Alfred Nobel Symposium
Energy in Cosmos, Molecules and Life
June 18-22, 2005

The chemistry of the universe

William Klemperer
Department of Chemistry and Chemical Biology
Harvard University, Cambridge MA 02138 USA

The discovery of the sharp line microwave emission from rotational transitions of polar polyatomic molecules in the direction of the galactic center [http://ieee.org/organizations/history_center/oral_histories/transcripts/townes.html] has changed our perception of the interstellar medium of galaxies from a low density atomic to a rich highly heterogeneous molecular universe. [http://antwrp.gsfc.nasa.gov/apod/lib/aptree.html]. We focus upon the chemistry of molecular clouds, large cold optically opaque structures with masses up to 10^6 that of the sun, showing that equilibrium predictions for abundances fail badly but that gas phase kinetic models can account for the rich organic chemistry that is observed. [http://www.ph1.uni-koeln.de/vorhersagen/] We discuss cosmic ray induced ionization of the major constituents H_2 and He followed by secondary reactions of their ions H_2^+ and He^+ with the components of the molecular clouds. In this scheme the primary repository of carbon is carbon monoxide. The highly exothermic reaction between He^+ and H_2 is sharply inhibited kinetically leading to the quantitative transfer of ionization of He to production of C^+ from the reaction $He^+ + CO = He + O + C^+$. Since the abundance of He is 10^3 that of CO this enhances production of the reactive species C^+ a thousand fold over direct cosmic ray dissociative ionization of CO . The growth of larger carbon chains and hydrocarbons is achieved through the reaction of C^+ with smaller organic species addition to smaller hydrocarbons. An example are the species C_3H_2 and C_3H, cyclic and linear ,which have as common ancestor the first aromatic $C_3H_3^+$.

The hydrogen molecular ion, H_2^+ reacts rapidly with H_2 forming the reactive species H_3^+. This species leaves many traces such as HCO^+, the major ion in molecular clouds. It also produces polar, observable, HN_2^+ and HCO_2^+ from reaction with the nonpolar and difficult to observe molecules N_2 and CO_2 , allowing estimates of their abundance. The direct observation of H_3^+ [http://fermi.uchicago.edu/] in dense molecular clouds as well as diffuse clouds is in good accord with estimates of cosmic ray fluxes. The molecular species observed in the galaxy are those observed in other galaxies indicating the chemistry to be universal.

The problem of a rich organic chemistry in the presence of excess oxygen is discussed in terms of refractory oxides and hydrates sequestering oxygen from the gas phase. Surveys of likely dominant species in cold molecular clouds , H_2O, and O_2 [http://cfa-www.harvard.edu/swas/] and CO_2 by the radio spectrum of the protonated ion HCO_2^+ show their abundance to be extremely small, less than 0.1% of the CO. The observation of abundant water in the hot core of the Orion molecular cloud [http://isowww.estec.esa.nl/science/] is one illustration of the change in chemistry of strongly heated regions where molecular abundances differ dramatically from the cold molecular clouds.

The isotopic fractionation exhibited by molecular enrichment of deuterium, known for over 30 years, is recently the focus of attention in very cold cloud cores in which CO, the primary destroyer of H_3^+ has condensed from the gas phase onto grains. There the ratio $ND_3/NH_3 = 10^{-3}$, compared with the cosmic abundance $HD/H_2 = 10^{-5}$,showing an enrichment of 10^{12}. We discuss hydrogen "chemistry" in terms of the production and destruction of H^+, H, H_2 and H_3^+, contrasting the processes in different epochs to obtain a picture of the formation of the first molecules.