

# FORMATION MECHANISM FOR INTERSTELLAR MOLECULES

PAUL HARTECK, ARTHUR BEAUDOIN, and ROBERT REEVES

*Chemistry Dept., Rensselaer Polytechnic Institute, Troy, N.Y. 12181, U.S.A.*

**Abstract.** The gas phase production of molecules in dust clouds in interstellar space may occur largely as H<sub>2</sub> formation on the interstellar grains, with relatively minor formation in the gas phase. The formation of more complex molecules, however, may be augmented by gas phase processes including (1) negative ions formed by radiative attachment of electrons, (2) direct radiative association of molecules and atoms, and (3) reaction of atoms and molecules with H<sub>3</sub><sup>+</sup> molecules.

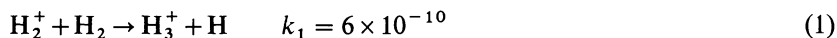
## 1. Introduction

The formation of molecules in interstellar space may be over a variety of different types of processes (McNally, 1968) which may be considered in two different categories, one for gas phase reactions and the other on interstellar grains. The latter type has been discussed in some detail (Watson and Salpeter, 1972). The gas phase reactions are probably playing a minor, but possibly crucial role in molecule formation by augmenting the production of the larger, more complex molecules. The simple molecular hydrogen may be largely produced on interstellar grains and evaporated into space. The more complex molecules if formed may not be so readily evaporated from the cold grains.

## 2. Discussion

In the region of the interstellar clouds, the density of hydrogen may be 10<sup>4±1</sup> molecules per cubic centimeter and an order of magnitude less, about 10<sup>3</sup>, for atomic hydrogen. Both H<sup>+</sup> and H<sub>2</sub><sup>+</sup> will be the major ions primarily formed with a typical steady state concentration of positive ions of about 0.05 per cubic centimeter (= 0.05 electrons cc<sup>-1</sup>). These may be formed by photo ionization, cosmic rays, or other processes, but are probably produced at about equal rates, possibly more H<sub>2</sub><sup>+</sup>, because of the greater amount of H<sub>2</sub> compared to H.

Under the rarified conditions the chemistry of the H<sub>2</sub><sup>+</sup> is interesting. The main reaction anticipated would be with H<sub>2</sub>.



Followed by:



The rate of formation of H<sub>3</sub><sup>+</sup> can be balanced with the rate of loss:

$$\frac{+dH_3^+}{dt} = k_1(H_2^+)(H_2) = \frac{-dH_3^+}{dt} = k_2(H_3^+)(e^-)$$

or

$$\frac{(H_3^+)}{(H_2^+)} = \frac{k_1(H_2)}{k_2(e^-)}$$

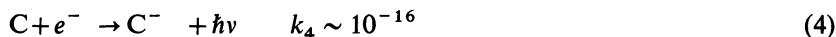
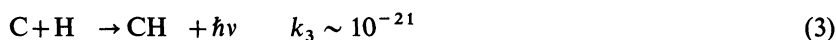
Assuming  $(H_2) = 10^4$  and  $(e^-) = 0.05$ , then

$$(H_3^+)/(H_2^+) = \frac{6 \times 10^{-10}}{10^{-7}} \times \frac{10^4}{(0.05)} = \sim 10^3.$$

The loss of  $H_3^+$  would be in the order of some years, while the  $H_2^+$  would be a few days.

(The rate of loss of molecular ions  $A_2^+$  or  $A_3^+ + e^-$  vs the rate of loss of atomic ions  $A^+ + e^-$  is high. So the  $H^+$  ions may be of an order of magnitude greater density than  $H_3^+$ . However, we don't know all processes by which the  $H^+$  will be consumed. The reaction  $H + H_2^+ \rightarrow H_2 + H^+$  would not normally compete with reaction 1, since  $H_2 > H$ ). We assume here conservatively that the  $(H_3^+) \sim 10^{-3}$ .

A series of reactions which produce molecules or molecular ions may be illustrated with the carbon atoms.



and the relative rates\*:

$$\begin{aligned} \frac{-dC}{dt} \cdot \frac{1}{C} &= k_3(H) = 10^{-21} \times 10^3 = 10^{-18} \\ &= k_4(e^-) = 10^{-16} \times (0.05) = 5 \times 10^{-18} \\ &= k_5(H_3^+) = 10^{-9} \times (10^{-3}) = 10^{-12}. \end{aligned}$$

Here it can be seen that reaction (5) is several orders of magnitude faster than the other two processes. Once formed the  $CH^+$  may react with the molecular hydrogen:

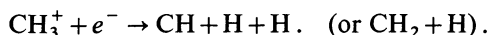


followed by



(The subsequent analogous reaction to form  $CH_4^+$  is endothermic and cannot occur under these conditions). The ion-electron reactions can then result in neutral CH radicals, e.g..

\* As fraction of carbon atoms lost per second.



The  $\text{CH}^+$  ion can combine with an electron under these conditions in about 10 yr ( $\text{CH}^+ + e^- \rightarrow \text{C} + \text{H}$ ), while it will probably react with  $\text{H}_2$  in a much shorter time – if  $k_6 \sim 10^{-11}$ , then with  $\text{H}_2 \sim 10^4$ , it would be a few months.

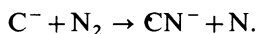
In themselves the positive ion reactions do not add new bonds, but rather act to rearrange these bonds. A reaction of the type (Rank *et al.*, 1971) forms a new bond, but for atom-atom interaction, it is known to be generally very slow. The more complex associations may be much faster. The reaction:



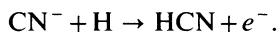
has been measured and is between  $10^{-15}$  and  $10^{-16}$  (Rolfes *et al.*, 1965). Rates of this order of magnitude or even faster may be expected for reactions of this complexity, i.e. forming triatomic or larger polyatomic atoms in association. If the association process were then about five orders of magnitude faster than that indicated for reaction (3), it could well compete with the  $\text{H}_3^+$  reactions of type (5).

Similarly the electron attachment process should be considered for the more complex molecule where attachment occurs with a higher probability. Such processes in the gas phase can yield molecules which are of relatively low boiling point, but could not reasonably evaporate if formed on interstellar grains which have relatively low temperatures.

The formation of nitrogen containing molecules may again be mainly on interstellar grains. Negatively ion reactions, however, may also contribute to the production of certain species. The reaction of  $\text{C}^-$  with  $\text{N}_2$  can produce the  $\text{CN}^-$  ion fragment:



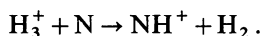
This reaction may be exothermic if the higher value (73.8 kcal) (Neale, 1964) of the electron affinity of CN is found correct, rather than the 64 kcal value sometimes cited (Napper and Page, 1963). The  $\text{CN}^-$  might react to produce HCN via



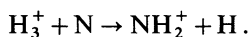
The source of additional CN and HCN may be from the N-atom attack on carbon compounds, well-known in the extensive literature on active nitrogen.

The reaction of  $\text{H}_3^+$  with molecular  $\text{N}_2$  is known to yield  $\text{HN}_2^+$  (Burt *et al.*, 1970), but this probably does not lead to any observed nitrogen compounds. Further studies by these workers may shed light on other important reactions and their mechanisms.

The positive ion reaction:



Seems to be endothermic and may be neglected. The alternate products might be considered since the reaction is then exothermic:



Although to our knowledge, this has not been observed.

Lind (1961) was an advocate of ion clusters as the explanation of many reactions in radiation chemistry. In his monograph, he quotes the paper by Magee and Funabaski (1959) which came to the conclusion that clusters in general don't account for the chemical reactions induced by ionizing radiation under laboratory conditions. However, after an exhaustive treatment of all types of binding energies, Magee and Funabaski conclude that "It is possible that specific ion-catalyzed reactions could be obtained between clustered molecules in the sense originally suggested by Lind."

At interstellar conditions, there will exist regions where the temperatures and particle concentrations are favorable for the formation of ion clusters. The clustering is obviously enhanced at low temperatures. If the cluster contains in the order of a few dozen particles then in the case of neutralization, the electrostatic forces will disappear and the energy of neutralization may 'evaporate' the clustered molecules or contribute to their activation as a complex. So larger molecules may be formed in the gas phase which could not originate by evaporation from a grain at low temperatures. In this respect, clusters would act as a hybrid of pure gas and grain surface reactions.

Magee and Funabaski emphasize that the experimental base is very minor in their theoretical considerations and the matter becomes even more complicated when we try to apply this theory to interstellar problems. However, it seems necessary and valuable to reconsider the cluster theory in the light of interstellar molecular formation.

### 3. Conclusion

The reaction types discussed seem to be adaptable to a series of chemical species found in interstellar space, and they are also in line with the observed amounts of these species, total pressures and particle concentrations in the clouds. A more detailed discussion will follow in another paper.

### Acknowledgement

This work was supported by a grant from the National Aeronautics and Space Administration, NGL 33-108-007.

### References

- Burt, J. A., Dunn, J. L., McEwan, M. J., Sutton, M. M., Roche, A. E., and Schiff, H. I.: 1970, *Chem. Phys.* **52**, 6062.
- Lind, S. C.: 1961, *Radiation Chemistry of Gases* (American Chemical Society Monograph No. 151), Reinhold Publishing Corporation, New York.
- Magee, J. L. and Funabaski, K.: 1959, *Radiation Res.* **10**, 622.
- McNally, D.: 1968, *Adv. Astron. Astrophys.* **6**, p. 173.
- Napper, R. and Page, F. M.: 1963, *Trans. Faraday Soc.* **59**, 1086.
- Neale, R. S.: 1964, *Phys. Chem.* **68**, 143.
- Rank, D. M., Townes, C. H., and Welch, W. J.: 1971, *Science* **174**, 1083.
- Rolfes, T. R., Reeves R. R., and Harteck, P.: 1965, *J. Phys. Chem.* **69**, 849.
- Watson W. D. and Salpeter, E. E.: 1972, *Astrophys. J.* **174**, 321.