

ANALYTICAL PYROLYSIS EXPERIMENTS OF TITAN AEROSOL ANALOGUES IN PREPARATION FOR THE CASSINI HUYGENS MISSION

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ABSTRACT

Comparative pyrolysis mass spectrometric data of Titan aerosol analogues, called "tholins", are presented. The Titan tholins were produced in the laboratory at Cornell by irradiation of simulated Titan atmospheres with high energy electrons in plasma discharge. Mass-spectrometry measurements were performed at FOM of the solid phase of various tholins by Curie-point pyrolysis Gas-Chromatography/Mass-Spectrometry (GCMS) and by temperature resolved in-source Pyrolysis Mass-Spectrometry to reveal the composition and evolution temperature of the dissociation products. The results presented here are used to further define the ACP (Aerosol Collector Pyrolyser)-GCMS experiment and provide a basis for modelling of aerosol composition on Titan and for the interpretation of Titan atmosphere data from the Huygens probe in the future.

INTRODUCTION

The presence of organics in Titan's atmosphere /1/ is confirmed by astronomical observations (Voyager), and has further been studied by laboratory simulations and theoretical models /2,3,4,5/. It is assumed that aerosols, mostly made of hydrocarbons and nitriles, are formed by UV photolysis and charged particles at high altitudes. Eddy diffusion, sedimentation and general circulation distribute these aerosols throughout the atmosphere of Titan. Whereas submicron particles dominate the upper atmosphere, larger molecules, absorbing in the visible, are expected in the lower regions.

The study of the constituents of these aerosols by Py-GC/MS (Pyrolysis Gas Chromatography/Mass Spectrometry) is part of the Cassini Huygens mission /6/. In order to understand the relationship between gas phase molecules and the heteropolymers which form the aerosols in Titan's atmosphere, Titan aerosol analogues, called "tholins", are created in the laboratory. The production of these tholins is performed in the laboratory by irradiation of simulated Titanian atmospheres with high energy electrons in plasma discharge /7/, spark discharge /8,9/ or by UV irradiation /10,11/. Compounds which have been previously detected by analysing various tholins with closed system pyrolysis techniques /12/ include: saturated and unsaturated aliphatic hydrocarbons, substituted polycyclic aromatic hydrocarbons, nitriles, amines, pyrroles, pyrazines and pyrimidines. The optical constants of these tholins /12/ are in good agreement with those for the Titan haze /5/. Every gas phase organic detected by Voyager (IRIS) could be reproduced with the above described technique in the laboratory /3,5,13/.

Assuming that the molecules created in the laboratory are similar to those found in Titan's atmosphere, our aim is to characterize the constituents of these polymers and to understand the relationship between gas phase atmospheric composition and condensed phases products like tholins. The atmospheric solids studies were undertaken by Temperature resolved in-source Pyrolysis Mass Spectrometry (TrisPyMS) and by analytical Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GCMS), both powerful techniques for the study of complex organic molecules on a microscale. Recent advances in the technique and the progress in understanding the relationship between chemical structure and flash pyrolysis products of polymers have been reviewed /14,15/. With these microscale analytical techniques we hope to find repeating substructures in the tholins and give an inventory of structural units.

Our analytical pyrolysis data can also further define the analytical specifications for the ACP/GCMS (Aerosol Collector Pyrolyser coupled to a Gas Chromatograph-Mass Spectrometer) on board the Huygens sonde, which is part of the forthcoming Cassini Huygens space mission /6/. This instrument will collect aerosol samples in 2 regions, respectively at 160 - 40 and 30 - 20 km altitude, which will be analyzed in situ by PyMS and PyGC/MS. The primary objectives of the ACP instrument are to determine the chemical composition, to derive relative abundances of condensed organics and to study the prebiotic environment in the atmosphere of Titan /6/.

TECHNIQUES

Tris PyMS: Time resolved in source Pyrolysis Mass Spectrometry

An aliquot of a tholin sample suspension in H₂O is applied to a Pt/Rh wire (0.1 mm diameter, 10 % Rh), dried in vacuo, giving about 5 µg on the filament. After insertion of the probe into the ion source (10⁻⁴ Pa, 180° C) of a Jeol DX 303 double focussing mass spectrometer, the wire was heated resistively at a rate of 16°C/s to a final temperature of 800 °C. Pyrolysis products are ionized at 16 eV EI, accelerated to 3 kV, separated through an E/B setup and post accelerated to 5 keV for mass analysis over a range of 20 - 1000 Da with a scan cycle time of 1 sec. Data are processed with a JMA DA 5000 data system and transferred to a SUN Sparc station for further analysis with the Kratos MACH3 software.

CuPy GCMS: Curie Point Pyrolysis Gas Chromatography Mass Spectrometry

PyGCMS was conducted with a FOM4-LX Curie point pyrolysis unit built into a HP 5890 Series II gas chromatograph connected to a Finnigan INCOS 50 quadrupole mass spectrometer. About 10 µg of sample (suspended in di-chloromethane) was applied to a ferromagnetic wire with a Curie point temperature of 770 °C (Fe). The ferromagnetic wire was inserted into a glass liner, flushed with argon gas to remove air and subsequently introduced into the pyrolysis unit where it is placed directly on a Kalrez ferrule with entrance to the gas chromatographic column. A high frequency coil around the glass liner was used to heat the ferromagnetic wire for 10 sec by induction through a 1 MHz frequency field. The wire is inductively heated to its Curie point temperature within 1 s. Desorbed pyrolytic fragments were flushed by the helium carrier gas into a 30 m lengths J & W DB 5 fused silica capillary column (film thickness 0.4 µm, ID 0.25 mm, 120000 theoretical plates for tetradecane). The GC oven was kept at - 10° C during pyrolysis and subsequently programmed to 300° C at a rate of 4° C/min. Compounds were ionized at 70 eV EI conditions and mass analyzed over a range of 35-500 Da. Data were transferred to a SUN Sparc station for processing on the Kratos MACH3 software.

Curie point pyrolysis online in the carrier gas guarantees a well defined temperature time history, a fast and reproducible heating of a small amount of sample and an immediate transport of volatiles away from the pyrolysis zone. Its advantage is that secondary condensation reactions are minimized and therefore a product distribution is obtained which better reflects the chemical structure of the original sample.

RESULTS AND DISCUSSION

So far PyGCMS data on tholins have been reported only with analytical pyrolysis in an closed system on a milligram scale /8/. We focus here on the analysis of these compounds with flash pyrolysis which represents an open pyrolysis system and an immediate outflow of volatiles.

We report here on two tholins produced in the laboratory at Cornell. One tholin (coded N₂/CH₄) is a sample of a film produced by a DC coronal discharge through a continuously flowing 90 % N₂/ 10% CH₄ atmosphere, at p = 0.2 mb /7/. The other tholin was produced in a 100 % methane atmosphere (coded CH₄) /16/. The samples have been kept in glass vials without further precautions against oxidation. Their exposure to the atmosphere may have introduced oxygen containing functional groups as seems to be evident from elemental analysis /13/.

Fig. 1 shows the summarized low voltage EI PyMS spectra of both Titan tholin produced from 90 % N₂ / 10% CH₄, and a 100% CH₄ tholin. The spectra are confined to the Huygens ACP/GCMS relevant m/z range from 10-200 with the full range of relevant peaks presented as an insert. The evolution of the compounds with temperature is compared in Fig. 2.

Summarized pyrolysis mass spectra (16eV)

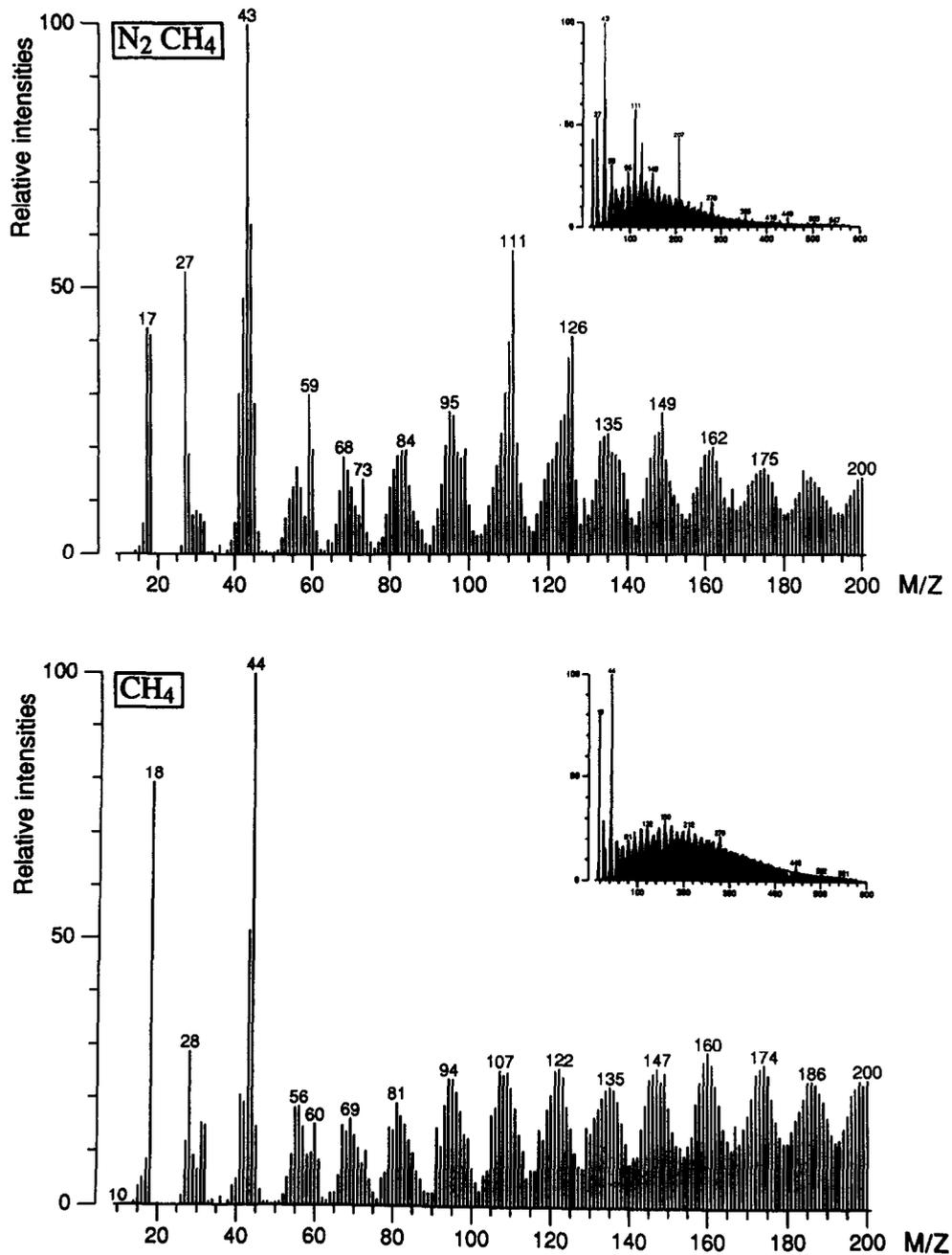


Fig. 1. Summarized pyrolysis mass spectra from N_2/CH_4 and CH_4 tholins. The high molecular weight region is shown as an insert.

The mass peak profile of compounds of the two tholins as a function of m/z is different and the CH_4 tholin shows higher relative intensities for compounds in the molecular weight region between 200 and 400 (see insert). The N_2/CH_4 tholin shows some peaks indicative of silicone grease contamination (m/z 207, 281, 355, 429) which was confirmed by the PyGCMS data. High peaks in both spectra are m/z 18 and 44 from CO_2 and H_2O (as shown by PyGCMS), which are clearly released at higher temperature, pointing to elimination from the tholin structure. Oxygen is an unintended building block of the molecules in the tholins investigated. Some oxygen-containing functional groups probably result from air exposure after the tholins were prepared but diffusion into the tholin preparation system during the long period of experiments can not be excluded. Both profiles show a high complexity of the spectra with a mass increment of 14 amu between peak maxima, pointing to structural units with a CH_2 chemical structure increment. There are no peaks in the spectrum corresponding to simple monomeric repeating units (as for example in the polystyrene polymer).

The difference between the TIC profiles of the tholins shows that the addition of N_2 in the reactive gas phase leads to a higher complexity in the tholin and the formation of many more constituents at different temperatures. The relatively narrow thermal dissociation peak in the CH_4 tholin points to a relative uniformity in the chemical bond strength. The N_2/CH_4 sample shows a larger fraction of compounds which evaporate from the filament.

The main dissociation event peaks at the same T_{max} as the CH_4 tholin, but the high temperature pyrolysis tail for the N_2/CH_4 sample indicates the presence of a significant amount of refractory matter.

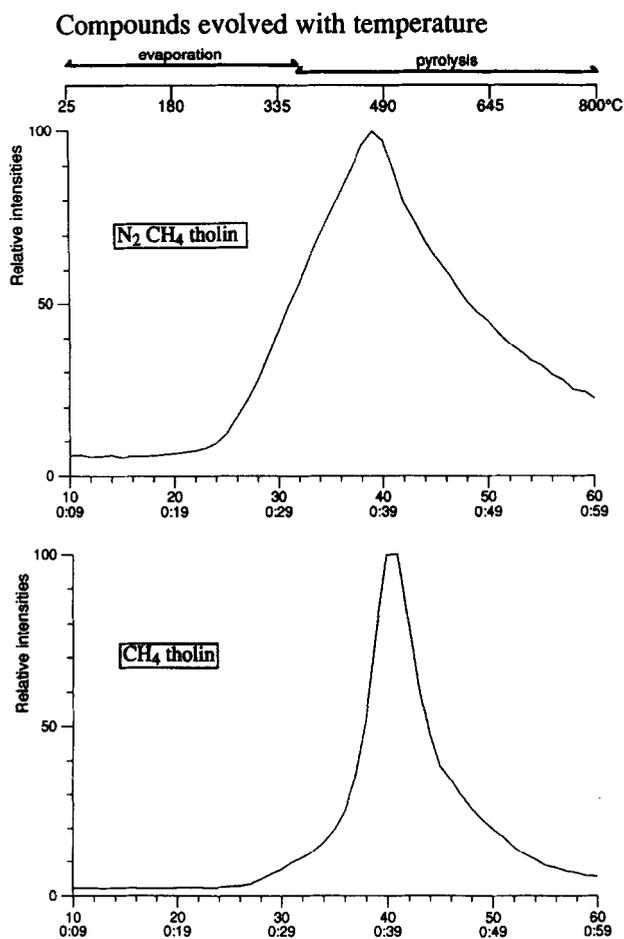


Fig. 2. Mass peak profile as a function of m/z of N_2/CH_4 and CH_4 tholins.

A detailed analysis of some of the peaks of the main compounds evolved with temperature (Fig. 3) of the N_2/CH_4 tholin shows that NH_3 and CO_2 and acetamide (CH_3CONH_2) are released at lower temperature, whereas acetonitrile (CH_3CN) is released at higher temperature and HCN is a dissociation product during the whole pyrolysis process. This seems to imply that the nitriles can form from rather thermostable substructures in the tholins.

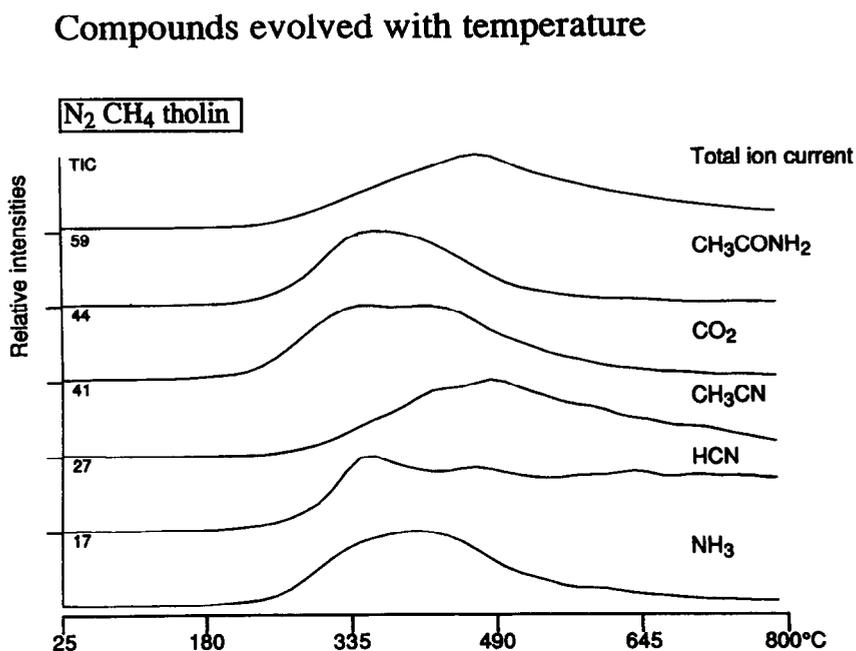


Fig. 3. Evolution with temperature of main peaks of a N_2/CH_4 tholin.

The complexity of these nominal PyMS spectra is such that without high resolution, providing the elemental composition of the mass peaks, only limited information can be extracted. We therefore relied on PyGCMS for the actual identification of individual compounds assuming that the GC chromatographic filtering of polar compounds would be limited. Initial experiments with Curie point filaments of $510^\circ C$ and $610^\circ C$ were found to give very limited thermal dissociation, but a Curie point filament of $770^\circ C$ did efficiently pyrolyse the samples. A cryofocussing of the pyrolysate at $-10^\circ C$ was found to be essential to obtain good resolution of the more volatile species. Polar compounds however were easily overloaded on this apolar column giving fronting peaks. The PyGCMS spectrum of the Titan tholin N_2/CH_4 is shown in Fig. 4, as an enlargement of the first 1500 scans with peak identifications. Though cryofocussing of the compounds could improve the resolution of the compounds at higher elution temperature, the resolution is still insufficient above scan 2000 (data not shown). This is due to the fact that many dissociation products are mostly polar and present with many isomers in small quantities. H_2O , acetic acid and HNCO form strongly fronting peaks with a width larger than 5 minutes. The main peaks in the GC are HCN, CH_3CN , acrylonitrile, propionitrile and longer chain branched and unsaturated nitriles. Many hydrocarbons were observed as methyl branched and monosaturated isomers with a low relative intensity. No saturated hydrocarbons were present in contrast to previously published closed system pyrolysis studies. Benzene, pyrrole, pyridine, pyrazine, pyrimidine and alkylated homologues were observed as small components of the pyrolysate mixture. A full account of all the data will be published elsewhere.

Surprisingly, a number of nitriles and aromatic nitrogen compounds were also found in the 100 % CH₄ tholin, probably due to air contamination during the preparation phase of the tholins. Methyl-branched and monosaturated hydrocarbons and aromatic hydrocarbons were the main dissociation products. The CH₄ tholin PyGCMS data also confirmed water and CO₂ as pyrolysis products. It must be pointed out that the Py MS and GCMS data do not correspond completely and it is evident that the GC column filtered out polar compounds in the higher MW range.

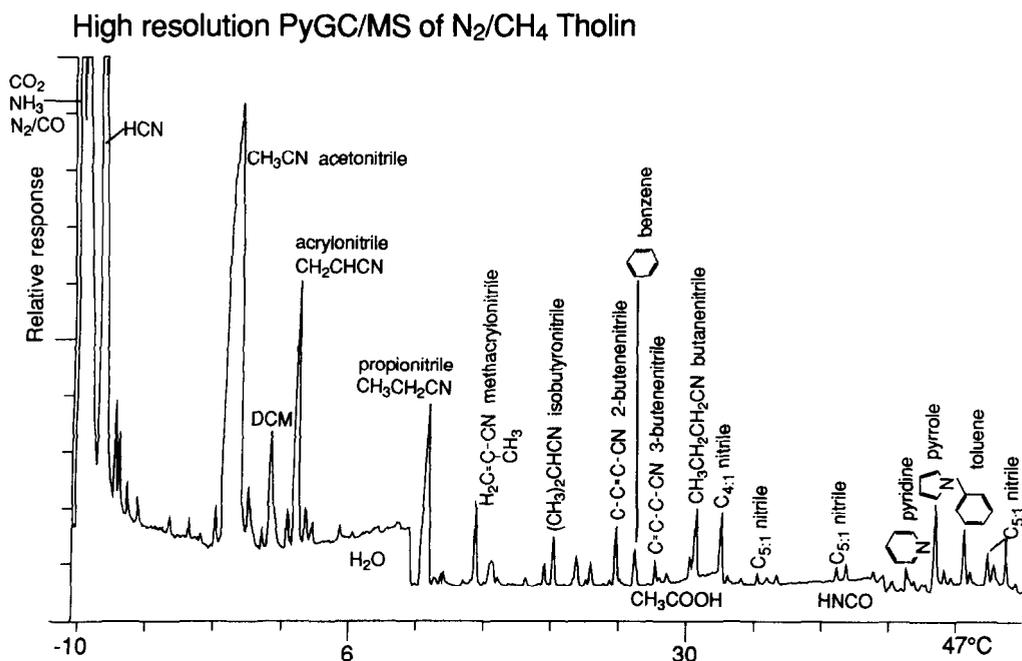


Fig. 4. PyGCMS chromatographic profile of a N₂/CH₄ tholin as an enlargement of the first 1500 scans with peak identification.

Thompson & Sagan /17/ have argued that tholins can be formed by the polymerization reaction of nitriles with unsaturated and radical species. The condensation reaction is based on the CN and hydrocarbon radical studies of Lichtin and Lin /18/. In case of a N₂/CH₄ mixture this can lead to a proposed substructure shown in Fig. 5.

Hydrolysis of such a substructure may be the source of amino acids, as shown for a Titan tholin /19/, and suggested by Thompson & Sagan /17/. Since anhydrous pyrolytic dissociation of N₂/CH₄ tholin leads to HCN and alkylnitriles as major dissociation products, we propose an unzipping reaction of this assumed N₂/CH₄ tholin substructure to explain the results. The suggested polymer is fragmented during the analytical pyrolysis process into the original gas phase constituents, HCN and RCN, which were formed in the plasma discharge experiments. This proposal implies that the experimental Titan gas phase composition is reflected in the constituents of the solids in such a way that the synthetic reaction can be reversed.

Other substructures generate unsaturated hydrocarbons under pyrolysis conditions, which show striking agreement with what is observed in the gas phase analysis of discharge experiments. The more aromatic hydrocarbons in the pyrolysate may result from the condensation of acetylenic hydrocarbons leading to dehydrogenated structural elements in the tholins. These ideas must be tested with less complicated synthetic conditions than those present in the Titan atmosphere simulation so far. The use of isotopically labelled primary gases may rule out some of the biases introduced by Earth atmospheric species diffusing into the tholins.

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