

CHEMISTRY IN DENSE INTERSTELLAR CLOUDS - DATA REQUIREMENTS

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ABSTRACT. Chemical models of dense interstellar clouds are reviewed with particular emphasis on recent results. The need for theoretical and experimental data on rate coefficients is pointed out and some observational studies are suggested.

1. INTRODUCTION

In this brief review I shall discuss some current research on the chemistry of dark, dense interstellar clouds. In particular, I shall restrict myself to the description of cold, quiescent clouds such as TMC-1 and L134N which have kinetic temperatures $\sim 10\text{K}$. Chemistry on grain surfaces and in evolving clouds is discussed elsewhere. Recent reviews of interstellar chemistry include those given by Herbst (1988) and Millar (1988). In the following section, I shall describe microscopic processes which may play important roles in the chemistry. Numerical results quoted in this section are taken from Millar (1988). In Section 3, I summarise recent chemical kinetic models of dark clouds, and finally in Section 4, give a brief list of data required.

2. MICROSCOPIC PROCESSES

2.1 Dissociative Recombination Branching Ratios

In models of interstellar chemistry, it has become standard practice to assume that when a molecular ion containing one or more hydrogen atoms, recombines with an electron, one or two hydrogen atoms, or possibly H_2 , is released. This viewpoint is supported to some extent by the phase space calculations of Herbst (1978) and Green and Herbst (1979). Thus, for example, the reaction $\text{H}_3\text{O}^+ + e$ results in the formation of OH and H_2O with a branching ratio, f , to OH generally assumed to ~ 0.5 . More recently, Bates (1986) has argued that dissociation occurs

through excitation of a particular valence bond and hence results in the disruption of one bond, unless polarisation bonds are present in the molecular ion. For example, he argues that $\text{H}_3\text{O}^+ + e \rightarrow \text{H}_2\text{O}$ only (i.e. $f = 0$) and $\text{CH}_5^+ (= \text{CH}_3^+ \cdot \text{H}_2) + e \rightarrow \text{CH}_2 + \text{H} + \text{H}_2$, but not $\text{CH}_4 + \text{H}$. Bates and Herbst (1988) have given a review of dissociative recombination. Millar et al (1988) have applied Bates' ideas to a variety of complex molecular ions using *ab initio* techniques to determine the position of the charge on the ions. In general, the electron is delocalised, so that several product channels, rather than one, can result from the recombination process. Millar et al. have used their calculated branching ratios in a detailed chemical kinetic model of a dense interstellar cloud, and find that the most important branching ratio is that value assumed for f . If $f = 0$, then H_2O is as abundant as CO, H_3O^+ is the most abundant molecular ion and OH and molecules such as O_2 , NO, SO, SO_2 , N_2 , N_2H^+ which form, directly or indirectly, from it, become much less abundant than their observed, or inferred, interstellar values. However, if $f = 0.1$, OH and its descendents are formed efficiently. The extra channels included for the dissociation of hydrocarbon ions tend to decrease the abundances of the hydrocarbons, though only at steady state ($> 5 \cdot 10^6$ yr), while the CI abundance at steady state can reach $\sim 6 \cdot 10^{-6}$ for $f = 0$, since CI is destroyed mainly by O_2 and OH which have low abundances in this case.

2.2 Radiative Association via Electronic Stabilisation

Bates (1987) re-analysed the low temperature experimental results of Barlow et al. (1984) on the $\text{CH}_3^+ - \text{H}_2$ radiative association reaction. In particular, Bates argued that the experiment was carried out at an effective temperature of $\sim 50\text{K}$ rather than 13K and hence that the CH_5^{++} collision complex must stabilise via electronic, rather than vibrational, stabilisation in order to account for the measured rate coefficient. Subsequently, Herbst and Bates (1988) described two methods by which electronic stabilisation might occur and estimated expected enhancements to the radiative association rate coefficients. It is not known, as yet, whether electronic stabilisation applies to any other systems of astrophysical importance.

2.3 Cosmic Ray Induced Ultraviolet Photons

Prasad and Tarafdar (1983) recognised that the cosmic ray ionisation of H_2 in dense clouds would result in the generation of a low flux of UV photons within the clouds. Sternberg et al. (1987) and Gredel et al. (1987) have calculated the resulting spectrum of photons and used them to determine photodissociation rates for CO and other molecules (Gredel et al. 1988). These rates depend upon a number of parameters, most importantly the grain albedo, ω , and, for CO which is destroyed by line photons, on the cloud temperature, T , and on the CO line widths. Typical photorates are $\sim (10 - 10^3)\zeta$ where ζ is the primary cosmic ray ionisation rate of H_2 . For $T = 10\text{K}$, $\omega = 0.5$ and $\zeta = 10^{-17} \text{ s}^{-1}$, the

inclusion of such photoprocesses affects abundances slightly, and then only at steady state. One important exception is CI whose abundance can increase by an order of magnitude or more as a result of CO photodissociation. Complex hydrocarbons have abundances reduced by at most a factor of five at steady state.

2.4 Large Molecules

Lepp and Dalgarno (1988) have explored the consequences of including a component of large molecules (LMs) - possibly the polycyclic aromatic hydrocarbons - in dense cloud chemistry. They find that the LMs take up almost all the electrons in such clouds with the result that $[LM^-] > [e]$ (here square brackets refer to abundance). Collisions of atomic and molecular ions with LM^- rather than with electrons become the dominant means of neutralisation. The reaction $C^+ + LM^- \rightarrow C + LM$ leads to a large abundance of atomic carbon, although it is unclear as to whether this reaction could lead to a $[CI]/[CO]$ ratio as large as 0.01 (Lepp and Dalgarno 1988). The recombination of complex ions and LM^- may occur by mutual neutralisation, that is a reaction in which dissociation of the ion does not take place (Bates and Herbst 1988), which, together with the increased CI abundance, enhances the formation of complex species. The major uncertainty in this model is the LM abundance which Lepp and Dalgarno treated as a free parameter.

3. RECENT CHEMICAL KINETIC MODELS

3.1 Complex Molecule Formation

Herbst and Leung (1988) have extended the hydrocarbon chemistry to include species such as C_mH_n ($m \leq 9$, $n \leq 2$), the cyanopolyynes up to HC_9N , CH_3C_6N and so on. Although laboratory data on many of the reactions in their scheme are lacking, they have based their chemistry on the processes thought to important, and well determined, in the production of less complex species. They find reasonable agreement between their calculated abundances and those observed in TMC-1 given the large uncertainties in the chemical network used. It appears that a relatively simple chemistry involving carbon-chain growth via C^+ and CI reactions can explain, in a general fashion, the type of species observed in TMC-1.

3.2 Deuterium Chemistry

Brown and Rice (1981, 1986) performed pioneering studies on detailed models of deuterium chemistry in dark clouds. Recently, Millar, Bennett and Herbst (1988) have updated and extended their model to include the effects of deuterium fractionation in more complex molecules and to study the sensitivity of fractionation to the choice of dissociative recombination branching ratios. Their detailed results showed that (i) for hydrocarbon

molecules, which are deuterated principally by CH_2D^+ and C_2HD^+ for $T > 20\text{K}$, the degree of fractionation actually increases with temperature in the range 30 - 70 K. This behaviour is opposite to that of species such as H_2O and NH_3 which are deuterated by H_2D^+ . Herbst et al. (1987) have shown that this behaviour is due to the competition between H_2 and HD in reactions with CH_3^+ and C_2H_2^+ . These two ions react with H_2 in radiative association reactions whose rate coefficients therefore decrease with increasing temperature, hence allowing HD reactions, whose rate coefficients are independent of temperature, to be more effective. At $T > 70\text{K}$, however, the degree of fractionation decreases because reactions of H_2 with the CH_2D^+ and C_2HD^+ ions dominate the loss of these species. (ii) As noted by Brown and Rice (1986), the fractionation of HCO^+ is strongly time dependent at $T = 70\text{K}$. At early times fractionation results from the reactions of deuterated hydrocarbon ions with O and CO whereas at steady state, the hydrocarbon ions have been processed into CO and deuteration, which is now via H_2D^+ , is inefficient. Observations of DCO^+ and HCO^+ in Orion indicate that this cloud has not yet reached a chemical steady state. (iii) Dalgarno and Lepp (1984) showed that the reaction $\text{D} + \text{OH} \rightarrow \text{OD} + \text{H}$ could lead to a large $[\text{OD}]/[\text{OH}]$ ratio at low temperatures. Millar, Bennett and Herbst (1988) find this ratio to be ~ 0.5 , although its value is uncertain due to some poorly known rate coefficients.

3.3 Carbon Isotope Chemistry

Langer and Graedel (1988) have included the chemistry of ^{13}C in dense cloud models and find some important differences from their earlier results (Langer et al. 1984). In particular, while ^{13}C enhancement occurs in CO and HCO^+ , trace carbon-bearing molecules are enhanced in ^{12}C but to a degree less than in their earlier work, though still larger than those observed. If cosmic-ray produced UV photons dominate the loss of CO, then isotope selective photodissociation of ^{13}CO will occur and may change the ratios calculated by Langer and Graedel.

4. DATA REQUIREMENTS

4.1 Theoretical and Experimental Determination of Rate Coefficients.

As discussed in Section 2.1, branching ratios for dissociative recombination reactions are highly uncertain and experimental work in this area is essential for a proper understanding of interstellar chemistry. There has been some dispute recently (Amano 1988) over the rate constant for the $\text{H}_3^+ + e$ reaction, but this reaction plays no important role in dense clouds because the H_3^+ ion is lost predominantly through reactions with species such as O, C, N, CO, H_2O , etc. Its value does have important implications for chemistry in diffuse clouds (van Dishoeck and Black 1988) and in Jupiter's atmosphere (Dalgarno 1988).

The most important recombination reaction in dense clouds is that of $\text{H}_3\text{O}^+ + e$, which can have significant effects on cloud chemistry if only H_2O is formed.

Low temperature data on neutral-neutral reactions are also needed. The reactions $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ and $\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}$ are important in determining the O_2 and CI abundances in dense clouds. Smith (1988) has given some general rules which can be used to indicate the presence of barriers at low temperatures while Wagner and Graff (1987) and Leen and Graff (1988) have estimated rate coefficients for several systems of astrophysical importance.

Structural information on ions is extremely important as Adams and Smith (1987) have pointed out in their study of the linear and cyclic forms of C_3H_3^+ . Such information is important in determining the HCN/HNC and linear - C_3H /cyclic - C_3H abundance ratios. It may also help us to understand the mechanisms by which the cyanopolyynes form. Lee and Amano (1987) have shown that protonated cyanoacetylene is linear, HC_3NH^+ ; hence, one expects the reaction $\text{HC}_3\text{N} + \text{H}_2\text{D}^+$ to produce the ion HC_3ND^+ upon deuteron transfer. In this case, it is difficult to see how DC_3N can result from dissociative recombination. The $[\text{DC}_3\text{N}]/[\text{HC}_3\text{N}]$ ratio should, therefore, not reflect the $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ or $[\text{DCO}^+]/[\text{HCO}^+]$ ratios but may be closely tied to ratios such as $[\text{CCD}]/[\text{CCH}]$ or $[\text{C}_3\text{HD}]/[\text{C}_3\text{H}_2]$, depending upon its exact mode of formation. Such isomeric effects, which may also be important in the DCN/DNC system, have not been included in any study of deuterium fractionation.

4.2 Observational Data Requirements

It has been the case that observational studies have given impetus to the development of particular chemical models and, of course, observations provide a test for such models. Perhaps the most important measurement to be carried out is a study of CI in cold, dark clouds. To date, there has been only one source detected, L134N, and one other source, TMC-1, searched (Phillips and Huggins 1981). The chemical models predict that the C_3H_3^+ ion is the precursor to HC_3N and $c\text{-C}_3\text{H}_2$ indicating that these species should be correlated to some degree, although the exact correlation should depend on the $[\text{N}]/[\text{e}]$ abundance ratio which can vary from source to source.

Detailed studies of particular molecular clouds are also of great value. Much observational data has been gathered for TMC-1, while Swade (1987) has studied L134N in great detail and presented evidence for a C/O abundance gradient within this cloud. Other studies such as this would be useful.

Finally there is evidence that, at least in hot core regions, the formation of complex molecules such as methanol, ethanol and dimethyl ether, is related to grain surface processes (Millar et al. 1988b). It is not clear,

as yet, whether the grains play any significant role in the production of molecules in cold clouds but observations of large molecules in these regions may eventually provide information on this point.

REFERENCES

- Adams, N. G. & Smith, D., 1987, *Ap. J.*, 317, L25.
 Adams, N. G., Smith, D. & Clary, D. C., 1985, *Ap. J.*, 296, L31.
 Amano, T., 1988, *Ap. J.*, 329, L121.
 Barlow, S. E., Dunn, G. H. & Schauer, M., 1984, *Phys. Rev. Letts.*, 52, 902.
 Bates, D. R., 1986, *Ap. J.*, 306, L45.
 Bates, D. R., 1987, *Ap. J.*, 312, 363.
 Bates, D. R. & Herbst, E., 1988, In: "Rate Coefficients in Astrochemistry" eds. T. J. Millar & D. A. Williams (Kluwer), p. 41.
 Brown, R. D. & Rice, E. H. N., 1981, *Phil. Trans. Roy. Soc.*, A303, 523.
 Brown, R. D. & Rice, E. H. N., 1986, *MNRAS*, 223, 429.
 Dalgarno, A. 1988, In: "Rate Coefficients in Astrochemistry" eds. T. J. Millar & D. A. Williams (Kluwer), p. 321.
 Dalgarno, A. & Lepp, S., 1984, *Ap. J.*, 287, L47.
 Gredel, R., Lepp, S. & Dalgarno, A., 1987, *Ap. J.*, 323, L137.
 Gredel, R., Lepp, S., Dalgarno, A. & Herbst, E. 1988, *Ap. J.*, in press.
 Green, S. & Herbst, E., 1979, *Ap. J.*, 229, 121.
 Herbst, E., 1978, *Ap. J.*, 222, 508.
 Herbst, E., 1988, In: "Rate Coefficients in Astrochemistry" eds. T. J. Millar & D. A. Williams (Kluwer), p. 239.
 Herbst, E., Adams, N. G., Smith, D. & DeFrees, D. J., 1987, *Ap. J.*, 312, 351.
 Herbst, E. & Bates, D. R., 1988, *Ap. J.*, 329, 410.
 Herbst, E. & Leung, C. M., 1986, *Ap. J.*, 310, 378.
 Herbst, E. & Leung, C. M., 1988, *Ap. J. Suppl.*, in press.
 Langer, W. D. & Graedel, T. E., 1988, *Ap. J.*, in press.
 Langer, W. D., Graedel, T. E., Frerking, M. A. & Armentrout, P. B., 1984 *Ap. J.*, 277, 581.
 Lee, S. K. & Amano, T., 1987, *Ap. J.*, 323, L145.
 Lee, T. M. & Graff, M. M., 1988, *Ap. J.*, 325, 411.
 Lepp, S. & Dalgarno, A., 1988, *Ap. J.*, 324, 553.
 Millar, T. J., 1988, In: "Molecular Astrophysics" ed. T. W. Harquist (Cambridge University Press), in press.
 Millar, T. J., Bennett, A. & Herbst, E., 1988, *Ap. J.*, in press.
 Millar, T. J., DeFrees, D. J., McLean, A. D. & Herbst, E. 1988a. *A. & A.*, 194, 250.
 Millar, T. J., Olofsson, H., Hjalmanson, A. & Brown, P. D., 1988b., *A. & A.*, in press
 Phillips, T. G. & Huggins, P. J., 1981, *Ap. J.*, 251, 533.
 Prasad, S. S. & Tarafdar, S. P., 1983, *Ap. J.*, 267, 603.
 Smith, I. W. M., 1988. In: "Rate Coefficients in Astrochemistry" eds. T. J. Millar & D. A. Williams (Kluwer), p. 103.
 Sternberg, A., Dalgarno, A. & Lepp, S., 1987, *Ap. J.*, 320, 676.
 Swade, D. A., 1987. Ph. D. Thesis, U. Mass. at Amherst.
 van Dishoeck, E. F. & Black, J. H., 1988. In: "Rate Coefficients in Astrochemistry" eds. T. J. Millar & D. A. Williams (Kluwer), p. 209.
 Wagner, A. F. & Graff, M. M., 1987. *Ap. J.*, 317, 423.