LABORATORY AND MODELING STUDIES OF CHEMISTRY IN DENSE MOLECULAR CLOUDS

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Abstract: A chemical evolutionary model with a large number of species and a large chemical library is used to examine the principal chemical processes in interstellar clouds. Simple chemical equilibrium arguments show the potential for synthesis of very complex organic species by ion-molecule radiative association reactions.

Theoretical models are used as key tools in obtaining an understanding of the chemistry occurring in interstellar clouds. These models have two major requirements for input: 1) the available observational abundances of the major elements, and the radiation field, and 2) both laboratory and estimated data on the physical and chemical processes which may occur in these clouds. The output of these models are then compared with observations and iterated to match observations as closely as possible in order to bound the possible chemistry. At this stage in the history of interstellar cloud chemistry, there is insufficient laboratory and observational data to produce models which are as realistic, accurate, or comprehensive as are (for example) the chemical models of the earth's upper atmosphere. The times are exciting nonetheless because it is precisely at this early stage that the learning rate is very high and discoveries tend to be major ones. In this spirit we have conducted two types of theoretical studies. In the first, we have constructed a large, time-dependent chemical model to complement the laboratory work which we have conducted in the past several years on ion-molecule reactions in interstellar clouds. The purpose of the large chemical evolutionary model is not to attempt simulations of the thermal, dynamic or chemical history of particular interstellar clouds. The major purpose is to examine in detail, in as comprehensive a manner as possible, the chemistry in interstellar clouds under a variety of conditions in order to determine what chemistry is of major importance in understanding observations of molecular abundances. In the second approach, we have used simple analytical chemical equilibrium arguments to examine the potential importance of new synthetic mechanisms for producing complex interstellar molecules. If found to be potentially important, then these mechanisms are

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included in the large model. The large model then identifies the most important production and loss mechanisms for any particular molecule under any set of cloud conditions. These major processes can then be used in dynamical and thermal models where the chemical reaction network must be limited. New directions are also obtained for laboratory measurements and suggestions can be made for observations.

In the large model, the chemical reaction network is not fixed and can change with time as the chemical environment changes. This is achieved by specifying an extraordinarily large library of chemical reactions and photoprocesses without any assumptions as to the importance of any single reaction for formation or destruction of a particular species. At present this library consists of over 1400 reactions amongst 137 species. The computer scans the library at suitable time intervals and selects which reactions in the library are significant under the prevalent conditions at the local time in cloud chemical evolution. The advantages of this approach are: 1) it is a time-dependent, chemical evolutionary model, 2) a large number of species can be managed and there are no a-priori assumptions concerning the reaction network other than the choice of reactions in the library, 3) the chemistry data base is large and can be readily changed and updated, and 4) the coupling of the chemistry between various families of species is not neglected.

The results which have been obtained using this model have been published elsewhere.[1,2] A major product of these models has been diagrams such as Fig. 1, which illustrates the major chemical processes in interstellar clouds and the chemical coupling between chemical families. Temperature, density, thermal history, chemical activation energies, and non-equilibrium effects are shown to be important in the case of particular interstellar molecules. The abundance of O_2 is critically dependent on the activation energies for the neutral reactions involved in its formation and destruction. In turn, the abundance of CN depends critically on the activation energies of the major loss reactions with O and O_2. The molecules C_2H and HC_2CN may be created quite early in the history of a dark cloud when the $C^+ \rightarrow CO$ conversion is still in progress. High abundances of these two species out of chemical equilibrium may be maintained at later times by a combination of lower cloud temperature and activation energies in major neutral loss processes. The NH_3 abundance may be very dependent on temperature, with higher abundances both at very low temperatures and at high temperatures. "Soft" recombination via radiative association of molecular ions (such as NH_3^+) with H_2 before recombination with electrons may lead to more efficient formation of NH_3, H_2CO, HCO and CH_3.

Radiative association other than the C^+-H_2 and CH_3^+-H_2 reactions were excluded from the large model. However, it was shown in discussion that the inclusion of certain radiative association reactions would relieve a number of problems with the model. A temperature dependent rate constant for the C^+-H_2 reaction is required in order to

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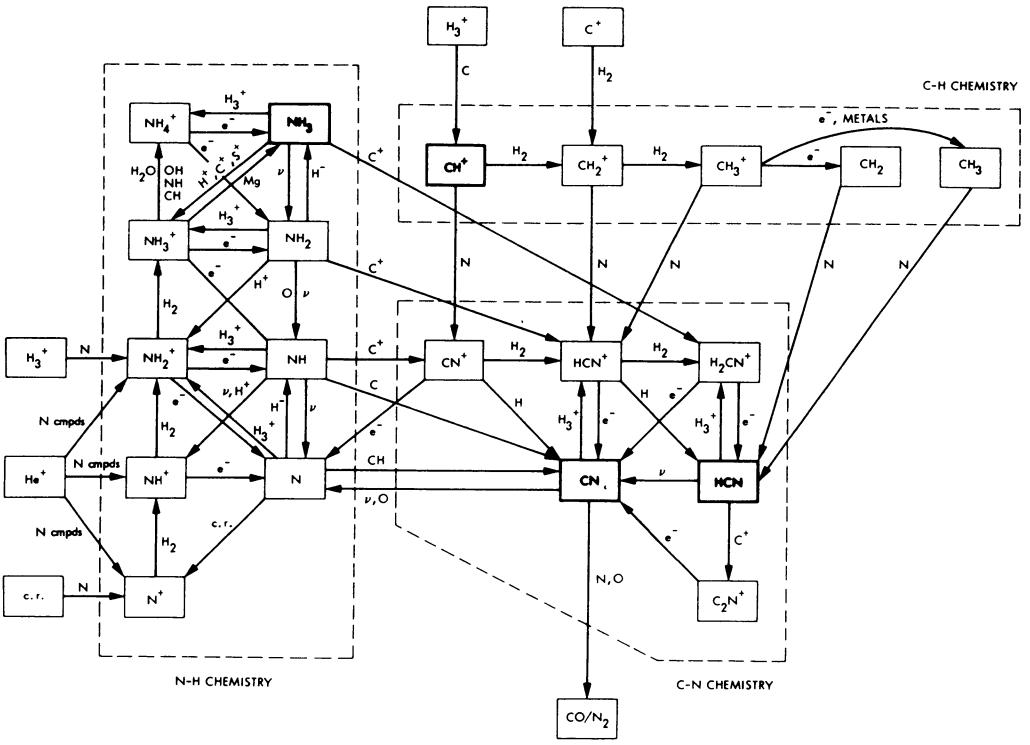

Figure 1

account for CH abundances in both diffuse and dense clouds, and large rate constants for both the C^+-H_2 and CH_3^+-H_2 reactions at low temperatures are required in order to reproduce the lower CO abundance in dark, low temperature clouds in comparison to Orion. The observed amount of HC_2CN and CH_3C_2H in dense clouds requires effective competition by the C^+-H_2 radiative association reaction (compared to the C^+-H_2O reaction) in order to provide sufficient precursor CH_n compounds (vs. CO) for formation of these species.

In addition to the large model, simple chemical equilibrium arguments have been applied which show the potential for the gas phase synthesis of very complex interstellar molecules by ion-molecule radiative association reactions. In addition to the radiative association reactions suggested by Smith and Adams[3], we have suggested[4] a larger set of reactions, not yet measured in the laboratory, which can account for the observed abundances of molecules such as CH_3OOCH, CH_3CHO, CH_3CH_2OH, CH_3OCH_3 and all of the presently observed complex molecules. The absolute and relative abundances of the cyanopolyynes, $HC_{2n}CN$, also can be explained[5] assuming certain ion-molecule radiative association reactions (Fig. 2). In this case, a laboratory measurement[6] has been made of the collisional analog of the initiating reaction:

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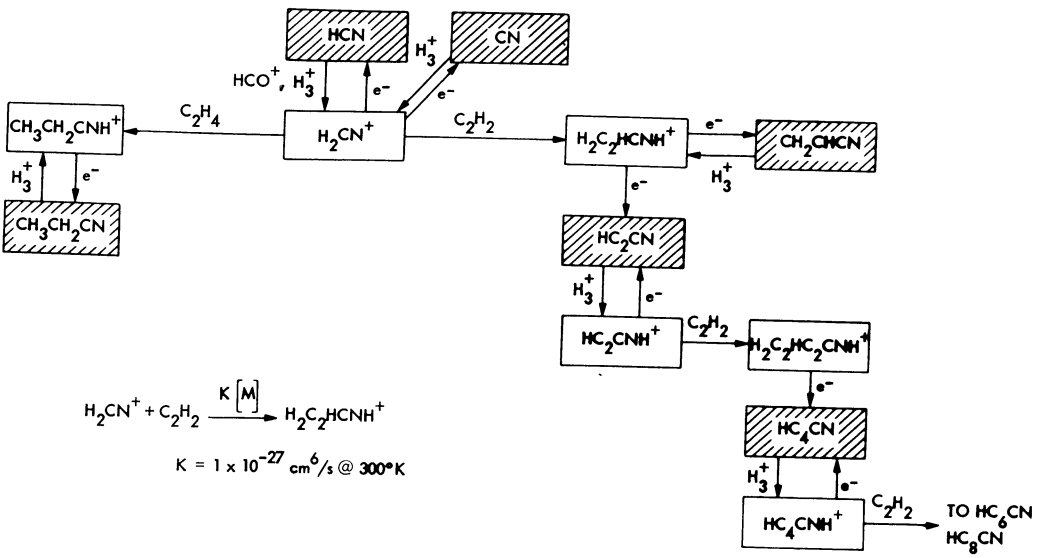

Figure 2

$H_2CN^+ + C_2H_2$. The laboratory and theoretical results thus far lend an optimistic view that gas phase ion chemistry may indeed be capable of synthesizing even the most complex of observed interstellar molecules.

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DISCUSSION FOLLOWING HUNTRESS

Tatum: How well are reaction rates known for such a large number of reactions, and whence are they obtained?

Huntress: For ion-molecule reactions, a number of groups are very active in producing the required data. There is flowing afterglow work at NOAA Boulder, the University of Birmingham and York University and ion cyclotron resonance work at the Jet Propulsion Laboratory. A great deal of the required data has been, and is being, obtained in these

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studies. For neutral-neutral reactions, there are no studies being conducted specifically for interstellar applications, but there is a large body of data available from a number of laboratories all over the world working mainly on Earth stratospheric chemistry. The lowest temperature data is not available, the data set is smaller and the activation energies are not well enough known, but the general features of this class of chemistry can be deduced. Dissociative recombination rates have been measured in microwave discharge work at the University of Pittsburg and in merged beam work at Western Ontario, but the product distributions for these reactions are a problem. Photodissociation and photoionization rates are also a problem, but John Black has compiled much of this data in his thesis. About 1/3 of the reactions in our chemistry library have been measured in the laboratory, another 1/3 are derived on the basis of analogies to known reactions, and another 1/3 are guesses. There is every expectation that the situation will constantly improve, given the large amount of laboratory and theoretical activity presently being conducted. For most of the simpler molecules in dense molecular clouds, say those with about five atoms or less, the rate constants for the major gas-phase production reactions are fairly confidently known.

Mouschovias: The goal of studies of interstellar chemistry is to reveal the physical conditions in interstellar clouds, and therefore to provide us with at least clues to the dynamical processes leading to star formation.

A question persistently recurs to me as I listen to detailed presentations (often to the point of saturation of the mind) on interstellar chemistry. Suppose that we have built the ultimate detectors, and carried out the most complete observational programs and associated calculations, so that we have detected every detectable molecular transition of every existing molecular species. We will then have a complete map of the physical conditions in dense clouds, such as the dependence of gas density and temperature on position within a cloud, the masses and shapes of clouds, etc. However, the question of what gave rise to these physical conditions will still remain. They are, certainly, determined by the dynamical processes of cloud formation, equilibrium, and collapse.

When these dynamical processes are considered, it becomes imperative to study in detail the effect of the interstellar magnetic field, whose energy density is larger than (or at least comparable to) any other interstellar energy density. It is disappointing to see that of the seventy or so papers selected for presentation at this symposium, not a single one deals with new observational information or new theoretical predictions concerning magnetic fields in dense clouds, and how observations of molecules can test these predictions. Apparently, the relation between dynamical processes (directly related to star formation) in magnetic clouds, and observable parameters, such as the velocity structure of a cloud, is not recognized or appreciated.

For example, we have predicted recently (1979, Ap. J., 230, 204) by exact analytical calculations that certain fragments within dense clouds should rotate in a *retrograde* sense with respect to the sense of their revolution about the axis of rotation of the cloud as a whole. (The evident significance of this prediction lies in the fact that it offers a natural explanation of possible retrograde rotation in stellar and

planetary systems as a purely magnetic phenomenon.) The range of fragment densities in which this effect takes place is from somewhat less than $10^4 cm^{-3}$ to somewhat greater than $10^6 cm^{-3}$. Since these are typical densities found in molecular clouds, one may look for retrograde spin of dense fragments by using optically thin molecular lines (such as ^{13}CO or an excited state of OH). Such evidence will reveal itself at the location of a fragment either as a "shoulder" on a plot of radial-velocity versus distance-from-the-rotation-axis, or as a reversal of the sign of the slope of such a curve.

A second new result of relevance to this meeting is an as yet unpublished time-dependent solution for ambipolar diffusion. We find that supersonic ion-neutral drift can be attained easily and very rapidly. If a significant fraction of grains are charged, inelastic collisions between charged and neutral grains can release molecules into the gas phase, as desired by Dr. Greenberg.

In summary, the interstellar magnetic field can largely determine the dynamics of dense clouds and, therefore, the physical conditions, which in turn determine the cloud chemistry. Molecular observations, on the other hand, can test the importance of magnetic effects in dense clouds.

Huntress: The goal of studies of interstellar chemistry is not just the derivation of the physical conditions in interstellar clouds. Another goal is to obtain an understanding of the evolution of organic compounds, from atoms and a radiation field in interstellar clouds, to prebiotic compounds in a primordial life-evolving ocean. How does the chemistry evolve in a collapsing interstellar cloud, and what is the resulting composition of a presolar nebula? How is that composition reflected in the early primitive atmospheres of newly-born planets? Studies of interstellar chemistry can yield clues to physical conditions in interstellar clouds because the chemistry is so sensitive to these physical conditions. Thus it is one goal of such studies, but it is not the one and only reason these studies are conducted.