC_4N cannot form appreciably from $C_3H_2^+ + HCN$ (low abundances), but is possibly expected via $C_4H_3^+ + N$ and will provide a useful diagnostic of the higher order hydrocarbon abundances. Likewise, the cumulene H_2C_3 is an isomer of the cyclic C_2H_2 and forms from $C_3H_3^+$, while H_2C_4 (not seen in TMC-1) forms via $C_4H_3^+$, which is evidently much less abundant than $C_3H_3^+$. It is likely that HC_nN and H_2C_n will have similar abundance patterns as a function of n , and also similar to those of $C_{n+1}H$, as each likely has the same hydrocarbon ion precursor. Finally, the C_nO family may form from the radiative association reactions of hydrocarbon ions with CO in the cold interstellar gas. The precursor ions are CH_3^+ and $C_2H_3^+$ for the C_2O (recently detected) and C_3O species. If C_5O (Turner 1990a) is confirmed, it will imply a significant abundance of $C_4H_2^+$ (or $C_4H_3^+$). A definite prediction either way is C_4O (high $C_3H_3^+$ abundance and high reaction rate with CO), while C_6O is also likely if C_5O is seen. Of course, the associated species H_mC_nO will also be present.

A sensitive search has been made for vinyl (CH_2CH), which should form simply from $C_2H_2^+$ via radiative association with H_2 , while C_2H forms directly from $C_2H_2^+$ by electron recombination. Thus $CH_2CH/C_2H \sim 1$ is expected from the given reaction rates, while $CH_2CH/C_2H < 0.06$ is observed. Results such as this underscore the limited predictability of the overall reaction scheme currently in use. Each reaction rate and branching ratio is open to question a priori.

2.2 OTHER SPECIES

Two additional transitions of H_3O^+ have now been seen, the 3_2-2_2 at 364.9 GHz (Wootten et al 1991) and the 3_0-2_0 at 396 GHz (van Dishoeck et al 1991). The abundance ratio is $1500 < H_2O/H_3O^+ < 6000$ in Orion(KL) and SgrB2, as compared with model values ranging from 2000 (Millar 1990) to 10^5 (Viala 1986). Here, the H_2O abundance is derived from observations of $H_2^{18}O$. The models assume a branching ratio of $H_3O^+ + e \rightarrow H_2O$ of 35 %, an upper limit to the measured value. If significant quantities of H_2O arise from grain mantle evaporation, then smaller values of the branching ratio will be required.

Additional Si compounds are predicted in the ISM by the chemistry model of Herbst et al (1989). SiN is not among them, as it is quickly destroyed by atomic O, but the closed shell species $HNSi$ may be expected, in view of the detection of SiN in IRC10216. A preliminary search reveals a line in W51M and SgrB2 corresponding to the $J = 6-5$ transition. If confirmed, then the Herbst et al model predicts abundances of several other Si species relative to $HNSi$: $HOSi^+$ (4), $HSiC_2$ (54), $SiCH_2$ (35), $Si_2C_2H_2$ (13), $SiCH_3$ (8), and SiC_3H (5), if the chemistry is early-times. If it is steady state, only $HOSi^+$ (0.4) and $HSiC_2$ (0.6) have abundances comparable with $HNSi$. The small dipole moments of many Si species make sensitive searches difficult. $HOSi^+/HNSi < 3.8$ has been established.

3. Interstellar Refractory-Element Chemistry

Ninety percent of all refractory-element grains condense in the innermost envelopes of evolved stars. The order of condensation is Al, Ti, Ca, Fe, (Mg,Si), P, (Na,K), S from highest to lower condensation temperature, so grains are layered. The remaining 10% of refractory elements are ejected into the ISM in atomic form, in fast winds from early-type stars, or supernovae.

Grains are ejected first into the warm diffuse ISM ($T \sim 10^4$ K, $n \sim 0.3 \text{ cm}^{-3}$, $\tau_{shock} \ll \tau_{acc}$, $\tau_{ph} \sim \tau_{acc}$; here τ 's are timescales for shock erosion of grains, accretion, and

photoprocessing). Measured extinctions $\delta = \log(X/X_{solar})$ of refractory elements show values of ~ -1.0 for Al, Fe, Ti, Ca, but smaller values (-0.1 to -0.6) for P, Mg, Na, Si, exactly as expected if shocks erode the outer grain layers down to the (Si,Mg) layers but leave the inner (Al,Ti,Ca,Fe) cores intact. Since $\tau_{ph} \sim \tau_{acc}$, simple hydrides forming on the surfaces quickly desorb and are photodissociated.

In the cold diffuse ISM ($T \sim 100$ K, $n \sim 30$ cm $^{-3}$, $\tau_{shock} \gg \tau_{acc}$, $\tau_{ph} \sim \tau_{acc}$, $\tau_{mix} \sim \tau_{acc}$), binding energies and photodesorption dominate the fate of accreted refractory elements. Binding energies are similar for the hydrides of O,C,N,P,S and possibly Mg, higher for Si, and much larger for Fe, Ti,Ca and likely Al. Accretion of refractory ice (and organic) mantles proceeds in this phase. Observed extinctions are all greater than in the warm medium, ranging from -0.7 for S, P, Mg, Na, to -3.6 for Ca. Si is at -1.6 .

In cold dense clouds, which evolve from the cold diffuse ISM, $T \sim 10$ K, $n \geq 10^3$ cm $^{-3}$, and $\tau_{chem} \sim \tau_{acc}$. Based on unsuccessful searches for PN and SiO, one has $(R/NH_3)_{cold} \ll (R/NH_3)_{warm}$, where R stands for refractory- element compounds, NH_3 for first-row compounds, which are readily seen in cold dense clouds. Eventually stars form in cold dense clouds, and evaporate the grain mantles. "Warm" refers to these regions. These two relations for cold dense clouds imply one of the following: i) all molecules desorb in some way (and gas-phase chemistry does not form SiO and PN at $T = 10$ K); ii) first-row species desorb while refractories do not; iii) no molecules desorb, and the presence of first-row species implies a longer accretion time, as a result of their chemistry. We favor iii).

A 3-layer picture of grains is usually envisioned (Leger et al 1985): a refractory, heavy-element core; a refractory ice mantle, mostly of H_2O ice, laid down by efficient binding of polar molecules during the cold diffuse ISM phase; and finally a volatile outer mantle (CO , N_2 , O_2 ,...) accreted during the cold dense cloud phase. Known binding energies of many substances indicate that atoms in general, as well as O_2 , N_2 , CO , CH_4 will accrete efficiently only during the cold dense phase, while all saturated hydrides (SiH_4 , PH_3 , H_2S , NH_3 , H_2O ...) and other polar molecules will accrete earlier and form the refractory ice mantle. Thus the non-polar group represents a gas phase "reservoir" with a long accretion timescale which allows continuation of the gas-phase chemistry observed in cold dense clouds. The cold dense cloud model of Herbst and Leung (1989) at $t = 3 \times 10^5$ yr shows the following "reservoir" amounts: N (99%), P(80%), O (57%), S (30%), Si (1%). All Si forms SiO while only 20% of P forms PN (or PO). This is why Si (SiO) is not observed, while the presence of many S-species implies that P compounds should be observable in cold clouds. We predict that PO (the principle P species formed by ion-molecule reactions) should be observable, and that the reaction $PO + N \rightarrow PN + O$ invoked to explain PN in warm star-forming regions does not proceed at $T = 10$ K.

In warm star-forming regions, refractory mantles (mostly H_2O ice will start to evaporate at $T \sim 90$ K, the outer volatile mantle earlier. All SiO and PN (PO) are accreted into the refractory ice mantle in the cooler phases. A central point is that the abundances of both SiO and PN, as observed in star-forming regions, are quantitatively explained in terms of the cosmic abundances (δ_c) of Si and P, the observed extinctions (δ_d) in the cold diffuse ISM, the conversion of 99% Si to SiO and 20% P to PN, and the evaporation of 4% of the refractory ice mantle in the case of Ori(KL). The relative abundances of molecules as observed in cold dense clouds and warm star-forming regions can be explained quantitatively on this picture by placing all Si, P, S species in the refractory ice mantle, and all N species in the outer volatile mantle, as expected on this picture. Then the fractional abundance X of any refractory element in Ori(KL) is given by $X = 0.04 \times 10^{-\delta_c - \delta_d}$. Values of $\delta_c + \delta_d$ are as follows: Mg (5.24), Si (6.13), Na (6.48), Fe (7.10), P (7.17), Al (7.72), Ca (9.38), Ti (9.88). Since Si and P species are observed, we predict that Mg species will be easily observable, and Na, Fe species also. Al is possible, while Ca, Ti are very unlikely.

Nothing is known of the gas-phase chemistry of Mg, Na, Fe, Al but in analogy with

that of Si (Herbst et al 1989) we expect oxides to dominate although they may convert to nitrides. MgO, NaO, and possibly AlO are not detected at expected levels. Here we assume surface molecules are destroyed in the gas phase after evaporation, and that ion-molecule processes start with the resulting atoms. If there are few ions in the dense, hot gas near massive protostars, surface molecules may survive; then full hydroxides are likely.

The detection of Mg (and Na, Fe) compounds, a strong prediction of this picture, would not only provide the first information on the chemistry of metals in the ISM (also poorly known terrestrially), but would provide insight into the lifecycles of grains, whose existence in the ISM is not clearly understood (Seab 1987).

4. Grain Chemistry

There is now much evidence of the importance of grain chemistry, of several types. Several molecular species are seen with abundances much greater than can be explained by gas-phase chemistry: i) complex species such as CH₃CHO, (CH₃)₂O, EtOH, CH₃OHCO, NH₂CHO, VyCn, EtCN in dense star-forming regions (Turner 1991a); ii) NH, recently identified in diffuse clouds (Meyer and Roth 1991); iii) fully saturated species such as H₂O, NH₃, HCN, CH₃CN in Orion(KL); iv) H₂CO in molecular cloud envelopes whose extinction is < 4 mag (Federman and Allen 1991). Other species such as D₂CO (Turner 1990b) are not producible at all via gas-phase chemistry, but have a natural explanation in terms of catalytic surface chemistry (Tielens 1983).

No detailed model of catalytic grain chemistry is currently possible, but a simple picture by Millar et al (1988) illustrates potentially useful predictions. For a molecular cloud with [H] > [O], ($n < 5 \times 10^4 \text{ cm}^{-3}$), mobile surface C atoms typically accrete H atoms and exist as H₃C-, which grow unidirectionally at low T. Thus H₃C-CH₃ and H₃C-O-CH₃ form readily. If the surface contains much CO, then H₃C-CO-CH₃ (acetone) is also likely. If, conversely, [H] < [O] ($n > 5 \times 10^4 \text{ cm}^{-3}$), then C-, HC-, H₂C- dominate the surface carbon, and these permit linear growth in two dimensions. It is also possible that on icy surfaces the mobilities $\mu(\text{N}) < \mu(\text{O}) < \mu(\text{C})$ (Iguchi 1976). Then in decreasing order of likelihood the following backbones may form: C-C-C or C-C-O; C-C-N; O-C-N or N-C-O. None of these will saturate with H atoms. Thus C-C-C may have the form H₃C-CH=CH₂ (propylene) and C-C-O the form EtOH. C-C-N forms EtCN or VyCN. Observationally, EtCN < EtOH ~ (CH₃)₂O in SgrB2 implies both H-rich and H-depleted regions occur within the observing beam. In the Orion hot core, EtCN >> EtOH, (CH₃)₂O implies H-depletion. In the Orion compact ridge, (CH₃)₂O >> EtOH, EtCN implies an H-rich region.

Of course, reactive species such as C₂H₂ should be plentiful on grains, and may hydrogenate to form H₃C-CH₃, or oxidize directly to form EtOH (Tielens, 1990) but *not* (CH₃)₂O. If $\mu(\text{N}) < \mu(\text{O})$, we expect EtCN < EtOH, contrary to the Orion case. The presence of surface carbon radicals rather than CO, C₂H₂ seems necessary to provide a non-restrictive surface chemistry, as suggested by the observations.

Deuterated forms of complex molecules likely provide the best test of surface chemistry. D-species reflect (D/H)_{gas}, if the addition and abstraction reactions of H and D are similar on surfaces. (D/H)_{gas} is largest for smallest [H]. Thus we predict D-EtCN, D-EtOH will be more abundance than D-(CH₃)₂O. In addition, for $p = \text{D}/(\text{D}+\text{H})$, we predict EtOD/EtOH = $p/(1-p)$, CH₂DCH₂OH/EtOH = CH₂DCH₂CN/EtCN = $3p/(1-p)$, while CHDCHCN/VyCN = $2p/(1-p)$, CH₂CDCN/VyCN = $p/(1-p)$. The CH₂DOH/CH₃OD ratio is also important in this context.

5. Shock Chemistry

Turner and Lubowich (1991) recently established directly the presence of hot molecular gas other than H₂ in a shocked region, namely H₂CO in IC443G. Subsequently, attempts to

test both non-dissociative and dissociative shock models have involved observations in IC443 of several species (SiO, SO, SO₂, CN, HCN) whose abundances are predicted to be similar in both types of shock, and other species (HCO⁺, H₂CO, C₃H₂) whose abundances are predicted to be very different. The first group is used to derive beam-filling factors, which are applied to the second group to deduce the nature of the shock. Both non-dissociative shocks (to explain H₂CO) and dissociative shocks (to explain HCO⁺ and C₃H₂) are implied, similar to the requirements for H₂ (Burton et al 1990). One new species, SO⁺, is predicted at detectable levels in the dissociative shock models of Neufeld and Dalgarno (1989). SO⁺ forms from SO and H⁺, and the low abundance of H⁺ in non-shocked regions explains why [SO⁺] is expected in shocked regions at 100 to 1000 times its normal interstellar value. Hence it provides one of few unambiguous tests of shock chemistry, as distinct from SiO or H₂CO, which may well be evaporated from grain mantles. In fact, [SiO] ~ 6×10⁻⁹ in IC443G, some 10³ to 10⁴ times smaller than predicted by shock models.

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