THEORETICAL CHEMISTRY

ERIC HERBST
Departments of Physics and Astronomy
The Ohio State University
Columbus, Ohio 43210-1106
USA

1. Introduction: CO and CI

Theoretical astrochemistry is concerned with the explanation and prediction of the abundances of the many likely and detected interstellar and circumstellar molecules. An updated list of the more than 100 detected gas-phase molecules is given by Herbst (1995). Carbon monoxide, by virtue of its ubiquity and high abundance, occupies a special place of importance.

As a guidepost for understanding the chemistry, quiescent dense interstellar clouds can be divided into shells or slabs of material of increasing density and visual extinction as one proceeds towards the cloud interior. Unlike ultra-violet photons, cosmic rays penetrate throughout the cloud and power a rich ion-molecule chemistry, especially in the high density interior. In outer layers, the dominant form of gaseous carbon is C^+ (CII) because of the diffuseness of the gas and the strength of the interstellar radiation field (Tielens & Hollenbach 1985). In intermediate layers ($A_V \approx 1 - 5$), a significant abundance of neutral atomic carbon (C or CI) exists. In the interior, with gas densities in the range 10^{3-5} cm^{-3} and large extinction, CO dominates. Indeed, gas-phase models show that CO is produced from precursor atoms in a relatively short time (Herbst & Leung 1989). By 10^5 yr, the CO fractional abundance has reached its asymptotic value, which depends both on metallicity and on the elemental depletions assumed. For cloud interiors in our galaxy, a fractional abundance of 10^{-4} is typically calculated, whereas for analogous cloud interiors in other galaxies, the value can be reduced by an order of magnitude or even more (Millar & Herbst 1990).

Once CO becomes the dominant carbon-containing molecule in the cloud interior, a small residual abundance of C (C/CO $\approx$ 0.001 - 0.01) is maintained via an indirect photodissociation of CO caused by cosmic rays (Prasad & Tarafdar 1983; Gredel et al. 1989). The small residual C abundance derives from the standard, or LIP (low ionization phase), solution to the differential equations governing the gas-phase chemistry; a more exotic solution, labeled the HIP (high ionization phase), exists in which the C/CO abundance ratio is considerably higher, approaching 0.1 (Flower et al. 1994). In the normal solution, the overall column density of C through the cloud is dominated by intermediate shells at times past 10^5 yr. This column density can be as large as 10^{-5} that of H_2 for times through 10^6 yr although it declines thereafter (Lee et al. 1995). The large C abundance calculated at times before steady state is achieved (10^{7-8} yr) may well explain C abundances towards relatively quiescent sources.

The shell-like C^+/C/CO structure discussed here is an idealization. Even if nearly spherical shells exist, there is the possibility of diffusion among them (Xie et al. 1995). To the extent that the interior of the cloud is clumpy, both diffusion between diffuse and dense gas and photon penetration from external photons will occur. Star formation and young stellar activity lead to still more photons. The net effect of all of these complications is to increase the internal abundances of C and C^+.

2. Gas-Phase Interstellar Chemistry

The ion-molecule picture (Herbst 1995; Herbst & Leung 1989; Millar et al. 1991; Bergin et al. 1995) of interstellar chemistry in cloud interiors leads to five successful general predictions, one of which, the high CO/H_2 abundance ratio, has already been mentioned. The second prediction concerns the abundances of protonated ions, which are calculated to be sufficiently large for various species to be observed. The detection of the protonated ions HCO^+, HN_2^+, $HOCO^+$, $HCNH^+$, and HC_3NH^+ is in good accord with the ion-molecule picture. The third prediction concerns metastable species, which are calculated to have abundances comparable to normal species. Known to chemists as isomers, metastable species have geometrical structures corresponding to local but not to global potential minima. The best known interstellar example is probably HNC. A more exotic example, l-C_3H, is calculated to lie above c-C_3H, where the designations 'l' and 'c' refer to linear and cyclic structures, respectively. Although metastable species are often especially reactive in the laboratory, their abundances are enhanced in ion-molecule chemistry for two main reasons. First, both stable and metastable species are typically produced via the dissociative recombination of precursor positive ions and electrons. The reactions are thought to lead to the breaking of differing chemical bonds; for example:

$$HCNH^+ + e^- \longrightarrow HCN + H; HNC + H. \tag{1}$$

Secondly, once produced, stable and metastable species react equally efficiently with abundant ions, typically on every strong collision.

Isotopic fractionation, leading to abundance ratios between so-called isotopomers and normal species very different from the abundance ratios of the isotopes themselves, represents the fourth strong success for the ion-molecule picture. Fractionation in the interstellar medium occurs at low temperatures because the direction of isotopic exchange reactions is critical if the exothermicity is large compared with the temperature. The fractionation of carbon is discussed by Langer in this volume. Here we consider deuterium fractionation. Consider, as an example, the exchange reactions

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2. \tag{2}$$

The left-to-right reaction is exothermic by 230 K, so that at temperatures considerably below this value, the right-to-left (endothermic) reaction occurs only slowly. Since, in the interiors of dense clouds, HD is the major repository of deuterium ($HD/H_2 \approx 3 \times 10^{-5}$), the above reaction system can produce a large H_2D^+/H_3^+ abundance ratio (≤ 0.10) which can then propagate throughout the ion-molecule network to produce large fractional abundances of an assortment of deuterated isotopomers, both ionized and neutral. This propagation is important because most ion-HD exchange reactions do not occur due to energy barriers. One ion produced from H_2D^+ is DCO^+, generated by the reaction

$$H_2D^+ + CO \longrightarrow DCO^+ + H_2. \tag{3}$$

The observed abundance ratio between this ion and its normal isotopomer is reproduced well by theory. The dissociative recombination of DCO^+ leads to a large abundance of atomic deuterium which, in turn, leads to another sequence of fractionation reactions. Detailed model calculations which include a variety of deuterium fractionation reactions show reasonable agreement with observation for many species in cold cloud cores (Millar et al. 1989).

The fifth successful prediction concerns the unsaturated (hydrogen-poor) nature of the chemistry. Many ions with more than 4–5 atoms do not react with H_2 because the reactions are endothermic. The result is that the ions cannot incorporate much hydrogen into their structures. Dissociative recombination then leads preferentially to very unsaturated neutral species such as bare carbon clusters and hydrocarbons with only one or two hydrogen atoms.

Despite these general areas of agreement between theory and observation, predictions of individual molecular abundances can be incorrect. This is not surprising; there are numerous chemical, physical, and astronomical uncertainties afflicting the model calculations. Among the chemical uncertainties is a lack of knowledge of the rates of many neutral-neutral reactions at low temperature. Among the physical uncertainties is a poor understanding of how species can be removed from grains once they stick to their surfaces. Among the astronomical uncertainties are the extent of clumpiness in the gas and the role of star formation in influencing the physical conditions and creating 'active' regions, discussed below.

One major uncertainty in ion-molecule model predictions is the extent of large molecule formation. Large molecules, here defined to be more than 4–5 atoms in size, are produced by long sequences of reactions, so that their predicted abundances are especially sensitive to uncertainties in the rates of individual reactions, many of which have not been measured in the laboratory. In particular, the uncertain role of neutral-neutral reactions strongly affects the calculated abundances (Bettens et al. 1995). In addition to this uncertainty, the calculated abundances of complex molecules show a time dependence which is quite distinct from that of smaller species. The latter reach their steady-state abundances by $10^4 - 10^5$ yr; the former reach peak abundances at this time but their abundances decrease sharply at still later times. For successful comparison with the observed abundances in molecule factories such as TMC-1 and L134N, calculated abundances at or near their peak values must be utilized. This peak at so-called 'early time' derives from the oxygen-rich nature of the elemental abundances chosen. The larger molecules are mainly carbon-containing in nature, and at late times virtually all of the carbon is consumed to produce CO. The time dependence may not be critical since it is difficult to see how large molecules can be kept off grains for more than 10^6 yr. Even so, investigators have increased the predicted abundances of complex species at late times by assuming that diffusion of atomic carbon occurs from outer shells or from diffuse gas in a clumpy interior.

Bettens & Herbst (1995) have recently extended the maximum size of molecules in gas-phase models from ≈ 10 atoms to upwards of sixty atoms. The synthesis of hydrocarbons has been taken from recent laboratory work, which shows that the growth of linear chains leads not to PAH's but, via isomerization, to large monocyclic rings, which then condense to form tricyclic rings, which finally isomerize to form fullerenes, including the famous C_{60}. Growth can even occur under diffuse cloud conditions (Thaddeus 1994). The production of PAH's occurs preferentially in C-rich circumstellar shells (Frenklach & Feigelson 1989).

3. Dust Observations and Chemistry

Along with other condensed-phase species such as water and methanol, CO is detected in grain mantles via broad absorption features in the infrared (Whittet 1993). A detailed examination of the CO feature at 4.67 μm in many sources shows that most CO is gaseous, with at most 25% in the condensed phase. In addition, the line does not correspond well in frequency with laboratory CO spectra taken in a water-ice-dominated environment. Rather, it is necessary to have a considerable amount of CO in a non-polar environment such as itself, O_2, and N_2 (Tielens et al. 1991). This implies a schizophrenic nature for grain mantles since water ice is known to dominate them, with H_2O (solid)/$H_2 \approx 10^{-4}$.

For dust temperatures under 20 K, the low abundance of non-gaseous CO cannot be explained by evaporation, which does not occur competitively. A variety of non-thermal desorption mechanisms for CO and other mantle molecules has been proposed (Williams 1993). We (Dzegilenko & Herbst 1995) have shown that CO can be desorbed from ice surfaces via an indirect mechanism in which infrared radiation at 3.05 μm excites an OH stretch, which relaxes via several channels, among which is the transfer of energy into the so-called librational (hindered rotational) mode of a neighboring CO molecule. The librational energy is strongly coupled to the physisorption mode between CO and the grain surface, and the sudden infusion of librational energy permits desorption of the CO in a time scale of picoseconds. Interestingly, the direct absorption of infrared radiation to excite the CO stretch has been measured not to lead to desorption since the two modes appear to be almost completely uncoupled.

The need for two environments for condensed-phase CO can be explained by time-dependent chemical effects. In the initial stages of a cloud, the gas is rich in atomic hydrogen, which is uniquely reactive on grain surfaces because of its rapid random (tunneling) motion from site to site. The formation of molecular hydrogen occurs when two surface H atoms collide with one another and deposit the energy released in chemical bond formation into the energy modes of the grain. In addition, H atoms can coalesce with slower moving heavy surface atoms such as O and N to produce the radicals OH and NH, which in turn react with additional H atoms. The process of association continues until saturation is reached, and species such as water and ammonia (NH_3) formed. Later in the cloud history, the gas-phase hydrogen becomes predominantly molecular, and the nature of the grain chemistry changes. Polar saturated species no longer dominate and frosting of molecules such as CO produced in the gas occurs, although the stability of these molecules is not guaranteed. Assuming that CO can be maintained on grain surfaces, the condensed-phase CO observations are consistent with a picture in which the inner mantle layers are rich in water and ammonia, while the outer layers contain the bulk of the CO.

A number of gas-grain chemical models, in which both gas and grain chemistry are followed along with adsorption and desorption processes, have been carried out (Hasegawa & Herbst 1993; Willacy et al. 1994). Most of these models use differential rate equations to describe the grain chemistry; however, it has just been realized by Tielens that these equations can be in error because they inappropriately average the discrete nature of the chemistry that occurs on small particles. We have recently begun to correct the rate equations; an alternative procedure, the Monte Carlo method, is appropriate for steady-state models (Tielens & Hagen 1982) but harder to implement for time-dependent calculations. With some current rate equation approaches, it is difficult to account for the non-polar environment of CO although others are successful (Willacy et al. 1994).

4. Active Regions

Star formation affects the chemistry in a variety of ways, which have been investigated in some detail. In the vicinity of low mass star formation, the dominant effect is an increase in the gas and dust density, which results in an increase in the adsorption rate on grains. In the absence of any large increase in the temperature, the grain mantles grow rapidly and the gas phase becomes depleted in molecules containing heavy elements, especially those molecules with relatively large surface binding energies. In the vicinity of high mass star formation, an increase in the temperature results in almost the opposite behavior - the grain mantles are almost totally desorbed and the gas is enriched in molecules produced previously via grain chemistry (Brown et al. 1988). These so-called 'Hot Cores' are discussed by Walmsley in this volume.

Photon-dominated regions (PDR's) represent another active area of extreme current interest (see Tielens & Hollenbach 1985; Sternberg & Dalgarno 1995; Hollenbach et al. 1991) since they represent the theoretical paradigm for explaining C^+ and C abundances in cloud interiors. In these regions, the radiation field is enhanced over the typical interstellar value, either by the presence of an external star near to the source, or, more likely, by internal newly-born stars. If clumpiness is neglected, the enhanced radiation field leads to shells similar to those discussed earlier, in which material near the radiation source contains carbon mainly in the form of C^+, material somewhat farther removed from the radiation source is rich in neutral atomic carbon, and material still farther removed contains excited CO. Models of PDR's also consider the thermal balance in these sources as well as their unusual chemistry. An example of the latter is the high abundance of the non-protonated ion CO^+. The addition of clumpiness to the models makes for a more complex picture with the external layers of clumps being strongly affected by the radiation. Most chemical models of PDR's have been steady-state in nature; the role of time-dependent effects remains largely unexplored. Somewhat akin to PDR's are cosmic ray-dominated regions (Farquhar et al. 1994), in which the effective cosmic ray ionization rate ζ is larger than the standard value, and X-ray dominated regions. These last two active sources may well be important in models of clouds in external galaxies.

Regions of high temperature possess perhaps the most distinct chemistry from standard quiescent sources. As the temperature rises, exothermic chemical reactions with activation energy barriers as well as endothermic reactions begin to occur. Regions beset intermittently by turbulence constitute one type of high temperature source; these are discussed by Falgarone in this volume. Shocked regions have been studied for some time, initially to explain the high abundance of CH^+ in diffuse clouds. These are now divided into two classes depending on magnetic field. In J-type shocks, the temperature rises rapidly to thousands of degrees and then relaxes slowly (Mitchell 1988; Neufeld & Dalgarno 1989). In C-type shocks, the rise in temperature is less dramatic but a two-fluid structure arises in which ions can stream with respect to neutrals, enhancing the importance of endothermic ion-molecule reactions (Roberge & Draine 1990; Pineau des Forêts et al. 1993). Modellers of high temperature regions should be cautious in utilizing thermal rate coefficients for high temperature processes measured in the laboratory; although excitation of internal degrees of freedom can preferentially power endothermic reactions, the available energy in shocks is mainly translational.

5. Summary and Future Prospcts

During its first twenty-five years, interstellar chemistry has made much progress, especially in the area of gas-phase processes. The general nature of the chemistry in dense cloud interiors is understood. Large models now exist to predict the gas-phase abundances of hundreds of species in quiescent sources as well as in a variety of active sources such as Hot Cores, PDR's, and shocks. Although the abundances of many molecules in different types of sources are predicted accurately by the models, many questions remain due to lingering chemical, physical, and astronomical uncertainties. Grain chemistry remains less well understood although progress is being made.

The future should see more progress in understanding the rates of chemical reactions and physical processes such as desorption. As the input into models becomes more secure, modellers will use their models to describe more complex physical situations, taking account of heterogeneities as well as their time dependence. Some dynamic models are already available (Prasad et al. 1991; Rawlings et al. 1992). The era of calculations with a single spatial point may soon end. Given the range of problems remaining, the next twenty-five years should witness substantial progress.

6. Acknowledgments

The support of the National Science Foundation is gratefully acknowledged.

References

Bergin, E. A., Langer, W. D., & Goldsmith, P. F. 1995, ApJ, 441, 222
Bettens, R. P. A., & Herbst, E. 1995, Int. J. Mass Spec. Ion Proc., in press
Bettens, R. P. A., Lee, H.-H., & Herbst, E. 1995, ApJ, 443, 664
Brown, P. D., Charnley, S. B., & Millar, T. J. 1988, MNRAS, 231, 409
Dzegilenko, F., & Herbst, E. 1995, ApJ, 443, L81
Farquhar, P. R. A., Millar, T. J., & Herbst, E. 1994, MNRAS, 269, 641
Flower, D. R., Le Bourlot, J., Pineau des Forêts, G., & Roueff, E. 1994, A&A, 282, 225
Frenklach, M., & Feigelson, E. D. 1989, ApJ, 341, 372
Gredel, R., Lepp, S., Dalgarno, A., & Herbst, E. 1989, ApJ, 347, 289
Hasegawa, T. I., & Herbst, E. 1993, MNRAS, 263, 589
Herbst, E. 1995, Ann. Rev. Phys. Chem., 46, 27
Herbst, E., & Leung, C. M. 1989, ApJS, 69, 271
Hollenbach, D. J., Takahashi, T., & Tielens, A. G. G. M. 1991, ApJ, 377, 192
Lee, H.-H., Pineau des Forêts, G., Roueff, E., & Herbst, E., in preparation
Millar, T. J., Bennett, A., & Herbst, E. 1989, ApJ, 340, 906
Millar, T. J., & Herbst, E. 1990, MNRAS, 242, 92
Millar, T. J., Rawlings, J. M. C., Bennett, A., Brown, P. D., & Charnley, S. B. 1991, A&AS, 87, 585
Mitchell, G. F. 1988, in Astrochemistry, ed. M. S. Vardya & S. P. Tarafdar (Dordrecht: Reidel), 87
Neufeld, D. A., & Dalgarno, A. 1989, ApJ, 344, 251
Pineau des Forêts, G., Roueff, E., Schilke, P., & Flower, D. R. 1993, MNRAS, 262, 915
Prasad, S. S., Heere, K. R., & Tarafdar, S. P. 1991, ApJ, 373, 123
Prasad, S. S. , & Tarafdar, S. P. 1983, ApJ, 267, 603
Rawlings, J. M. C., Hartquist, T. W., Menten, K. M., & Williams, D. A . 1992, MNRAS, 255, 471
Roberge, W. G. & Draine, B. T. 1990, ApJ, 350, 700
Sternberg, A., & Dalgarno, A. 1995, ApJS, 99, 565
Thaddeus, P. 1994, in Molecules and Grains in Space, ed. I. Nenner & L. Trojanowski (New York: Am. Inst. of Physics), 711
Tielens, A. G. G. M., & Hagen, W. 1982, A&A, 114, 245
Tielens, A. G. G. M., & Hollenbach, D. J. 1985, ApJ, 291, 722
Tielens, A. G. G. M., Tokunaga, A. T., Geballe, T. R., & Baas, F. 1991, ApJ, 381, 181
Whittet, D. C. B. 1993, in Dust and Chemistry in Astronomy, ed. T. J. Millar & D. J. Williams (Bristol: Inst. of Physics), 9
Willacy, K., Williams, D. A., & Duley, W. W. 1994, MNRAS, 267, 949 (1994).
Williams, D. A. 1993, in Dust and Chemistry in Astronomy, ed. T. J. Millar & D. J. Williams (Bristol: Inst. of Physics), 143
Xie, T., Allen, M., & Langer, W. D. 1995, ApJ, 440, 674