CHEMISTRY OF HIGH TEMPERATURE SPECIES AT LOW TEMPERATURE

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Part A Positive Ion Chemistry

Hydrocarbon positive ions in low temperature media, such as liquid argon and liquid xenon, are particularly fascinating species. We have found that in concentrations of a percent or less, methane readily polymerizes when a solution in liquid argon is irradiated with cobalt 60 gamma radiation. It forms a polymer with general formula of $C_{20}H_{40}$ which is very similar to that found earlier in solid methane at liquid nitrogen temperatures.(1)

It is our present suggestion(2) that the mechanism of polymerization may involve the Auger transition in the argon atom, i.e. the polymer is formed only when an inner electron in argon is ionized. The resulting explosion caused by successive Auger transitions would produce a congregation of positive argon ions in the immediate vicinity of the original point of internal level excitation and each of the ions would then be neutralized by electron transfer from methane solute since the argon ionization potential is higher. Thus about 20 methane ions would be produced within a radius of a few 10's of Angstroms of the original site. The subsequent neutralization of these ions by electrons being a fast or vertical process (in the sense of the Franck-Condon Principle) would cause dissociation of the methane to form radicals and fragments such as CH, CH_2 and CH_3. These then would subsequently recombine for there would be little else for them to do. This theory is still under experimental test. We are studying the effects on the isotopic composition of the polymer versus that or the other principal product ethane, and we are further studying the small effect od diluting the methane on the molecular weight of the polymer.

The ability of hydrocarbon ions to react at low temperatures in the presence of ionizing gamma radiation has been well known for a long time in that the hardening of the plastic polymer polyethelene by gamma rays has been well studied. It is our present belief that this too is an ionic process in most part.[3] Though once again, to say that the proof is complete would be an exaggeration. It would seem on balance that at low temperatures ionic processes may be dominant and that at ordinary temperatures they are very, very important in radiation chemistry in general.

Part B Carbon Vapor at Low Temperature

Our studies of the chemical reactions of carbon vapor with cold benzene and with diamond surfaces will be discussed. It is clear that carbon atoms are able to react with benzene even at 77°K. It is not certain that trace amounts of oxygen may not be involved in a critical way also.

Our attempts to prepare to grow diamonds by evaporating carbon vapor on to seed diamonds under high vacuum conditions will be described and any progress towards this goal discussed. It seems clear that the quality of the vacuum may be all important in this process. We indeed are using this as an example of the possible chemical value of the extremely high vacua that are attainable in the space chambers in the aerospace industry and in the laboratories such as Jet Propulsion Laboratory and, of course, in orbiting satellites. It seems to us that we should be able to develop a chemistry of surfaces, which has been highly inhibited because of air, if we take the pains to eliminate air and this may be a chemical benefit of the space environment.

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(1) Chemistry of Positive Ions. VI. Positive-Ion Chemistry in Solid Methane. Donald R. Davis, W. F. Libby and W. G. Meinschein. J. Chem. Phys. 45, 4481-(1966).

(2) Polymer Production in the Gamma Radiolysis of Methane in Liquid Argon. W. F. Libby, Peter Hamlet, Jai Mittal and Jeffrey Moss. To be published in The Journal of The American Chemical Society.

(3) The Chemistry of Ionic States in Solid Saturated Hydrocarbons. Larry Kevan and W. F. Libby. Advances in Photochemistry, Vol. 2, Interscience Publishers, New York, 183-(1964).