Elemental composition, solubility, and optical properties of Titan’s organic haze

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Received 18 August 1995; revised 26 December 1995; accepted 26 December 1995

Abstract. It is found that solid organic material produced by electrical discharge in a simulated Titan atmosphere (10% CH₄, 90% N₂) has an elemental composition corresponding to CₓHₓNₓ. Immersion in liquid ethane followed by filtration indicates that the organic solid is insoluble in ethane and it is supposed, in methane. An upper limit is placed on the soluble fraction of 0.03% by mass. When the mixing ratio of CH₄ is varied from 10 to 100% it is found that the organic solid produced becomes progressively darker in the ultraviolet and violet (0.2-0.4 μm) compared to the visible and near-infrared (0.4-0.75 μm). The optical properties are variable by more than a factor of 2 between experiments. Sedimentation of solid haze material on the surface of Titan represents a comparatively small loss for carbon. For nitrogen, however, the loss rate of 10¹⁸ N atoms cm⁻² s⁻¹ in haze material is greater than 10% of the total production of N in the upper atmosphere.

1. Introduction

Earth based observations have long indicated that Titan has an atmosphere with CH₄ present in it (Kuiper, 1944; Trafton, 1972). Coupled with the reddish appearance of the satellite this led to the suggestion that solid organic aerosols were being produced in Titan’s atmosphere by CH₄ photolysis (Sagan, 1974). Observations of the geometric albedo were used to deduce the optical properties of the Titan haze and indicated that the material is dark in the violet and ultraviolet and relatively bright in the visible and near-infrared (Rages and Pollack, 1980). With the Voyager 1 fly-by in 1980, the presence of N₂ in Titan’s atmosphere was confirmed and nine organics heavier than CH₄ were detected (Kunde et al., 1981).

Laboratory simulations in which gas mixtures with the composition of Titan’s atmosphere are irradiated with UV light, electrical discharge, or energetic electrons have produced a solid organic material—termed tholin—which has optical properties similar to those derived by Rages and Pollack (1980). The first, and most detailed, study of this sort is the work of Khare et al. (1984) in which the real and imaginary indices of refraction were determined for a tholin produced from the passage of a DC electrical discharge through a mixture of 10% CH₄-90% N₂ at standard temperature and a pressure of 0.2 mb.

Following up on the work of Rages and Pollack (1980), more sophisticated microphysical models (McKay et al., 1989; Toon et al., 1992; Rannou et al., 1995) have been developed to compute the geometric albedo of Titan and, by comparing with observations, determine the optical properties of the haze. The results indicate that using the refractive indices of Titan tholin produced in the laboratory (Khare et al., 1984) produces a remarkably good fit to the geometric albedo spectra (Sagan et al., 1992). This lends credence to the notion that the material produced in the simulations is accurately representing the Titan haze material. These microphysical models suggest that the haze production rate is about 10⁻¹⁴ g cm⁻² s⁻¹ (McKay et al., 1989). The haze material is ultimately deposited on the surface and represents a net sink for C and N atoms. To assess the importance of this sink it is necessary to know the C and N concentrations in the haze material.

In addition, the haze plays a key role in the thermal structure of Titan’s atmosphere. Its presence in the upper atmosphere is an important source of heating (McKay et al., 1989). By absorbing a significant fraction of the incoming sunlight and allowing thermal infrared radiation to escape easily, the haze generates an antigreenhouse effect which cools the surface (McKay et al., 1991). Although the haze strongly influences the surface and atmospheric temperatures, its effects have been ignored (Lunine and Rizk, 1989), or held constant (McKay et al., 1993) when considering the climate history of Titan. If the conditions in the atmosphere change, then the optical
properties and total production rate of the haze may vary. Such a change would alter the energy absorption in the upper atmosphere and on the surface.

The haze is not uniformly distributed on Titan and changes with season. During the Voyager 1 fly-by, the northern hemisphere was observed to be darker than the southern hemisphere by approximately 20% (Sromovsky et al., 1981) and one half orbit later the relative brightness of the hemispheres on Titan was reversed (Caldwell et al., 1992). Based on steady state calculations, Pollack et al. (1980) and Allen et al. (1980) suggested that the solar flux controls the production rate of the organics from which the haze forms and therefore seasonal and solar cycle changes in solar flux would change the haze reflectivity. However, Hutzell et al. (1993), using a time dependent calculation, have shown that the response of the haze is too sluggish to respond to changes in production rate. Taking a different approach, Courtin (1992) suggested that the hemispheric asymmetry on Titan could be due to changes in the optical properties of the haze material, without changing the number or size of the particles. Compositional changes in the haze are plausible given observed changes in the organic gases (Coustenis and Bézard, 1995) from which the haze is formed. Hutzell et al. (1996) have recently shown that an alternative explanation for the haze variability is that the atmospheric circulation redistributes the haze affecting both the particle size and column mass and thus changing the reflectivity of the atmosphere.

To further understand the properties of the haze we have conducted a series of laboratory experiments producing Titan tholin. We have investigated the elemental composition of tholin and its solubility in non-polar hydrocarbons (ethane). We have also measured the optical properties as a function of the CH4 concentration in the initial gas mixture. In the following sections we present these results and consider the implications for our understanding of Titan.

2. Results

Tholin was produced in a simulated Titan atmosphere comprised of 10% CH4, with the balance N2, via electrical discharge from a tesla coil similar to the experimental setup reviewed in Sagan et al. (1984). The three liter reaction vessel was energized with three sets of tungsten electrodes, each with a 0.5 cm arc gap. The pressure in the vessel was maintained at slightly above ambient (∼1150 mb) with gas flow-through at a rate of approximately 3 cm³ min⁻¹. The apparatus was operated at room temperature continuously for three weeks and accumulated a film of brown material (tholin) on the walls. Several hundred milligrams of tholin was scraped off the walls of the reaction vessel for use in experiments.

Ethane was liquified from high purity gaseous ethane in a condenser cooled with liquid nitrogen. The tholin (350 mg) was added to 75 ml of liquid ethane and stirred vigorously for 15 min. This phase of the experiment took place inside an air tight, dry hood in order to minimize water condensation. The temperature of the liquid ethane during the dissolution of the tholin was held between 95 and 110 K. The mixture was filtered through a 0.2 μm Teflon filter which had previously been cooled with liquid nitrogen. The filtrate was then allowed to warm to room temperature. A control was performed in which all experimental procedures were duplicated exactly, except that no tholin was added to the liquid ethane. By visual inspection the filtered ethane was as clear after filtering as it had been before the sample was added. Any residual material in the control was below the measurement limit of 0.1 mg. No residue could be detected after filtering the mixture of tholin and ethane. Our formal detection limit was 0.03%. We note that any impurities in the ethane, or any colloidal particles passing through the filter, would result in an overestimation of the soluble fraction. Thus, we believe that our result is a conservative upper limit on the fraction of laboratory tholin that is soluble in liquid ethane. We stress that this is an upper limit and the true value may be orders of magnitude lower. We note that the tholin material was highly soluble in other solvents. Ethylene glycol and dimethylsulfoxide became visibly brown when tholin was dissolved into them. Evaporation of the solution indicated solute concentrations of 3 and 1 mg ml⁻¹, for ethylene glycol and dimethylsulfoxide, respectively. Water, ethanol, and methanol also dissolved tholin, and the solution became a brownish color. For these solvents the solute concentration was about 0.5 mg ml⁻¹. Some solubility was noted in hexane, but the amount was difficult to quantify. No solubility was detectable in benzene. Spectral absorption of the solution compared to the pure solvent confirmed the presence of tholin in solution. Spectral features were seen in the 1.9–2 μm range in the ethanol, ethylene glycol, and dimethylsulfoxide. In the UV (0.2–0.3 μm), features were seen in the ethanol and hexane solutions. No systematic study of these results was undertaken but they do indicate that the soluble fraction differs for each solvent.

Three separate experiments were conducted in which samples of tholin material, produced as described above, were analyzed for elemental composition. The analyses were performed by Desert Analytics Laboratory (Tucson, Arizona) using a Perkin Elmer 240 CHN Analyzer. Each sample was divided into three aliquots for replicate measurements. The results are shown in Table 1. Oxygen

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%O</th>
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<td>5.79</td>
<td>14.2</td>
<td>12.0</td>
</tr>
<tr>
<td>Duplicate</td>
<td>67.2</td>
<td>5.74</td>
<td>14.2</td>
<td>12.0</td>
</tr>
<tr>
<td>Triplicate</td>
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<td>5.74</td>
<td>14.2</td>
<td>12.0</td>
</tr>
<tr>
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<td>5.46</td>
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<td>9.3</td>
</tr>
<tr>
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<td>5.33</td>
<td>15.8</td>
<td>9.8</td>
</tr>
<tr>
<td>Triplicate</td>
<td>66.2</td>
<td>5.34</td>
<td>15.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Tholin #3a</td>
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<td>4.38</td>
<td>8.4</td>
<td>11.8</td>
</tr>
<tr>
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<td>4.28</td>
<td>8.5</td>
<td>11.7</td>
</tr>
<tr>
<td>Triplicate</td>
<td>62.1</td>
<td>4.27</td>
<td>8.4</td>
<td>11.1</td>
</tr>
<tr>
<td>Assumed values</td>
<td>66</td>
<td>5.5</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

*Produced by tesla coil discharge in 10% CH4, 90% N2 at standard pressure and temperature, see text.
*aThere was a noticeable level of residue on combustion of tholin #3 which may account for the low N levels.
Curves are shown for the Khare et al. (1987) values for 100% CH, which represent the range of those measurements.

Fig. 1. Transmission of a thin film of tholin material produced from mixtures with a range of CH, to N, concentrations. All results have been normalized to 0.9 at 0.75 μm. Multiple solid lines for 20, 70, and 100% CH, show repeated measurements of a single film. For 10 and 50% (dotted lines) results from two separate experiments are shown. The values of Khare et al. (1984) for Titan tholin are shown as the short-dashed line. Two curves are shown for the Khare et al. (1987) values for 100% CH, which represent the range of those measurements.

is present in the analysis but not in the initial gas mixture. It is probable that the tholin material oxidizes when exposed to air at the conclusion of the experiment. We treat this as a simple addition of O atoms to the mixture and assume that the C and N values do not change. In obtaining averaged results, we relied on samples 1 and 2 because sample 3 left a residue after combustion in all three aliquots. Our averaged results have a C/N value of 5.13.

In a separate set of experiments we prepared tholin as described above except that the CH, mixing ratio was varied from 3 to 100%. In each case a quartz slide was placed inside the reaction vessel. After a thin film of material had accumulated on this slide it was removed. Spectral absorption was measured from 0.2 to 0.75 μm with a Cary Model 14 Spectrometer. The transmission of the slide before deposition of the tholin film was recorded as a baseline. Because the thickness of the film was not determined the results were normalized to a fixed value (0.9) at a reference wavelength (0.75 μm). A representative set of these results is shown in Fig. 1, in which transmission is plotted over the wavelength range considered. These cases were selected because they included duplicated experiments and repeated measurements on an individual slide. On a given film the measurements from different locations and from reversing the slide gave very consistent results after normalization (see the curves for 20, 70, and 100% CH, in Fig. 1). However, different experiments with the same initial amount of CH, produced a wider spread in the results (see curves for 10 and 50% CH,). With variations in absorption of more than a factor of 2, Khare et al. (1987) reported optical properties of film made in pure CH, at 0.13 mbar using a radio-frequency discharge. They also found that the results varied by factors of more than 2. The range of their results are shown in Fig. 1. In comparing these results it is important to note that by normalizing all curves to 0.75 μm the shape of each curve depends only on the rate of change of the optical properties with wavelength. Also shown in Fig. 1 is the transmission computed for the optical properties of Titan tholin as reported by Khare et al. (1984) for a 10% CH, mixture (the same normalization at 0.75 μm has been applied). The Khare et al. tholin is darker than all other spectra regardless of the amount of CH, This discrepancy is discussed further in Section 3.

3. Discussion

3.1. Tholin elemental composition

Sagan et al. (1984) reported an elemental composition by weight for Titan tholin of 48% C, 6.4% H, 29% N, and 17% O. The details of the analysis or the production method were not given other than the statement that they were produced with a tesla discharge at a pressure of >10 mb. If we assume that the oxygen is an oxidative contaminant, due to exposure to air which only adds O atoms without releasing either H, C, or N then it can be simply removed from the mass balance. This gives a C/N of 1.93. It is also possible to derive an elemental stoichiometry by dividing each weight percent by the molecular weight and multiplying by a constant to obtain integer values. We find that a factor of 2 gives the approximate stoichiometry C,H,N. The same procedure applied to our results in Table 2 gives C,H,N, after the O present is removed. Coll et al. (1995) have reported on tholin produced in a tesla coil discharge and found an elemental composition of C,H,N. These results are compared in Table 2. These results vary considerably, the C/N ratio varies from 2 to 11. The H/C ratio varies much less, ranging from 1 to 1.6. Understanding the C/N ratio of the Titan haze has important implications for photochemical models of the haze formation. It may be possible to use the elemental ratios to indicate the chemical mechanisms of tholin formation; for example, HCN and C,H, polymerization will give very different elemental ratios.

On Titan the starting species for photochemical processes are CH, and N,. The C/N ratio of CH, and N, in Titan’s upper atmosphere is ~0.01—much smaller than the laboratory results. However, this comparison is misleading and a more useful approach would be to consider the production rate of C and N containing species from the dissociation of CH, and N, (McKay and Toon, 1992). Based on the recent modeling results of Toublanc et al. (1995), the total dissociation rate for CH, is 1.3 × 10 cm s while the production rate of N from both UV light and magnetospheric electrons (Strobel et al., 1992) is 8.4 × 10 cm s giving a C/N ratio of 15. The ease with which CH, is dissociated compared to N, easily explains the observed differences.

Table 2. Comparison of elemental composition of tholin

<table>
<thead>
<tr>
<th>Reference</th>
<th>Stoichiometry</th>
<th>C/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>C,H,N</td>
<td>5.5</td>
</tr>
</tbody>
</table>
more than offsets the much larger fraction of N$_2$ in the atmosphere. However, the major sink for light (C$_n$ or N$_n$, $n \approx 2$) hydrocarbon species, produced from CH$_4$ photolysis, is condensation and not transformation into heavier organics. Hence, as the heavier organics ($n = 5$) are produced from the lighter ones the C/N ratio observed in Titan's atmosphere diminishes. For values of $n > 5$ condensation is no longer a significant sink and it is likely that these organics are quantitatively transformed into tholin. Thus, estimates of production for these large species is an effective estimate for haze production. Yung \textit{et al.} (1984) used this approach to estimate the haze production rate. They included a series of reactions that produce hydrocarbon “polymer” with a net mass production rate of about $2 \times 10^{-14}$ g cm$^{-2}$ s$^{-1}$, in rough agreement with the value determined from haze models as discussed above. This suggests that it is indeed possible to use photochemical models to predict the haze production rate without explicitly modeling organic molecules heavier than about 6—which appears to be impractical anyway due to the combinatorial increase in the number of distinct molecules possible as $n$ increases. However, N containing components of the haze, not included in the Yung \textit{et al.} model, need to be considered.

Table 3 compares the photolysis rate of CH$_4$, the dissociation rate of N$_2$ and the production rate of tholin in terms of total mass, carbon atoms, and nitrogen atoms. The CH$_4$ and N$_2$ dissociation rates are from Toublanc \textit{et al.} (1995), the haze production rate is from McKay \textit{et al.} (1989). The elemental composition of the haze material is based upon laboratory tholin as shown in Table 2 using an average value of the C/N ratio of 4. As is evident from the values in Table 3, the production of tholin on Titan is a minor sink for C but not for N. About 12% of the N produced is lost as solid organic material. This sink of N atoms is large enough that it must be accounted for in a self consistent way in photochemical models of Titan’s atmosphere. It is likely that the computed profiles of HCN will be altered when this additional sink of N is included. This could be important because the HCN profile determined by Tanguy \textit{et al.} (1990) is currently used to infer the eddy diffusion coefficient (Toon \textit{et al.}, 1992; Toublanc \textit{et al.}, 1995).

3.2. Solubility

The results of this study indicate that there is little or no polymeric organic material dissolved in hydrocarbon lakes or oceans on Titan. This result is consistent with the deduction by Raulin (1987) based on a list of Titan tholin components collected from both theoretical and laboratory studies. Using thermodynamic modeling to determine the solubility of specific organics in a liquid phase mixture of ethane, methane, and nitrogen, Raulin determined that the oceans of Titan may be very rich in dissolved organics, with concentrations between $10^{-6}$ and 1 M. His model predicts that the soluble component contains aliphatic Cl–C7 hydrocarbons, alkenes, alkynes, aromatics, and nitriles. These light organics have condensation temperatures well below standard temperature, and mostly below the 180 K temperature in Titan’s stratosphere. Thus, their incorporation into the laboratory tholin, and possibly the Titan haze, is not possible. For the polymeric compounds expected in tholin, Raulin (1987) found virtually no solubility. For the relatively refractory N-heterocyclic compounds adenine and pyrimidine, Raulin (1987) found solubilities of $10^{-5}$ and $10^{-3}$ M, respectively—undetectable in the present experiments. These are the only compounds, other than polymers, considered by Raulin (1987) that have condensation temperatures above 290 K. For polymers, Raulin (1987) concluded that only polyethylene would be soluble and then only in relatively pure CH$_4$. Overall then, the theoretical analysis of Raulin (1987) is in good agreement with our negative results concerning the solubility of tholin in liquid ethane. However, the indication of solubility of volatile organics suggests that it is important to redo these experiments with temperatures and pressures accurately simulating the upper atmosphere of Titan (180 K, $10^{-4}$–0.1 mb) followed by solubility tests in cryogenic hydrocarbons without warming the sample.

The results of our solubility tests indicate that tholin material is much more soluble in polar solvents (water, ethanol, methanol, glycol, and dimethylsulfoxide) than in non-polar solvents (ethane, hexane, and benzene). The insolubility of haze material in non-polar compounds has implications for the condensation of ethane and methane in Titan’s atmosphere. The efficacy of heterogeneous condensation depends on the contact angle between the condensate and the condensation nuclei (Moses \textit{et al.}, 1992). On Earth, compounds which are hydroscopic have contact angles that are small while for hydrophobic substances (like Teflon) the contact angles are large. Our results suggest that the tholin particles will have large contact angles with condensing ethane and methane. Courtin \textit{et al.} (1995) has suggested that this could result in supersaturations of ethane of over 500 in Titan’s stratosphere and supersaturations of methane of over 2 in the troposphere. More direct experiments aimed at invest-

<table>
<thead>
<tr>
<th>Process</th>
<th>Mass (g cm$^{-2}$ s$^{-1}$)</th>
<th>N (cm$^{-2}$ s$^{-1}$)</th>
<th>C (cm$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C from CH$_4$ photolysis</td>
<td>$2.6 \times 10^{-13}$</td>
<td>---</td>
<td>$1.3 \times 10^{10}$</td>
</tr>
<tr>
<td>N from N$_2$ dissociation</td>
<td>$2.0 \times 10^{-14}$</td>
<td>$8.4 \times 10^{4}$</td>
<td>---</td>
</tr>
<tr>
<td>Tholin production</td>
<td>$10^{-14}$</td>
<td>$1 \times 10^{4}$</td>
<td>$4 \times 10^{4}$</td>
</tr>
</tbody>
</table>

Assuming C$_{39}$H$_{66}$N, C/N = 4
ing the condensation of ethane and methane on tholin are indicated by these considerations. Organics other then methane and ethane, for example HCN, may also condense on the haze particles and these may affect the surface properties of the particles with respect to condensation of ethane and methane.

3.3. Optical properties and composition

It is likely that the optical properties (and hence presumably the elemental ratios) of tholin depend on the CH₄ to N₂ ratio in the initial gas mixture. This is confirmed by the results shown in Fig. 1, where there is a clear trend toward UV darkening with increasing CH₄ concentration. An unexplained feature of our results is the disagreement between the optical properties of the tholin produced in this study with that reported by Khare et al. (1984), and also shown in Fig. 1.

There are at least two implications of these results. First, the darkening in the violet and ultraviolet with increasing CH₄ probably reflects a change in the relative abundance of the dissociation products (e.g. HCN, C₂H₂, and heavier organics) that lead to the formation of the haze material. The value of the C₂H₄/HCN ratio observed in Titan’s stratosphere is ~ 15 and it varies with latitude, with values near 4 at 70 N (Coustenis and Bézard, 1995). Our results for the elemental composition of tholin (Section 1) indicate that C is more readily incorporated into the solid organic than N, even when the mixing ratio of CH₄ is low. As the CH₄ mixing ratio increases it is likely that the elemental composition of the solid material produced changes, with the C/N ratio becoming progressively larger.

A second result apparent in Fig. 1 is that the optical properties of the films produced in this experiment do not agree with those of the Titan tholin of Khare et al. (1984). The latter are much darker in the UV compared to the visible than any of the films produced here. Our results for 100% CH₄ are within the range of values reported by Khare et al. (1987): specifically both sets of data have similar wavelength dependence—we cannot compare the magnitude of the absorption. However, these results are both much darker in the violet compared to the visible than the results reported by Scattergood and Owen (1977), who found that proton irradiation of a CH₄/H₂ mixture yielded a colorless liquid. All films in our experiments were brownish colored. These results together with the differences in the elemental composition noted in the tholin (Table 2) suggest that the elemental composition and the optical properties of Titan tholin depends on the experimental conditions under which it is produced. Differences in material properties between tholin produced with different energy sources has been noted by Sagan et al. (1984).

It is difficult to simulate a planetary atmosphere in a laboratory reaction vessel. Even if the temperature, pressure, and energy sources are faithful replicates of the real atmosphere, the walls of the container can produce spurious effects. To some extent wall effects can be mitigated by continuous flow experiments (Sagan et al., 1992). Most simulations of Titan tholin, including those reported here, fail to reproduce the conditions in Titan’s upper atmosphere. The temperature in the region of haze formation is 180 K and as the particles settle to the surface they experience only colder temperatures. Thus, many compounds that are volatile at room temperature would condense in a proper simulation. The pressure at which haze formation occurs on Titan is not well constrained. Considering the available energy sources and condensation temperature for organics, Sagan and Thompson (1984) suggested that the haze production would be above 0.1 mb. From microphysical models, McKay et al. (1989) deduced that it could be from 10⁻⁴ to 0.1 mb. Most laboratory simulations operate at much higher pressures. Finally, the tesla discharge is not a good simulation of the dissociation processes that are occurring on Titan. The dissociation of CH₄ is achieved primarily by solar UV (Yung et al., 1984) while N is produced well above the altitude of haze formation by magnetospheric electrons (Strobel et al., 1992). It is important to note, that the Khare et al. (1984) optical properties on which many current models rely were derived from tholin produced at standard temperature and pressure of 0.2 mb. The laboratory gas phase organics that best match the observed minor constituents on Titan were synthesized at 0.2 mb: the results are much poorer for simulations at higher pressures (Thompson et al., 1991).

Understanding the dependence of optical properties on gas composition may be important in understanding Titan’s past history. In Titan’s upper atmosphere the mixing ratio of CH₄ depends on the temperature and pressure of the tropopause cold trap. Climate models suggest that both of these may have changed over time primarily as a result of secular increases in solar luminosity (McKay et al., 1993). However, McKay et al. (1993) found that during the past few billion years these effects tended to compensate: lower tropopause temperatures were associated with lower tropopause pressures and the stratospheric CH₄:N₂ varied only from 0.5 to 2%. Larger values may have been obtained early in Titan’s history when accretional heating would have driven CH₄ into the atmosphere. For example, for an accretional heating of 600 erg cm⁻² s⁻¹, the atmosphere becomes dominated by CH₄ (McKay et al., 1993).

4. Conclusions

We have conducted laboratory simulations of Titan tholin in order to understand the elemental composition, solubility properties, and optical properties of this material. Based on our results we draw the following conclusions.

1. The elemental composition of tholin produced from a 10% CH₄~90% N₂ gas by electrical discharge at room temperature and pressure has an elemental composition corresponding to C₁₂H₁₁N₂.
2. The production of haze material represents a comparatively small sink for photochemically produced C atoms. For N the haze material may be an important loss term, accounting for over 10% of the total. Including this loss term for N may have significant effects on
the computed HCN profile and hence on derived eddy diffusion coefficients.

3. Tholin is virtually insoluble in liquid ethane and, by inference, liquid methane. This implies that tholin particles are poor nuclei for ethane and methane condensation. However, these solubility experiments need to be repeated with tholin produced at the low temperatures (180 K) and pressures (10^{-4}–0.1 mb) of Titan's stratosphere and then cooled to surface conditions (95 K).

4. The optical properties, in particular the violet and ultraviolet absorption, of tholin material depends on the CH\(_4\)/N\(_2\) ratio in the initial gas mixture and the production conditions and method used. The optical properties vary more significantly than the elemental composition. In general, increasing CH\(_4\) results in enhanced violet and ultraviolet absorption compared to the visible.

5. There is significant variability of tholin produced by different groups and under different conditions (factors of 2–10). The implications of this variability for producing a realistic and repeatable Titan tholin warrants further study.

Laboratory simulations can be a powerful tool in understanding the organic chemistry of Titan’s haze. The determination of the optical properties of Titan tholin by Khare et al. (1984) has been one of the most useful results from simulations of planetary atmospheres. It has formed the basis for diverse radiative transfer calculations and photochemical models. Many problems now current in the study of Titan can be advanced with more definitive laboratory simulations of Titan tholin. Better understanding of the haze material is essential to coupling photochemical and microphysical models. Furthermore, heating by the haze dominates the thermal balance and drives the atmospheric circulation. In addition, the analysis of the results from the upcoming Huygens Probe mission to Titan, which will collect and analyze haze particles, would benefit from a careful laboratory simulation.

Acknowledgements. This paper is dedicated to the memory of Tom Scattergood who remained interested in these topics throughout his career and who contributed substantially to the experimental work on Titan at NASA Ames Research Center and the results presented here. Joan Mathog performed the solubility experiments. Cindy Giver provided valuable assistance in the spectral analysis. The preparation of this paper benefited from many valuable discussions with François Raoult and his group at LISA. Subventions from NASA's Exobiology program supported this work.

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