Reactions in the Sublimations of Matrix-Isolated Cosmic Ice Analogs: A Laboratory Study Utilizing 1:1:100 $CO+H_2O+N_2$ and $CH_4+H_2O+N_2$ Cosmic Ice Analogs

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Question

Could sublimation processes on nitrogen containing icy worlds like Pluto lead to the formation of new astrobiologically relevant chemical species?

Background

- Pluto and Triton have N_2 ices on their surfaces [1,2].
- Pluto in particular can undergo large temperature changes due to its orbit and rotation, which can lead to the sublimation of N_2 ices [1].
- Solid N_2 is not particularly reactive: it was used as a matrix material to trap reactive intermediates when matrix isolation techniques were first developed [3].
- We think planetary bodies could act as giant matrix isolation experiments, trapping reactive molecules formed in the gas phase on the planetary surface.
- These trapped molecules could then react when the N_2 sublimates and be trapped in a new ice type. Some of these new molecules might be astrobiological relevant due to the potential of forming large organic molecules.

Experiment

Experimental Conditions: ~10^{-7} Torr, ~6 K, KBr/BaF_2 Optical Discs (Substrates)

1. The initial gas mixture is created in a gas manifold by observing the partial pressures of each gas (1:1:100 C source + H_2O+N_2, where C source is either CO or CH_4).
2. Background scans in the mid-IR and UV-Vis range are made. The gas mixture is introduced into the main vacuum apparatus (see Fig. 1). The gas is irradiated with either an electric or microwave discharge.
3. Once deposition finishes, new spectroscopic scans are made in the aforementioned ranges. The N_2 ice is then sublimated by raising the temperature up to ~45 K in ~5-10 K increments over ~45 minutes.
4. A water ice is formed after sublimation and new spectroscopic scans are taken. The system is allowed to go back up to room temperature while a residual gas analyzer scans the products sublimating from the water ice.

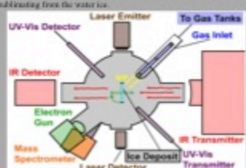

Figure 1 *The Experimental Setup*

A bird's eye view of the experimental apparatus, which consists of a 6" cylindrical vacuum chamber. The main tool used for analysis was an FTIR spectrometer (red). The center object is the optical disc and cold finger that could be turned 360 to face any instrument of interest.

Results

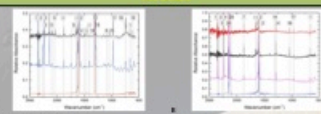

Figure 2 *The Initial Ice Deposit*

The IR spectrum from 2500-500 cm^{-1} for both the 1:1:100 C Source+H_2O+N_2 mixtures. These spectra show the initial, matrix-isolation-like results. (A) C Source = CH_4; Black – Microwave Irradiation; Blue – Tesla Coil; Red – No Irradiation. (B) C Source = CO; Red and Black – Microwave Irradiation; Purple – Tesla Coil; Blue – No Irradiation.

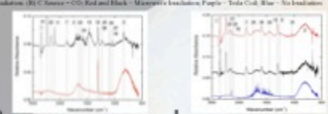

Figure 2 *Post-Sublimation Water Ice*

The spectra here show the new ice that is formed upon sublimation of the solid N_2 leaving behind a H_2O ice. (A) C Source = CH_4; Black – Microwave; Red – No Irradiation (B) C Source = CO; Red and Black – Microwave Irradiation; Blue – No Irradiation.

Table 1 *Identified Molecules*

The molecules from the above spectra are identified here. Molecules in red showed up in the N_2 ice first. The yellow shading indicates molecules that were identified in the H_2O ice, but not the N_2 ice due to not knowing their positions in the N_2 ice. Lastly, green indicates that the molecule appeared in the H_2O ice, but not the N_2 ice even with the position of the molecule available in the literature.

Discussion

- Carbon suboxide (C_3O_2) was the only truly novel product formed in the sublimation of the N_2 ice. However, it is an astrobiologically important one and has been observed on comets and meteorites [8]. C_3O_2 is astrobiologically significant because of its polymerizing potential [19], its biological role as an ATPase deactivator [20], and its other biological role in reducing oxidative damage [21].
- Also, C_3O_2 has a red tint to it. Therefore, the molecule could be one of the tholins contributing to Pluto's appearance at its sublimation regions. The reddish tint of the molecule made some early planetary scientists think Mars was predominantly C_3O_2 [22].
- One can calculate the amount formed by calculating the column density, $N = 2.303 \int A(\nu)d\nu / A$, where the numerator is the integrated band area and A is the intrinsic absorbance value. We formed ~1.5-1.8 x 10^{16} molecules cm^{-2} in both experiments. This corresponds to a rate formation of ~3.6 x 10^{14} molecules cm^{-2} min^{-1}. If similar conditions are found on Pluto then based off the time that a particular point on the surface is facing the Sun, we would form ~1.8 x 10^{16} molecules cm^{-2} per Plutonian day or ~1.8 x 10^{-6} g cm^{-2} per Plutonian day.
- Charged molecules were also formed, which may be important for grain chemistry. In the Interstellar Medium, where the gravity of small grains is effectively nonexistent, electromagnetic forces could help or repel other grains or charged ions/molecules.

Discussion

- Other molecules were also formed, of course, but they have been previously observed from similar gas mixtures or experimental conditions. Other astrobiologically relevant molecules include:
  - HNCO → Could be involved in the formation of amino acids.
  - HCN → Could be involved in the formation of either nucleotides or amino acids.
- Slow sublimation produced the cleanest spectra (Fig. 3). Fast sublimation techniques seemed to eject the water molecules along with the other gases that sublimate below 45 K.
- Lastly, the technique proved to be experimentally valuable. It was shown that matrix-isolated molecules could later react upon sublimation and be trapped in a new ice: similar processes may be at work on planetary bodies like Pluto or stellar nurseries.

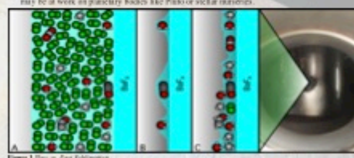

Figure 3 *Slow vs. Fast Sublimation*

(A) The initial deposit containing the 1:1:100 mixtures. (B) Upon quick sublimation, many of the newly formed molecules are also ejected. (C) On the other hand, slow sublimation techniques lead to cleaner spectra and formation of a new ice that traps other chemical species.

Conclusion and Future Work

- C_3O_2, an astrobiologically relevant molecule, was formed upon the sublimation of the N_2 ice, which could be responsible for the observed coloration found on Pluto along with other tholins.
- Negatively charged species were also formed, which may have important implications for grain chemistry.
- Repeating experiments with other matrix materials: CO, CO_2, CH_4, and O_2. Adding other experiment techniques: particle radiation, photon radiation, sublimating non-matrix isolation materials away, introducing new reagents post-sublimation, and so forth. The ultimate goal is to create solid-state analogs of wet lab organic chemistry techniques (Fig. 4).

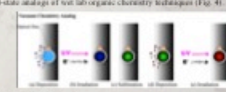

Figure 4 *Utilizing Wet Lab Chemistry Analogs*

(a) The initial deposition could be regarded as an analog for the initial mixing of chemicals, (b and e) irradiation as introducing an energy source, (c) sublimation as evaporation, and (d) further deposition of new reagents as mixing in new chemicals to a reaction vessel.

References

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