EXPERIMENTAL STUDIES CONCERNING

EQUILIBRIUM AND NON-EQUILIBRIUM SYSTEMS

IN PRE-BIOLOGICAL ATMOSPHERES

PROGRESS REPORT COVERING THE PERIOD

MARCH 1, 1966 TO AUGUST 31, 1966.

FOR GRANT NO. 21-002-050

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

from

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

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The following progress has been made on Grant No. 21-002-059, covering the period March 1, 1966 to August 31, 1966.

Gas mixtures representing a wide range of C:H ratios have been subjected to the plasma discharge and the product mixtures are being examined. It has been found by gas chromatography that they contain a large number of polynuclear aromatic hydrocarbons in small quantities. To aid in the identification of these compounds, most of the commerically available unsubstituted polynuclear aromatic hydrocarbons have been run in the gas chromatograph under the conditions best suited for separation of the product mixtures. It was found that the log of the relative retention times gives a straight line when plotted against the boiling points, and a smooth curve when plotted against the number of carbon atoms. These plots, together with chromatograms of the product mixtures, afford some information on reaction products for which no standards are available for direct comparison. A number of specific compounds have been identified.

A number of theoretical calculations have been carried out to serve as an aid in evaluating the experimental results.

The following table gives computed Equilibrium Concentrations of Selected Compounds which, under certain conditions, should be present in greater than 1% mole fractions.

Temperature	Pressure	Aromatics Excluded	Aromatics Included
300°K	10^{-6} Atm.	Methane H_2 1,3-Butadiene Cyclohexane	Asphalt Methane H_2
	1 Atm.	Methane H_2 Acetylene Cyclohexane 1,3-Butadiene Cyclohexene Methylcyclohexane	Asphalt Methane H_2

Temperature	Pressure	Aromatics Excluded	Aromatics Included
300°K	100 Atm.	Methane H_2 Acetylene Cyclohexane 1,3-Butadiene Cyclohexene Methylcyclohexane	Asphalt Methane H_2
500°K	10^{-6} Atm.	Methane H_2 Acetylene Ethylene Propyne 1,3-Butadiene Isoprene Cis-piperylene Trans-piperylene Cyclohexene	Asphalt Methane H_2
	1 Atm.	Methane H_2 Acetylene Ethane Cyclopentane Cyclohexane Propyne 1,3-Butadiene Isoprene Cis-piperylene Trans-piperylene Cyclohexene Methylcyclohexene	Asphalt Methane H_2
	100 Atm.	Methane H_2 Acetylene Cyclopentane Cyclohexane Propyne 1,3-Butadiene Isoprene Cis-piperylene Trans-piperylene Cyclohexene Methylcyclohexane	Asphalt Methane H_2
700°K	10^{-6} Atm.	Methane H_2 Acetylene Ethylene Propyne	Asphalt Methane H_2

Temperature	Pressure	Aromatics Excluded	Aromatics Included
	1 Atm.	Methane H_2 Acetylene Ethylene Ethane Propene Propyne Allene 1,3-Butadiene Isoprene Cis-piperylene Trans-piperylene Cyclohexene	Asphalt Methane H_2
	100 Atm.	Methane H_2 Acetylene Ethane Propane Cyclopentane Propene Propyne Allene 1,3-Butadiene Isoprene Cis-piperylene Trans-piperylene Cyclohexene Methylcyclohexane	Naphthalene Asphalt Methane
$1000^{\circ}K$	10^{-6} Atm.	H_2 Acetylene	Asphalt H_2 Acetylene
	1 Atm.	Methane H_2 Acetylene Ethylene Propene Propyne Allene 1,3-Butadiene Isoprene Cis-piperylene Trans-piperylene	Benzene Naphthalene Asphalt Methane H_2
	100 Atm.	Methane H_2 Acetylene Ethylene Ethane Propene Butane	Benzene Naphthalene Asphalt Methane H_2

Temperature	Pressure	Aromatics Excluded	Aromatics Included
		Propyne Allene 1,3-Butadiene 1,4-Pentadiene Isoprene Cis-piperylene Trans-piperylene Cyclohexene	

The preparation of a book entitled "Thermodynamic Equilibria in Pre-biological Atmospheres" is in its final stages and should be finished sometime during the Fall of 1966.

The following represents completed work, reported in part previously but now completed and published:

"Thermodynamic Equilibrium and the Inorganic Origin of Organic Compounds", R.V. Eck, E.R. Lippincott, M.O. Dayhoff, Y.T. Pratt, Science, 153, 3736, 628 (1966).

Theoretical and experimental support is presented for the hypothesis that many organic compounds may form under conditions of thermodynamic equilibrium. This possibility must be considered along with special effects of selective catalysts, radiation, and degradation from biological matter, in explaining the origin of organic compounds in carbonaceous chondrites. Similar considerations may apply to solar nebulas and planetary atmospheres. The equilibrium distribution of organic compounds at temperatures between 300°K and 1000°K and pressures of 10^{-6} to 50 atm for the C—H—O system have been computed. At moderate temperatures and low pressures, conditions where graphite production is inhibited, aromatic compounds may form even in the presence of large excesses of hydrogen. Such conditions exist in the solar nebula and in the atmospheres of some of the major planets. Equilibrium concentrations of a large number of compounds at 1000°K with nitrogen, sulfur, and chlorine added to the system have also been determined.

In some cases, a limited equilibrium method is employed in which these few compounds which form with the most difficulty are excluded from the computations, while representatives of all other families of compounds are included. This approach is shown to the useful in the interpretation of certain experimental data in which complete equilibrium has not been attained. We have also found that gases, activated to the plasma state by a high-energy radio frequency field, recombine on cooling to yield product mixtures which are in qualitative agreement with those predicted by the equilibrium computations. We believe that such products can be profitably studied as if at a metastable limited equilibrium.