CHEMISTRY OF THE OUTER PLANETS

S.U.N.Y. Stony Brook - NASA Ames Research Center
Co-operative Agreement NCC 2-311

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ABSTRACT

The general purpose of the work performed under this project was to investigate various aspects of past or present chemistry in the atmospheres of the outer planets and their satellites using laboratory simulations. Three areas of study were investigated during the period of this co-operative agreement: 1) Organic chemistry induced by kinetically 'hot' hydrogen atoms in the region of Jupiter's atmosphere containing the ammonia cirrus clouds; 2) The conversion of NH$_3$ into N$_2$ by plasmas associated with entry of meteors and other objects into the atmosphere of early Titan; and 3) The synthesis of simple hydrocarbons and HCN by lightning in mixtures containing N$_2$, CH$_4$ and NH$_3$ representing the atmospheres of Titan and the outer planets. The results of the studies showed that: 1) Hot hydrogen atoms formed from the photodissociation of NH$_3$ in the atmosphere of Jupiter could account for some, but not most, of the chemistry that takes place in and just below the ammonia cirrus cloud region; 2) The thermalization of hot (=3 eV) hydrogen atoms in atmospheres predominated by molecular hydrogen is not as rapid as predicted by classical elastic collision theory; 3) The net quantum loss of NH$_3$ in the presence of a 200 fold excess of H$_2$ is 0.02, much higher than was expected from the amount of H$_2$ present, 4) The conversion of NH$_3$ into N$_2$ in plasmas associated with falling meteors is very efficient and rapid, and could account for most of the N$_2$ present on Titan today; 5) The yields of C$_2$H$_2$ and HCN from lightning induced chemistry in mixtures of CH$_4$ and N$_2$ is consistent with quenched thermodynamic models of the discharge core but that the yields of C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$ and other hydrocarbons are much higher than predicted by the model; and 6) Photolysis induced by the ultraviolet light emitted by the gases in the hot plasma may account for some, if not most, of the excess production of C$_2$H$_6$ and the more complex hydrocarbons.
Introduction

The fact that the outer planets possess extensive atmospheres has been known for a long time. Galileo first observed the complexity of the atmosphere of Jupiter with his homemade telescope in 1608. Since then more sophisticated and extensive observations have been made confirming the complexity and diversity of the objects (and their atmospheres) in the solar system. These observations, which still continue to be made, were certainly demonstrated by the photographic images returned to us by the Voyager spacecraft which flew past the outer planets (except Pluto) and their satellites this past decade.

The first evidence that the outer planets possessed complex atmospheres was the observation by Galileo of the colors in the atmosphere of Jupiter. With the development of better telescopes, similar observations were made of the other outer planets. Development of spectroscopic techniques and of equipment that could be attached to telescopes led to the detection and identification of the species that we now know comprise the atmospheres. The atmosphere of Jupiter, for example, contains about 88% molecular hydrogen (H₂) and 11% helium (He), along with smaller amounts of methane (CH₄), ammonia (NH₃), simple hydrocarbons and hydrogen cyanide (HCN). Many other compounds such as more complex hydrocarbons and nitriles (CN containing compounds) and materials that may be very complex or even polymeric must also be present. The latter of these species are evidenced by the presence of aerosols in the atmospheres of Jupiter and the outer planets. Reviews of our knowledge regarding the atmospheres of the outer planets are given in Trafton (1981) and Hunten et al. (1984).

The presence of these molecules and aerosols and the fact that some of them are colored imply that active chemistry of atmospheric species is either occurring now and/or has occurred in the past (Scattergood and Owen, 1977). Condensation of simple compounds such as CH₄ and NH₃ from the solar nebula result in clear or white ices and not colored aerosols. Also, compounds such as acetylene (C₂H₂) and HCN are not expected from simple thermodynamic condensation of species expected to have been present in the primordial solar nebula. How were these species formed? Can modeling of the chemical processes in planetary atmospheres be used to predict the compositions of the atmospheres that we cannot presently determine from the
earth but may be able to analyze by probes sent to the outer planets in the future? To help answer questions like these, laboratory research efforts in the areas of hot atom induced chemistry and synthesis of organic compounds by electrical discharge in planetary atmospheres were carried out as described below.

The discoveries of a thick atmosphere on Saturn's satellite Titan and the tenuous atmosphere on Neptune's satellite Triton indicate that studies of the chemical evolution of the outer planets is no longer limited to the atmospheres of the giant planets. Titan has an atmosphere that is more extended than that of the Earth and, like that of the Earth, is primarily composed of nitrogen (N\textsubscript{2}). Many simple organic compounds including CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and HCN are present in the atmosphere along with at least three haze layers, one of which is responsible for the satellite's yellow-orange color. Little is known about the chemical nature of the hazes, but their presence indicates the occurrence of active chemistry, at least in the past.

The presence of such an extensive atmosphere on Titan raises the question about the sources for atmospheres on solar system bodies, in particular that of Titan. Such a small satellite, even with a surface temperature of only 94 K, would not likely capture such a thick atmosphere (Owen, 1982). Two basic hypotheses have been proposed to explain Titan's present atmosphere. One suggests that the atmosphere is original and the initial NH\textsubscript{3} was converted into N\textsubscript{2} by photolysis (Atreya et al., 1978). The other suggests that the N\textsubscript{2} and other volatile gases were trapped in water clathrates and then released later to form the present atmosphere (Lunine et al., 1989). Neither of these models can fully account for all of the details known about Titan's current atmosphere. Another possibility is that Titan did accrete an atmosphere containing NH\textsubscript{3} which was subsequently converted into N\textsubscript{2} by processing of the atmosphere in plasmas associated with infalling objects such as meteors. Much more work needs to be done to understand how the atmosphere was formed and evolved.

To help answer some of the questions raised above, laboratory based investigations of three areas were done: 1) Organic chemistry induced by kinetically 'hot' hydrogen atoms in the region of Jupiter's atmosphere containing the ammonia cirrus clouds; 2) The conversion of NH\textsubscript{3} into N\textsubscript{2} by plasmas associated with entry of meteors and other objects into the atmosphere of early Titan; and 3) The synthesis of simple hydrocarbons and HCN by lightning in mixtures containing N\textsubscript{2}, CH\textsubscript{4} and NH\textsubscript{3} representing the atmospheres of Titan and the outer planets. The results of each of these studies have been published in the scientific literature (see the list of
Hot Hydrogen Atom Chemistry on Jupiter

The occurrence of active chemistry in the atmospheres of the outer planets has been evidenced by observations from ground-based telescopes and by spacecraft. Further support for the occurrence of chemical processes (past or present) comes from models of the condensation of planetary bodies from the primordial nebula, which predict that only simple molecules such as H₂, He, CH₄, NH₃, etc. should be expected to be present in planetary atmospheres in observable quantities. Many sources of energy useful in initiating chemical reactions are available to planetary atmospheres. Such sources include ultraviolet light (λ<2500Å), electrical discharges, particle bombardment, and heat. Of these, UV light is considered to be the most important because of its higher energy fluences. Observations and computational modeling show that the atmosphere of Jupiter (and probably of the other outer planets) to be chemically stratified so that solar radiation of different wavelengths will penetrate to different levels in the atmosphere. This leads to photolysis of CH₄, NH₃, phosphine (PH₃) and hydrogen sulfide (H₂S) at different altitudes. In the upper atmosphere direct photolysis of CH₄ produces the hydrocarbon products which have been observed. Ammonia, however, is frozen out lower in the atmosphere and is not available for reaction with CH₄ or its photoproducts. Another mechanism must be responsible for the formation of organic nitrogen species (e.g., HCN).

In the region of the NH₃ cirrus clouds, direct photolysis of CH₄ is unlikely due to the shielding by CH₄ in the overlying atmosphere. Another way of making the CH₃ radicals necessary to react with the NH₂ radicals formed from photolysis of NH₃ is abstraction of H from CH₄ by kinetically 'hot' hydrogen atoms, also formed from photolysis of NH₃. The CH₃ and NH₂ radicals can then react with each other and other species to form HCN and more complex CN compounds. The major criticisms of this scenario are that the efficiency of the abstraction reaction is too low and that the hot hydrogen atoms are too rapidly thermalized by molecular hydrogen and other gases for hot hydrogen atoms to be effective in initiating chemistry.

To investigate these problems, a number of experiments were carried out in which NH₃ (at a pressure of 4 torr) was photolysed with isotopically labeled methane
(CD$_4$) in the presence of varying amounts of H$_2$ (pressures from 0 to 800 torr). The deuterated form of methane was used to allow monitoring of the reaction. The overall abstraction of D from CD$_4$ was measured by the production of HD, i.e.,

$$\text{H}^* + \text{CD}_4 \rightarrow \text{CD}_3 + \text{HD}.$$ 

Monitoring of the changes in NH$_3$ and, consequently, H$^*$ were done by measuring the decrease in the amount of NH$_3$ during the photolysis. The measurement accuracy was found to be ±10%. After the photolysis, the gas mixtures were each divided into 4 equal aliquots and the HD (and H$_2$ that was either added or present with the HD) were separated from the reactants and other products. The amounts of HD produced were measured using a stable isotope mass spectrometer specifically designed to measure hydrogen. From these data and the amounts of NH$_3$ lost, the efficiencies of the abstraction reaction and of the thermalization of H$^*$ were determined.

Briefly, the results of the experiments showed that the thermalization of hot H$^*$ by H$_2$ was much less efficient than expected based upon simple elastic collision theory. This is qualitatively indicated in Figure 1, which shows the yield of HD as a function of the initial pressure of H$_2$ in the mixture. From the figure, the yield of HD does not decrease linearly with H$_2$ pressure, and is still significant even for pressures of H$_2$ as high as 800 torr ([H$_2$]/[NH$_3$] = 200; the Jovian ratio is ≈500). From calculations using probability theory of the expected versus experimental yields, a measure of the thermalization of H$^*$ can be made. Our results show that about 10 to 11 collisions between the hot hydrogen atoms and molecular hydrogen are required to reduce the energy of the H$^*$ below that required for abstraction of D from CD$_4$. Classic theory predicts total thermalization in just 3 collisions. Finally, from Figure 1 it can be seen that even at high pressures of H$_2$, the production of HD (and abstraction of D from CD$_4$) still occurs. This suggests that if a significant amount of hot hydrogen atoms can be made in Jupiter’s cirrus cloud region, then chemistry induced by these atoms should occur and that some of the CN compounds found there may be due to hot atom chemistry. More detailed descriptions of this work have published in the scientific literature (Aronowitz, et al., 1981 [theory]; Aronowitz et al., 1986 [experiments]).

Although not one of the original purposes of this project, a determination of the effect of H$_2$ on the quantum loss ($\phi$) of NH$_3$ photolyzed at 1849Å was made. The results are shown in Figure 2. The value of 0.28 for no hydrogen agrees with values found in the literature. However, the important result relevant to chemistry of outer planet atmospheres is that $\phi$(NH$_3$) = 0.02 is still significant even for [H$_2$]/[NH$_3$] = 200.
Origin of N\textsubscript{2} in Titan's Atmosphere

Titan is an unusual outer solar system satellite in that it has a substantial atmosphere and that the atmosphere is dominated by molecular nitrogen. Based on cosmochemical arguments, in particular that hydrogen was the major component of the primordial solar nebula and that the stable low temperature forms of carbon and nitrogen are CH\textsubscript{4} and NH\textsubscript{3}, respectively, Titan should have accreted an atmosphere of mostly H\textsubscript{2}, CH\textsubscript{4}, and NH\textsubscript{3}. Water, the stable form of oxygen, would have frozen out onto the surface or in the interior. Most of the H\textsubscript{2} would have escaped over time due to the satellite's low gravity, leaving an atmosphere consisting of CH\textsubscript{4} and NH\textsubscript{3} with smaller amounts of other gases, argon for example (Owen, 1982). As mentioned above, however, Titan's atmosphere is made up of CH\textsubscript{4} and N\textsubscript{2} (Hunten et al., 1984).

Recently an argument was made on kinetic grounds that the form of nitrogen in the solar nebula had been N\textsubscript{2} and not NH\textsubscript{3} (Prinn and Fegley, 1981). Also, the form of carbon would have been carbon monoxide (CO) and not CH\textsubscript{4}. If this were the case, then the original atmosphere would have consisted of N\textsubscript{2} and CO, not N\textsubscript{2} and CH\textsubscript{4} as found today. Hence, Titan's atmosphere presents a dilemma in that it contains species consistent with equilibration of the nebula at both high (for N\textsubscript{2}) and low (for CH\textsubscript{4}) temperatures.

Assuming that the kinetic arguments were valid, how would such an atmosphere have been acquired? The present surface temperature of 94 K is not low enough for direct condensation of N\textsubscript{2} and CO. To solve this problem, water-ice clathrates containing large amounts of these species have been postulated (Lunine et al., 1989). However, there are difficulties with this model. The maximum vapor pressure of N\textsubscript{2} above a clathrate surface at 94 K is only 1.5 torr (Lunine and Stevenson, 1985), much less than the 1.5 bar present today. Also, if enough N\textsubscript{2} were incorporated in the clathrate to give the present N\textsubscript{2} abundance, then there should be a large amount of CO and an even larger amount of CH\textsubscript{4} in the atmosphere as CH\textsubscript{4} is more readily incorporated into water-ice clathrates than are CO and N\textsubscript{2}.

Some recent studies suggest that Titan may have formed in the outer portion of the nebula surrounding Saturn (Lunine et al., 1989). In this nebula, the form of nitrogen might have been NH\textsubscript{3}, which would have been directly accreted into Titan's
atmosphere resulting in an atmosphere of CH$_4$ and NH$_3$. If this were the case, then how was the present N$_2$ formed? One hypothesis is that the original NH$_3$ was photolysed by solar UV light over time to produce the N$_2$ found there today. However, during the early history of the solar system, the solar nebula may have been too dense to permit penetration of UV light to the region of Saturn, and the surface temperature of Titan may have been too low for much NH$_3$ to have existed in the (upper) atmosphere. Also, there may have been hazes in the upper atmosphere, like there are today, that could have blocked the UV light necessary to photolyze the NH$_3$.

During the early stages of Titan's history, the atmosphere would have been bombarded by meteors and other nebular debris. Plasmas, generated during passage of these objects through the atmosphere, are known to be efficient initiators of chemical processes. Also, these objects would have reached the lower part of Titan's atmosphere where NH$_3$ would have been most abundant. Hence, bombardment of the atmosphere by meteors and other nebular debris might have been an effective way of converting the original NH$_3$ into the present N$_2$.

To evaluate this scenario, a number of experiments were done in which mixtures of CH$_4$ and NH$_3$ were subjected to laser-induced plasmas (LIP), simulating the plasmas associated with infalling meteors in Titan's early atmosphere. These plasmas were generated by a 10 Hz pulsed Nd-YAG ($\lambda = 1.06 \mu$m) laser with about 0.2 J per pulse. After irradiation, the amounts of N$_2$ and H$_2$ (and some simple hydrocarbons) produced were measured by gas chromatography using a thermal conductivity detector and their yields as a function of the energy absorbed by the gas were determined. The yields of N$_2$ as a function of the initial concentration of NH$_3$ in the mixture are shown in Figure 3. Also shown are the yields calculated from a simple high temperature quenched equilibrium model for three 'freeze-out' temperatures.

Using the yield for $X$(NH$_3$) = 0.1, the results suggest that meteor impacts could have generated as much as 12 bar of N$_2$, more than enough to account for the N$_2$ present today. This conclusion was also reached independently from a computational model of shock-initiated chemistry in the atmosphere (Jones and Lewis, 1987). However, the assumptions about the total energy delivered to the atmosphere by infalling meteors and the effects of plasma made H$_2$ accumulated in Titan's atmosphere may not be valid, possibly resulting in much lower yields of N$_2$ from this process. A discussion of these effects and a more detailed presentation of this model and the experiments have been published in the open literature (McKay et al., 1988).
Production of Organic Compounds in Plasmas

The chemistry in planetary atmospheres that is induced by processes associated with high-temperature plasmas is of broad interest because such processes may explain many of the chemical species observed in these atmospheres. There are at least two important phenomena that are known to generate plasmas (and shocks) in planetary atmospheres: lightning and meteor impacts. For both phenomena, rapid heating of atmospheric gases leads to the formation of a high-temperature plasma which emits radiation and produces shock waves that propagate through the surrounding atmosphere. These processes initiate chemical reactions that can transform simple gases into more complex compounds. These compounds may, in part, account for the variety of gases and aerosols known or believed to exist in the atmospheres of the outer planets and of the satellites Titan and Triton.

In order to study the production of organic compounds in plasmas and shocks in a primitive atmosphere, a series of experiments were done in which various mixtures of $N_2$, $CH_4$ and $H_2$, modeling the atmosphere of Titan, were exposed to discrete sparks, laser-induced plasmas, and ultraviolet light. For the spark experiments, an apparatus capable of producing discrete 20 KV sparks across a 4.5 cm gap was used. The energy density of these sparks was about $10^4$ J/m, which is within an order of magnitude of that of terrestrial lightning. For the laser experiments, a Nd-YAG laser ($\lambda = 1.06 \, \mu m$) producing a 10 Hz pulsed beam containing about 0.2 J per pulse was used. The photolysis experiments were carried out using the light produced by the sparks but the test mixture was contained in a cell with MgF$_2$ windows to isolate the gases from the shock but not the ultraviolet light.

As was expected for high-temperature plasmas, the molecules produced in highest yield in both the spark and laser experiments were HCN and $C_2H_2$, followed by ethane ($C_2H_6$), ethylene ($C_2H_4$), and propane ($C_3H_8$) in order of decreasing yield. When compared to the yields predicted by a simple high-temperature quenched thermodynamic equilibrium model, those for HCN and $C_2H_2$ are in fair agreement, as shown in Figure 4. However, the agreements for $C_2H_6$ and the other hydrocarbons were poor and became increasingly worse with product complexity (carbon number). This indicates that a more comprehensive theory is needed, as processes other than
equilibrium cooling from a high temperature gas must be occurring.

Our experiments suggested that perhaps photolysis by ultraviolet light emitted from the plasma is an important process in the synthesis. To test this hypothesis, experiments were done in which the mixtures were exposed to the light from the spark but not to the shock or high-temperature plasma. As expected from known results of the UV photolysis of $\text{CH}_4$, $\text{C}_2\text{H}_6$ was the major product, followed by $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, and $\text{C}_3\text{H}_8$. After correction for the diminution of the light from the spark due to system geometry and absorption by the cell windows, the photolysis yields can be compared to the spark yields, as shown in Figure 5. From the figure, it can be seen that the production of $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_4$ may be almost entirely accounted for by photolysis. $\text{C}_3\text{H}_8$ may also be made primarily by photolysis as the yield predicted by the quenched equilibrium model is more than 5 orders of magnitude smaller than that observed in the experiments. Hence, the results of these experiments demonstrate that the thermodynamic equilibrium theory does not adequately model chemistry in lightning and plasmas associated with meteor impacts and that at least photolysis must be included. A detailed description of the results of these experiments and their implications to chemistry in planetary atmospheres has been published in the journal *Icarus* (Scattergood *et al.*, 1989).

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References


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QUANTUM YIELD OF HD AS A FUNCTION OF HYDROGEN PRESSURE FOR VARIOUS PRESSURES OF METHANE

Photolysis of NH₃ + CD₄ + H₂ at 1849 Å

- P (CD₄) = 40 mm Hg
- P (CD₄) = 20 mm Hg
- P (CD₄) = 10 mm Hg

HD Quantum Yield x 1000 (molecules / photon)

Hydrogen Pressure (mm Hg)

Figure 1
QUANTUM LOSS OF NH₃ AS A FUNCTION OF HYDROGEN PRESSURE

Photolysis of NH₃ + CD₄ + H₂ at 1849 Å

Figure 2

Hydrogen Pressure (mm Hg)

Quantum Loss (Molecules / Photon)
CONVERSION OF NH$_3$ TO N$_2$ BY LASER-SUPPORTED SHOCKS IN NH$_3$–CH$_4$
MIXTURES MODELING EARLY TITAN

EXPERIMENTAL CONDITIONS:
MIXTURES: NH$_3$ + CH$_4$
PRESSURE: 760 torr
TOTAL ENERGY: ~ 150 J

Figure 3
EXPERIMENTAL vs. THEORETICAL YIELDS PREDICTED FROM LIGHTNING IN A MODEL TITAN ATMOSPHERE

MIXTURE: 96.8% N2, 3.0% CH4, 0.2% H2
MODEL: HIGH TEMPERATURE SHOCK (2000-3000 K)

*: Values are averages of all spark experiments.

Figure 4
PRODUCTION OF HCN AND HYDROCARBONS BY LIGHTNING:
IMPORTANCE OF PHOTOLYSIS TO THE SPARK PROCESS

MIXTURE: 96.8% N2, 3.0% CH4, 0.2% H2
PRESSURE: 760 torr.

Values shown are averages of all experiments.

* Spark includes shock + photolysis + other processes.

** Photolysis was accomplished using the light emitted by the sparks.

Figure 5