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CHEMISTRY OF THE OUTER PLANETS

Investigations of the Chemical Nature of the Atmosphere of Titan

NASA Ames Research Center - SUNY at Stony Brook
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Thomas W. Scattergood
Department of Earth and Space Sciences
SUNY at Stony Brook
Stony Brook, New York 11794

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CHEMISTRY OF THE OUTER PLANETS

INTRODUCTION:

This cooperative agreement is part of a continuing collaboration between the Planetary Biology Branch of NASA Ames Research Center and S.U.N.Y. at Stony Brook on the chemistry of the outer planets, in particular that which is occuring or may have occured in the past in the atmospheres of Jupiter, Saturn, and Saturn's satellite Titan. Past work has included study of hot-atom chemistry in the Jovian atmosphere, production of laboratory synthesized materials as candidates for Titan aerosols, and comparison of infrared spectra of natural and commercially prepared compounds with observations of the outer planets and their satellites. Under this cooperative agreement, these studies have been continued, but with the planning now underway for sending a probe to Titan to analyze its atmosphere, the emphasis of the past (and future) research has been on the chemistry of Titan's atmosphere. This mission, now referred to as the Cassini mission, is planned to be launched in 1994 for arrival at Titan by 2002, and will carry instruments that will, among other things, analyze the chemical composition of the gaseous and aerosol components of the atmosphere. In order to prepare for this mission, as much information as possible about the nature of Titan's atmosphere must be obtained in order to intelligently design the instruments to be carried on the probe.

Most of what is known about the composition and structure of Titan's atmosphere was obtained by the two Voyager spacecraft, along with observations from ground-based telescopes. The vertical structure of the atmosphere, as currently envisioned, is shown in Figure 1. In the upper atmosphere, above about 200 km, an ultraviolet absorbing haze layer has been observed. The composition of this haze is not known, but the gas phase is dominated by nitrogen (~97%,) with small amounts of methane (~3%) and hydrogen (~0.2%.) Other species that have been detected (in trace amounts) include the hydrocarbons ethane, propane, acetylene, diacetylene, and methylacetylene, the nitriles hydrogen cyanide, cyanoacetylene, and cyanogen, and two oxygen containing compounds, carbon dioxide and carbon monoxide (Hunten, etal., 1984.) All of these species exist above Titan'svisible red-orange cloud deck, located about 160 km above the surface. Below this cloud layer little is known about the atmosphere, except that the surface pressure and temperature are 1.6 bar and 94 °K, respectively (Hunten, et al., 1984.) Because the temperature of the atmosphere drops below the liquification point of methane at about 45 km (see Figure 1,) a methane cloud layer is believed to exist there, but this has not yet been observed. From simple rainout of species produced in the upper atmosphere, the region below the visible clouds should contain at least all of the compounds listed above, and, if other types of chemistry are occuring there (Borucki, McKay and Whitten, 1984,) many other organic compounds may also be formed, perhaps to form aerosols chemically more complex than liquid methane droplets.

The present plans for the Cassini mission call for the Titan probe to become subsonic and its instruments to be deployed at about 200 km above the surface. Consequently, all measurements of the chemical composition of the atmosphere will be confined to the region below the visible clouds. In order to learn about what compounds might be found in this region, experiments have been carried out to determine the nature of the gaseous (and aerosol) species that are formed when a model Titan atmosphere is subjected to electrical discharges, a process proposed to occur in the lower atmosphere (Borucki, McKay and Whitten, 1984.)

PRODUCTION OF GAS PHASE SPECIES:

Using a spark facility, consisting of two aluminum electrodes enclosed in a rectangular chamber of 13 liter volume, a set of preliminary experiments has been carried out on a mixture (96.8% N_2, 3.0% CH_4, 0.2% H_2) modeling the atmosphere of Titan. This mixture was subjected, in five separate experiments, to various numbers of sparks. These five centimeter long sparks averaged 362 joules each, resulting in energy densities of about 10^4 joules/meter, appoximating that of terrestrial lightning. Samples of the mixtures before and after each set of sparks were taken and analysed for hydrocarbons and hydrogen cyanide. The yields of the various products were determined and compared to yields predicted by a simple high-temperature equilibrium shock model, in order to eventually refine the model as a predictor for lightning produced species in planetary atmospheres.

The yields of C_2H_6, C_2H_4, C_2H_2, C_3H_8 and HCN that were determined from the experiments are shown in Figure 2. The dominant products, regardless of the number of sparks, were acetylene and hydrogen cyanide. The yield of C_2H_2 (in molecules/joule) was found to be the same (to within experimental error) for all numbers of sparks, indicating that this species is a primary product of the lightning generated shock. Similar behavior with spark number, but with lower yields, was observed for C_2H_6, C_2H_4 and C_3H_8. HCN, however, was found to increase markedly with the number of sparks. This suggests that in addition to direct formation of HCN, an intermediate species is formed that leads to the formation of HCN. Further work needs to be done in order to further understand this process.

Comparison of the experimental yields with those predicted by the model are shown in Figure 3. The theoretical calculations were done by C.P. McKay of the Solar System Exploration Branch at Ames. The rather good agreement between model and experiment for HCN and C_2H_2 is readily apparent, but the agreement for C_2H_4 and C_2H_6 is poor, at best, and becomes increasingly worse with greater complexity of the product (no calculations have yet been done for C_3H_8.) These results suggest, for ethane and propane, that their formation may be due to secondary processes, such as photolysis. Work will continue to study this hypothesis.

THE NATURE OF THE AEROSOL MATERIAL:

Using the same mixture that was used in the spark experiments discussed above, solid/liquid materials were produced from laser detonated shocks. Shocks produced from nanosecond pulses of a very high energy 1.04 μm laser are being investigated at Ames as electrodeless models for lightning (Borucki and McKay, 1985.) This method was chosen here due to the greater ease in producing the amounts of material required for analysis. The analysis of the waxy reddish-brown material was done by pyrolytic gas chromatography. The system used in this study is schematically shown in Figure 4. Small amounts of the material were introduced into an evacuated furnace at room temperature. The material was then stepwise heated under vacuum, allowed to equilibrate for three minutes at each temperature, and samples of the headspace gases were taken. The temperatures chosen for this study were 20°C, 250°C, 450°C and 700°C. Analyses of the gases were carried out by injecting known amounts of the gas, using a Valco loop sampling valve, onto a custom prepared Porapak-like column at 105°C and detecting the components with a meta-stable ionization detector.

Few products were observed until the temperature of the sample was raised to 450°C. At this temperature, over 20 species were found, as shown in Figure 5. Of these 20 compounds, eleven have been identified by comparison of their retention times to those of known compounds. These species are listed in the Figure, and include hydrocarbons up to butane and several nitriles, at least HCN and CH_3CN. The slight hump near the end of the chromatogram has the same retention time as benzene, which could be an important finding in light of the detection of the molecule in the Jovian atmosphere. Further work to determine the identities of the remaining peaks and if more complex products are formed will be done.

CONCLUSIONS:

It is clear from the experiments that a variety of complex organic molecules can be produced by lightning in a Titan-like gas mixture. The dominant products were found to be acetylene and hydrogen cyanide, with smaller amounts of many other species. Any aerosol produced by lightning initiated processes will consist of a complex mixture of organic compounds, many of which should be easily identified by pyrolytic GC. Work will continue to expand the data base of molecules produced by lightning and other processes in order to assist in the design of appropriate analytical instruments for the upcoming Saturn/Titan mission and any other planetary probes.

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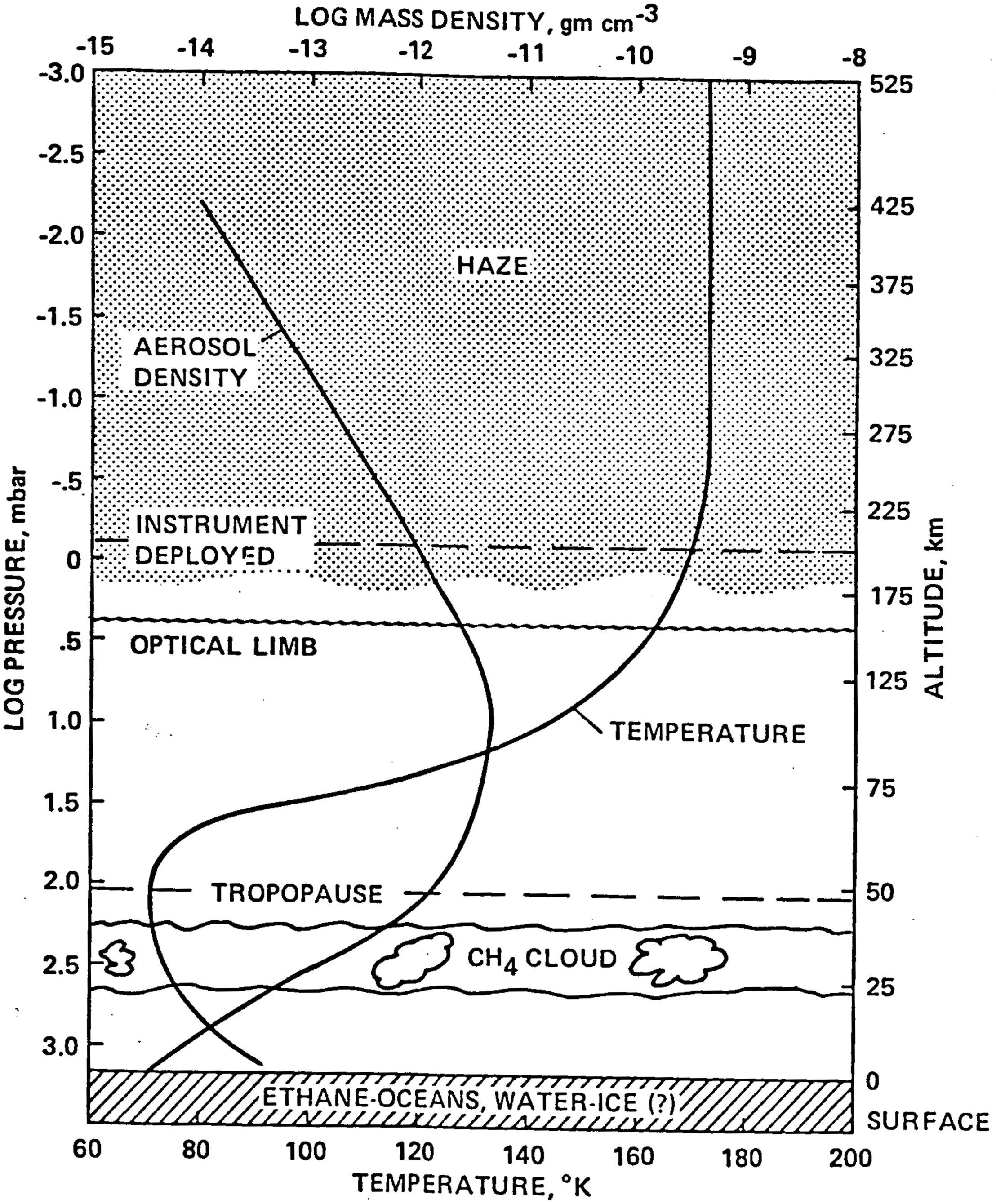
Figure 1

THE ATMOSPHERE OF TITAN



PRESSURE-TEMPERATURE PROFILE FROM LINDAL et al., 1983
DENSITY PROFILE FOR AEROSOLS, FROM TOON, et al., 1985

Figure 2

EXPERIMENTAL YIELDS FROM ELECTRICAL DISCHARGES IN A MODEL TITAN ATMOSPHERE

MIXTURE: 96.8% N_2, 3.0% CH_4, 0.2% H_2

$\bar{E}$ = 362 J/SPARK, P = 1 atm

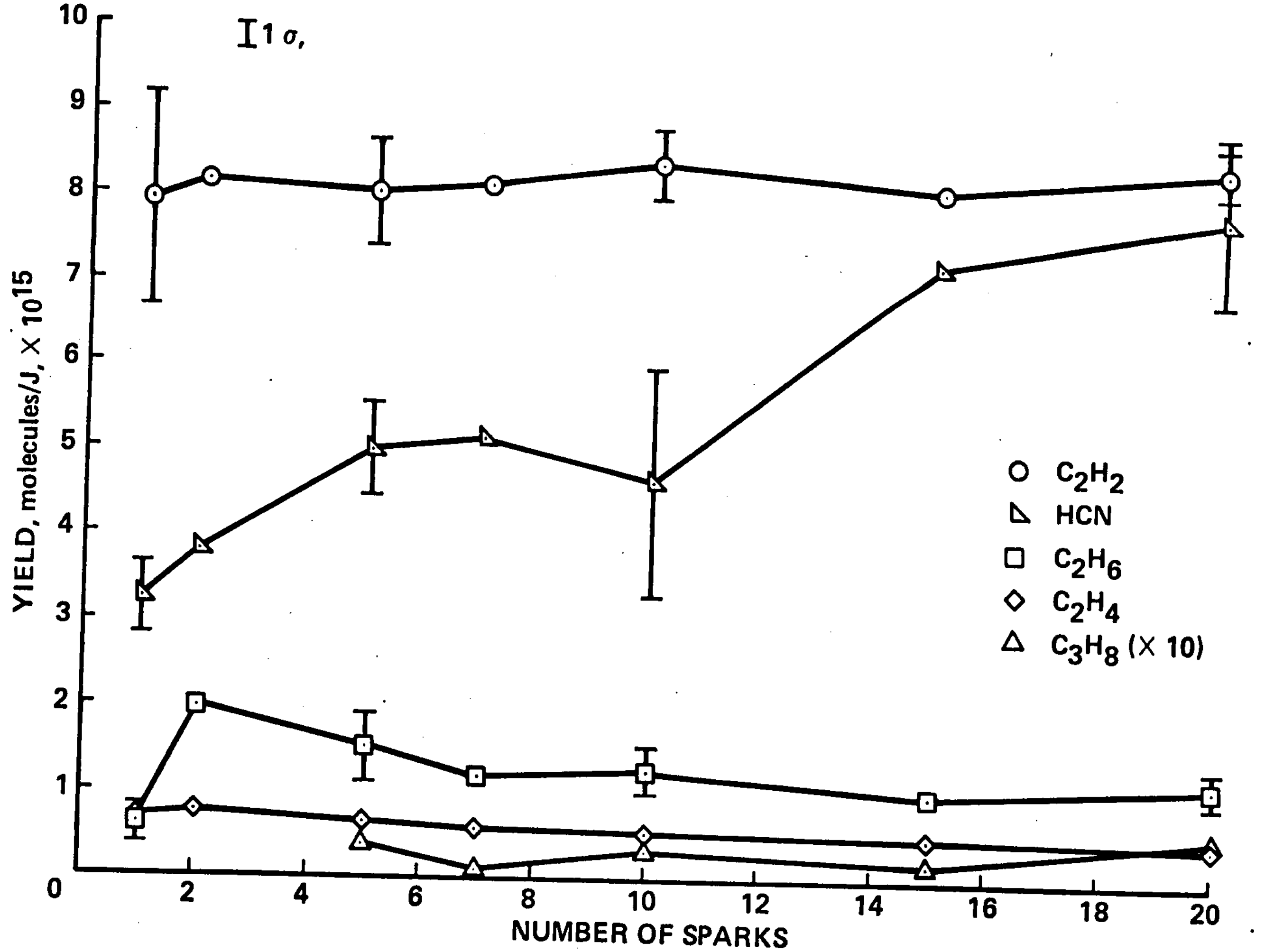
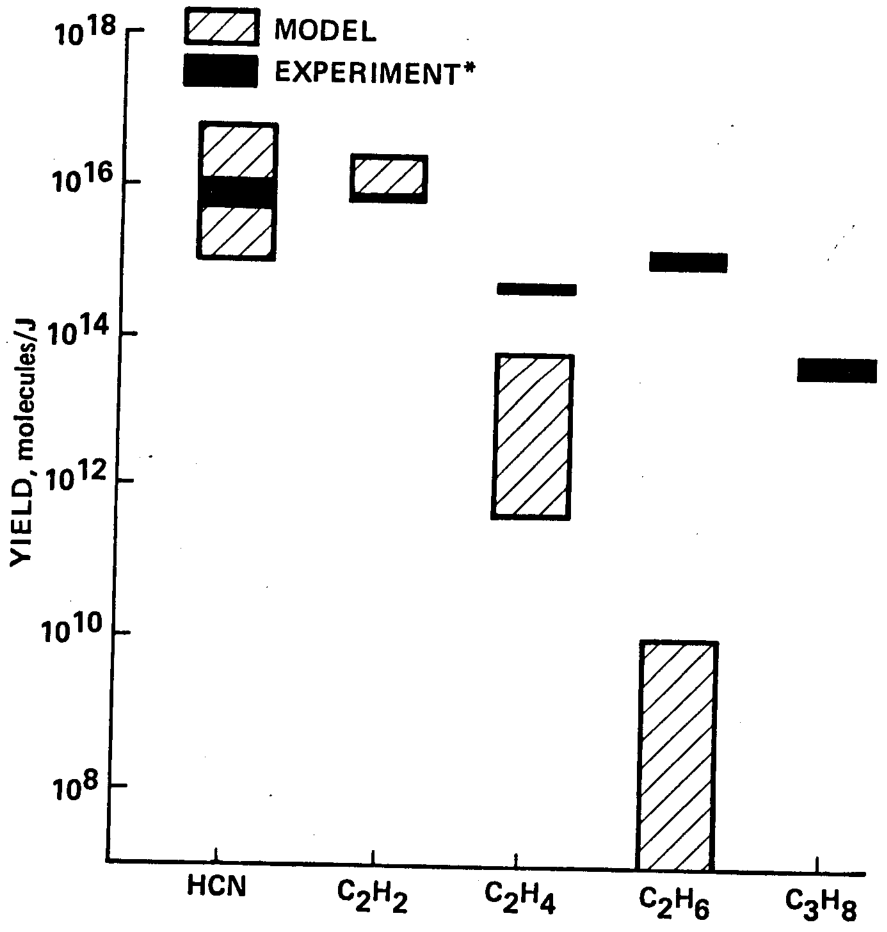


Figure 3

EXPERIMENTAL vs. THEORETICAL YIELDS PREDICTED FROM LIGHTNING IN A MODEL TITAN ATMOSPHERE

MIXTURE: 96.8% N_2, 3.0% CH_4, 0.2% H_2

MODEL: HIGH TEMPERATURE SHOCK (2000-3000 K)



*: DATA ARE FROM 20 SPARK EXPERIMENT.

Figure 4

SCHEMATIC OF SYSTEM USED FOR PYROLYSIS AND ANALYSIS OF MODEL TITAN AEROSOLS

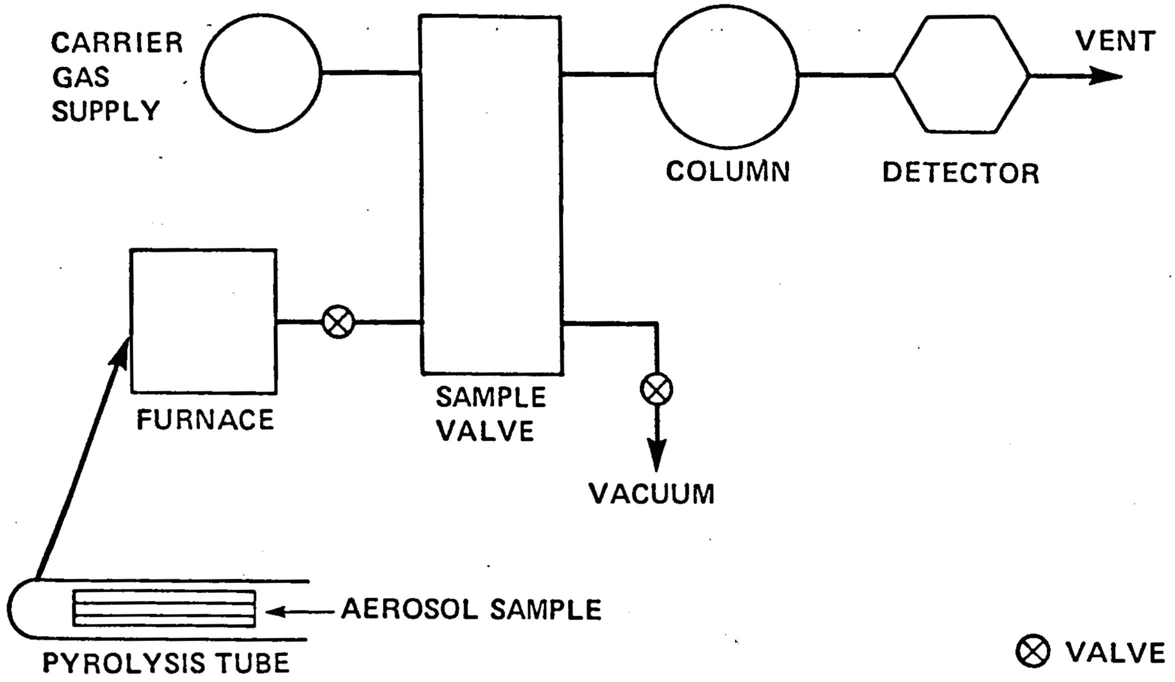


Figure 5

PYROLYSIS OF MODEL TITAN AEROSOL AT 450°C

Initial mixture:

96.8% N_2
3.0% CH_4

0.2% H_2

Peaks identified:

1. Methane
2. Ethylene
3. Ethane
4. Acetylene
5. Propane, propylene
6. Cyanogen, allene
7. Methylacetylene
8. Isobutane
9. Butane
12. Hydrogen cyanide
17. Acetonitrile