Surface Reactions in Interstellar Space

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Abstract. It is impossible to explain the abundances of some gas-phase and most condensed-phase interstellar molecules without the use of grain chemistry. Nevertheless, grain-surface chemistry is relatively poorly understood for a variety of reasons. Our current knowledge of this chemistry and its use in interstellar models is discussed along with specific needs for future research.

1. The Need for Grain Chemistry

Although the abundances of most gas-phase interstellar molecules can be explained reasonably well via gas-phase chemistry, there are some notable exceptions. The most abundant molecule in space – molecular hydrogen – can only be formed by the surface recombination of neutral hydrogen atoms. The detection of interstellar ice mantles consisting mainly of water ice, but with other abundant species such as carbon monoxide, carbon dioxide, and methanol cannot be reasonably explained unless surface chemistry is invoked; depletion of gas-phase material is insufficient (Ruffle & Herbst 2000a,b). The gas-phase abundances in hot cores are best explained by the evaporation of these ice mantles.

2. Uncertainties and Models

There is clearly a role for surface chemistry in modelling the chemistry of interstellar clouds (Allen & Robinson 1977; Tielens & Allamandola 1987; Williams 1993). Yet the state of the laboratory discipline is such that there are many problems, and these problems are only aggravated by our lack of knowledge of the detailed nature of dust particles. There are six main uncertainties to be dealt with:

(i) *the size distribution and topological nature of grains.* The chemistry occurring on small grains is likely to be different from that on large grains (Tielens 1993), while the chemistry occurring on fluffy grains is likely to be more complex than that on spherical grains.

(ii) *the chemical nature of the surface on which reactions occur.* Surface reactions are governed mainly by two parameters - the energy required to desorb from the surface (E_D) and the energy required to diffuse from one surface site to another (E_b). These depend strongly on the chemical nature of the surface. For example, using E_D and E_b, we estimate the maximum temperature for efficient conversion of atomic to molecular hydrogen in dense clouds to range from 10 K

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on olivine to $\gg 300$ K on graphite.

(iii) *the mechanism or mechanisms of chemical reaction.* There are at least two mechanisms - the Langmuir-Hinshelwood (diffusive) mechanism, in which two thermal species diffuse towards each other, and the Eley-Rideal mechanism, in which a gas-phase species lands atop a rather inert and strongly-bound surface species. In addition, there is a variant of the Eley-Rideal mechanism known as the "hot atom" process, in which a gas-phase atom hits the surface and skims along it before quickly finding a reaction partner. The dominance of a particular mechanism is determined by the adsorbate, surface, and temperature. Finally, there is the problem of photo-chemistry, in which interstellar photons can break up unreactive surface molecules and form reactive ones.

(iv) *the types of chemical reactions.* It is normally assumed that the dominant surface reactions are association reactions, in which reactive neutral species stick to one another by giving off excess energy to the grains. But often normal exothermic channels (two or more products) are competitive and branching fractions are rarely determined.

(v) *mathematical problems associated with small particles.* With large numbers of surface species on sizeable surfaces, the diffusive mechanism is easily handled by rate equations akin to their gas-phase analogues (Pickles & Williams 1977). But on small surfaces with few reactive particles, the rate equations are not necessarily correct (Charnley 1997, 1998; Tielens & Hagen 1982).

(vi) *the role of non-thermal desorption of heavy species.* Unless non-thermal mechanisms are active, heavy species will not leave the grain surface in cold regions and the gas phase will be depleted of heavy material on time scales much shorter than cloud lifetimes.

All of these problems have been dealt with at most partially in current generations of models. For example, our models (Ruffle & Herbst 2000a,b) contain diffusive chemistry only on spherical grains of one radius (0.1μ), with a variety of surface materials, and a network of surface reactions consisting mainly but not exclusively of association reactions. The rate equations are modified in an empirical (and not totally satisfactory) way to deal with small particles (Caselli et al. 1998), while non-thermal desorption is assumed to occur upon cosmic ray excitation of grains. Photochemistry has recently been included but at highly uncertain rates. Improvements in all of these areas will be undertaken in the next few years, based, it is hoped, on new generations of experiment and theory.

Our current gas-grain models of cold (10 K) dense interstellar clouds are capable of reproducing most gas-phase observations and do show the existence of mantles consisting mainly of water ice, but with large amounts of CO and methanol (depending on conditions). We are currently working towards an understanding of the large abundance of CO_2, which has so far eluded us. Extension of the model to sources at higher temperatures may require a better method of treating the mathematical problems associated with small dust particles.

3. Future Needs

The formation of H_2 has been studied on assorted surfaces in some detail experimentally (Katz et al. 1999) and theoretically (Farebrother et al. 2000;

Parneix & Bréchignac 1998). To improve the reliability of current models, laboratory/theoretical efforts directed at the following additional problems would also be desirable:

• rates/mechanisms of reactions involving H (and D) atoms and heavy species at a variety of temperatures and on a variety of surfaces
• rates of surface reactions involving two heavy species
• experiments on actual dust particles rather than large cold surfaces
• experiments on non-thermal desorption
• development of a proper and useful mathematical treatment for surface reactions on small surfaces with few reactive particles (the so-called "accretion" limit).

Relevant experiments and calculations in these areas are being performed and planned in a number of laboratories. In addition, our knowledge of interstellar dust is improving. By the time of the next General Assembly, we can expect much progress in this area.

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