INTERSTELLAR CHEMISTRY : THE REACTIONS OF H_3^+ WITH HYDROCARBONS

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The largest chemical factories in the universe lie within the diffuse clouds of dust and gas that exist between the stars. It can be argued that within these interstellar clouds (dense and diffuse), most of the chemistry in the universe takes place[1]. ‘Dense’ is of course only a relative term; typically dense clouds have particle densities that are of the order of 10^4 to 10^6 per cubic centimetre and temperatures between 10-50K. It is perhaps surprising that any molecules at all can be observed in the interstellar medium (ISM), in view of the low particle densities and extreme cold, yet in excess of 100 species have been observed, the largest containing up to 13 atoms. Conventional chemical reactions with activation barriers are prohibitively slow under these conditions, and so cannot play a significant role in the formation of these observed molecules. However, it is known that reactions between ions and molecules can be very fast even at low temperatures, which makes ion-molecule reactions an important contributor to the chemistry of the universe.

Molecular hydrogen is by far the most abundant species in both diffuse and dense molecular clouds. When molecular hydrogen is ionised the dominant ion formed is H_3^+. H_2 also has an extremely low proton affinity (423.4kJ mol^{-1})[2] which means that practically all collisions of H_3^+ with a molecular species result in the transfer of a proton. These factors combine to make the chemistry of H_3^+ extremely important to the ISM.

Conventional wisdom has it that when proton transfer is exothermic, it proceeds rapidly (usually at the gas kinetic rate), and earlier investigations have borne this out for H_3^+ [3]. However, because of the low proton affinity of H_3^+ these reactions are extremely energetic and many possible exothermic product channels are available. The formation of vibrationally excited H_3^+ ions has also hampered previous experimental studies[3] of these reactions as it provides extra energy for the reaction and could drive even more dissociative processes. The current work aims to examine the rates and products of the reaction of H_3^+ with various hydrocarbons, especially those with less than 3 carbon atoms, in an attempt to ascertain how the available energy is partitioned in the products and what implications this has for the theories of molecular formation in the ISM.

The reactions of H_3^+ have been examined in a flowing afterglow selected ion flow/drift tube(FA/SIFDT) using H_3^+ formed in one of two ways. The first method involves the formation of ions with a microwave discharge on pure hydrogen and then mass selection and injection of only the H_3^+ ion. This method forms vibrationally excited H_3^+ (v=1)[4]. The second method involves the injection of krypton ions into a hydrogen carrier, which results in H_3^+ as shown in reactions (1) and (2). This latter method guarantees ground state ions as reaction (1) is slightly endothermic and thus there is not enough energy in reaction (2) to produce any vibrational excitation[5].

$$Kr^+ + H_2 \Rightarrow H_2^+ + Kr \quad (1)$$
$$H_2^+ + H_2 \Rightarrow H_3^+ + H_2 \quad (2)$$

The reactions of H_3^+ with the smaller hydrocarbons (C_nH_m $n \leq 3$) are mostly dissociative with many involving the elimination of one or more hydrogen molecules or a methane neutral. Almost all reactions have more than one dissociative channel and as expected all proceed at or near the theoretical collision rate in either helium or hydrogen carrier gas. Complications as a result of the use of the different carriers will also be discussed.

1.Herbst, E. Annu. Rev. Phys. Chem. 1995, 46, 27.
2. Lias, S.G. *et al*. J. Phys. Chem. Ref Data. 1988, 17, supplement 1.
3. Anicich, V.G. J. Phys. Chem. Ref. Data. 1994, 22, 1469.
4. Spanel, P. Smith, D. Int. J. Mass Spectrom. Ion Proc. 1993, 129, 163.
5. Smith, D. Spanel, P. Chem. Phys. Lett. 1995, 211, 454.