PRODUCTION OF HEXAMETHYLENETETRAMINE IN PHOTOLYZED AND IRRADIATED INTERSTELLAR COMETARY ICE ANALOGS

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ABSTRACT

We report hexamethylenetetramine (HMT) detection in organic residues resulting from $H_2O : CO : CH_3OH : NH_3$ ices submitted to UV photolysis or proton irradiation. This is the first time HMT is detected after proton irradiation of an interstellar or cometary ice analog, whereas this molecule was suspected to be a characteristic signature of UV versus ion processing. This result strengthens the probability of HMT presence in the interstellar medium and in comets, where it may eventually be detected with the COSAC (COmetary Sampling And Composition) experiment on board the upcoming *Rosetta* mission.

Subject headings: astrochemistry — comets: general — ISM: molecules — methods: laboratory — space vehicles: instruments

1. INTRODUCTION

Unraveling the nature of the organic components of interstellar dust and comets is critical to understanding the chemical evolution of materials from the interstellar medium to the solar system. A classic laboratory approach to this problem is to start with various ice mixtures at ∼10 K and photolyze with vacuum ultraviolet, irradiate with charged particles, or simply warm the ices, simulating the processing of ice-mantled dust in molecular clouds or the solar system. When warmed to room temperature, these processed icy mixtures leave a residue, which is generally presumed to be a close analog of the organic mantles of dust in molecular clouds (see, for instance, Greenberg 1982, Allamandola, Sandford, & Valero 1988, or Cottin, Gazeau, & Raulin 1999 for reviews on that subject).

Three kinds of energetic processing occur on icy coated dust grains in interstellar clouds or in the outer layers of comet ices in the solar system. In interstellar clouds, icy coated dust particles are subjected to processing by

1. Charged particles: Galactic cosmic rays.
2. UV photons: Lyα photons from neighboring stars in the diffuse outer regions or UV photons induced by Galactic cosmic rays in the inner regions of dense clouds.
3. Thermal processes: cycling between the cold dense cloud center and warmer diffuse regions.

In the solar system, the outer layers of comets undergo the same processes:

1. Charged particles: Galactic cosmic rays, mainly in the Kuiper belt and the Oort clouds. This process has the largest effect on the outer few meters of the nucleus.
2. UV photons: solar UV, mainly in the inner solar system when the comet is close to the Sun. This process would affect the outer few micrometers of the nucleus.
3. Thermal processes: during the formation of the solar system (depending on the region in which the comet accretes) and in the inner Solar system (when the comet approaches perihelion).

As a result of the diversity of environments involved, constraining the degrees to which different processes affect cosmic ices is a highly convoluted problem. Differences between the products synthesized during processing, according to the energy sources, could give information on the history of comets. So far the laboratory experiments have emphasized the analytical method (infrared spectroscopy, liquid and gas chromatography, mass spectroscopy, etc.) to detect the widest range of synthesized molecules rather than the form of the deposited energy (Cottin et al. 1999).

The facilities at NASA's Goddard Cosmic Ice Laboratory are equipped with a Van de Graaff accelerator and a UV lamp system so that ices can be processed using both protons and UV photons. Results can be compared using the same analytical method. Thus, a direct comparison of synthesized compounds is possible, with the aim of finding if the production of a molecule can be an indicator of the processing history of ices. The first set of data comparing UV photolysis and ion irradiation of ices at Goddard showed that the yield of major products was similar for a simple ice containing H_2O and CO_2 (Gerakines, Moore, & Hudson 2000) but different for pure CO (Gerakines & Moore 2001).

Among the complex organic refractory molecules that have been synthesized during cometary and interstellar ice analog experiments, polyoxymethylene [POM; $(CH_2-O)_n$] and hexamethylenetetramine (HMT; $C_6H_{12}N_4$) seem to be of prime interest. POM and polymers of the same family have been detected when ice mixtures containing formaldehyde and ammonia are slowly warmed to room temperature, without any photolysis or ion irradiation processing (Schutte, Allamandola, & Sandford 1993a, 1993b). After UV photolysis of ices such as $H_2O : CH_3OH : CO : NH_3$ (10 : 5 : 1 : 1), POM-like polymers have also been detected, but HMT represents ∼60% of the organic residue at 300 K (Bernstein et al. 1995). Thus, it looks like POM is a good indicator for thermal processing of ices, while HMT plays the same role concerning UV photolysis. HMT is of particular interest since it forms amino acids when acid-hydrolyzed (Wolman et al. 1971).

Bernstein et al. (1995) suggested that ion irradiation of a mixture of $H_2O : CH_3OH : CO : NH_3$ would not lead to the production of HMT. Rather than a conversion of CH_3OH into H_2CO, which is the first step toward HMT formation during photolysis, acetone would form, leading to the production of linear molecules such as polyamino-dimethyl-methylene

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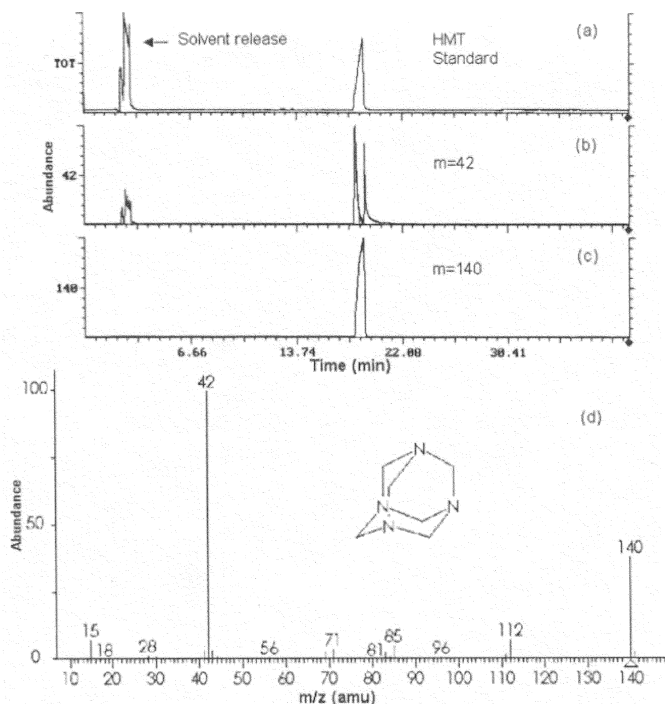
FIG. 1.—Chromatogram of HMT injected in an MXT-1 column (see text for details). (a) Total chromatogram. It shows the sample is released 19 minutes after injection. The same retention time for mass 42 is shown in (b) and for mass 140 in (c). (d) Mass spectrum of HMT (from the National Institute of Standards and Technology Mass Spectral Database). Characteristic peaks for HMT are 42 and 140 amu.

(PADMM; $[-C(CH_3)_2-NH-]_n$). HMT would then be a signature of UV processing, and PADMM a signature of proton processing. This hypothesis originated with a tentative infrared identification of acetone in irradiated water ice containing methanol by Baratta et al. (1994), which was repeated by Moore, Ferrante, & Nuth (1996) and Palumbo, Castorina, & Strazzulla (1999). However, Hudson & Moore (2000), recently showed that there is no evidence of acetone formation in proton-irradiated methanol ices. Instead, H_2CO has now been identified in both $H_2O : CH_3OH$ and $H_2O : CO$ ices. Therefore, HMT formation in proton-irradiated ices was expected in irradiated $H_2O : CH_3OH : CO : NH_3$ ices and has been confirmed by the results reported in this Letter.

For the first time, we present the analysis of two organic residues originating from the same ice composition. One residue was from UV-photolyzed $H_2O : CH_3OH : CO : NH_3$ ice and the second residue from the same ice after ion irradiation. This Letter focuses specifically on HMT formation, in order to check the hypothesis that HMT is a specific signature of UV-processed ice. Analysis of other organic compounds will require new analytical developments and is in progress.

2. EXPERIMENT

The experimental setup has been described in detail by Hudson & Moore (1995) and Moore & Hudson (1998, 2000). A gas mixture is condensed onto an aluminum cold mirror ($T < 20$ K) in a vacuum chamber ($P \sim 10^{-8}$ torr). Gases are mixed in a glass bulb, and the concentration of each is determined by its partial pressure. The resulting ice is assumed to have the same composition as the gas phase. The ice thickness is determined by measuring laser interference fringes during deposition. The typical rate is 3–5 μm hr^{-1}. Ice can be photolyzed

with a UV lamp (average energy: 7.4 eV; flux: $\sim 3 \times 10^{14}$ photons cm^{-2} s^{-1}) or irradiated with 0.8 MeV protons from a Van de Graaff accelerator. Source and purity of used compounds are the following: triply distilled H_2O with a resistance greater than 10^7 ohms cm; CO, Matheson research grade, 99.99%; CH_4, Matheson research grade, 99.999%; NH_3, Matheson anhydrous, 99.99%; CH_3OH, Sigma-Aldrich HPLC grade, 99.9%; HMT, Fluka, greater than 99.5%.

Two sets of experiments have been performed with the same ice composition: $H_2O : CH_3OH : CO : NH_3$ (10 : 5 : 1 : 1). This composition was chosen to be the same as the one studied in Bernstein et al. (1995) and includes the most abundant interstellar and cometary molecules with the exception of CO_2 and H_2 (Ehrenfreund & Charnley 2000). During the first set of experiments, two successive ~ 0.5 μm ice layers were photolyzed each during 9 hr, in order to repeat Bernstein et al. experiment. Ices where very thin to ensure UV processing throughout the whole ice depth. The second experimental set consists of an ~ 10 μm ice sample, irradiated with 0.8 MeV protons. This energy has a penetration range of ~ 20 μm and will process the whole ice depth. Irradiation processing therefore is more efficient than UV processing at producing a larger amount of organic residue. Dose estimates for UV photons are described in Gerakines et al. (2000) and for protons in Moore & Hudson (1998). The proton irradiation dose has been set to be equivalent to the UV energy deposited, i.e., roughly 25 eV molecule^{-1}.

Organic residues were recovered from the aluminum mirror with methanol. Analyses were performed using a Varian Saturn II gas chromatograph–mass spectrometer (GC-MS). GC separations were performed on an MXT-1 (Restek) capillary column (length = 30 m, internal diameter = 0.18 mm, inner coating = 0.6 μm). Analysis settings were: column inlet pressure = 17 psi (relative to the atmospheric pressure), $T_{column} = 60°C$ (0–5 minutes) and then 20°C minute^{-1} until 160°C, $T_{injection} = 300°C$, $T_{transfer to MS} = 200°C$. This column and settings were chosen specifically for the detection of HMT. Detection was performed with a Finnigan-Varian mass spectrometer, with an ion trap (1–650 amu; resolution: 1 amu). Secure GC-MS identification of HMT is achieved by comparing the retention time of standard HMT with the retention time of peaks resulting from the organic residue injected with the same analysis settings and by matching the mass spectrum with the HMT reference mass spectrum (Fig. 1). Blank experiments are performed before each organic sample injection in order to check the contamination level of the column.

3. RESULTS AND DISCUSSION

GC-MS analyses of residues from both UV-photolyzed and ion-irradiated $H_2O : CH_3OH : CO : NH_3$ ices are shown in Figure 2. Concerning the UV sample, there is no clear indication of HMT in the total chromatogram (Fig. 2a). This is due to the very low amount of residue recovered after the photolysis experiment. Nevertheless, its presence is clearly revealed on the specific plots (Figs. 2b and 2c) for masses 42 and 140 (main HMT MS fragments), both of which show a peak at the same retention time as measured for the HMT standard. The peculiar shape of the peaks is not clearly understood. It is probably due to the high polarity of amino groups such as in HMT, which interact badly with stationary phases of GC columns. Identification of HMT is confirmed by the mass spectrum sampled on peaks 42 and 140 attributed to HMT (Fig. 2d). Masses detected with amu > 140 are due to recombination in the ion
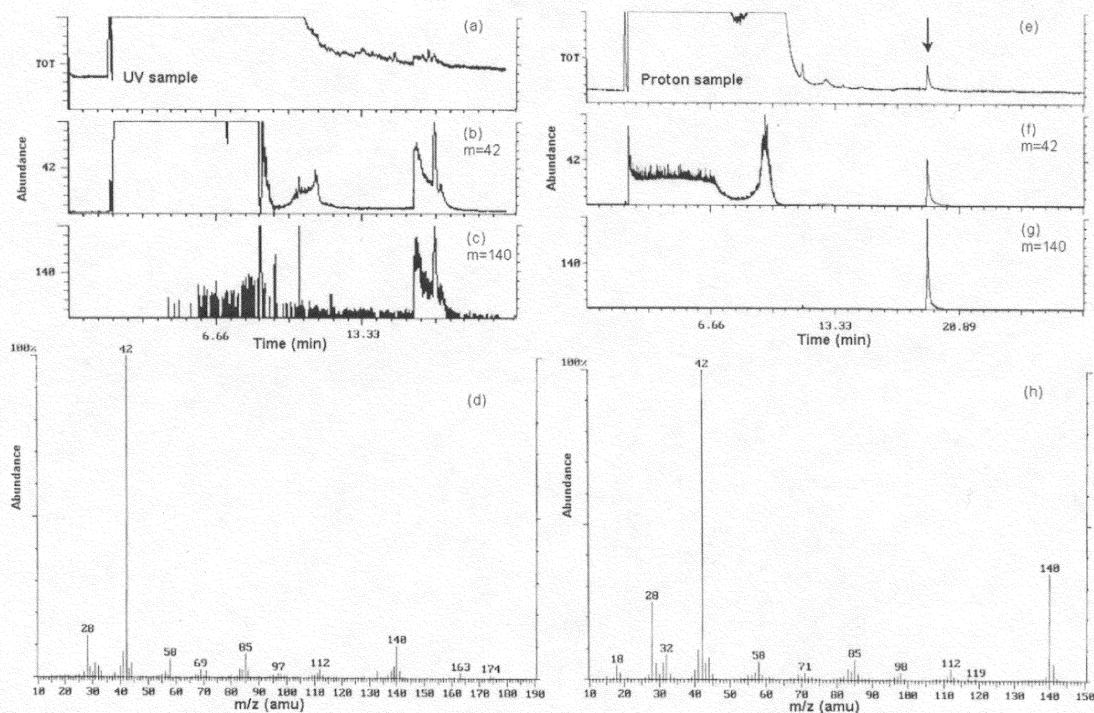
FIG. 2.—Chromatograms collected during analysis of UV-processed residue (*left panels*) and proton-processed residue (*right panels*). Upper panels are the total chromatogram compared to the two characteristic masses of HMT 42 and 140. Lower panels show the mass spectra corresponding to the peaks associated to HMT.

trap of the spectrometer. This detection is consistent with Bernstein et al. (1995).

The proton-processed ice was much thicker than the UV one; therefore, the amount of residue is larger, ensuring a better signal, as shown in the right panels of Figure 2. HMT is clearly detected in the total chromatogram thanks to its retention time, 19 minutes (Fig. 2e). This detection is confirmed by specific plots for masses 42 and 140 (Figs. 2f and 2g) and by the mass spectrum sampled on the peak attributed to HMT (Fig. 2h). No trace of substituted HMT (HMT skeleton with a CH_3, OH, CHO, or COOH group instead of one H, which should result in a parent mass of 154, 156, 168, and 184, respectively) has been so far detected in our samples (spectra not shown).

Thus, HMT is detected in both samples and should henceforth not be considered as a characteristic signature of a specific process. According to the mechanism described in Bernstein et al. (1995), the first stage toward its synthesis is the production of H_2CO by oxidation of CH_3OH. This can be achieved by UV photolysis (Allamandola et al. 1988) or proton irradiation (Hudson & Moore 2000). But CO in water also produces formaldehyde by UV (Allamandola et al. 1988) or proton processes (Moore, Khanna, & Donn 1991). Experiments starting with ^{13}C-labeled methanol reported in Bernstein et al. indicated that the carbon in HMT originated from methanol rather than from CO. But this is certainly due to a more efficient conversion rate of methanol into formaldehyde than CO into formaldehyde. Then ices containing only one carbon source (CO or CH_3OH) should yield production of HMT but with a higher efficiency with CH_3OH. Addition of CO_2 in the initial ice mixture should not induce any effect regarding HMT production as no detectable amount of H_2CO is reported after UV (Gerakines et al. 1999) or proton (Moore et al. 1991; Brucato, Palumbo, & Stazzulla 1997) irradiation of $H_2O : CO_2$ ices.

Our results strengthen the probability for the presence of HMT in the interstellar medium as being one product of radiation chemistry (UV and charged particles) between the most abundant interstellar molecules detected so far. But its actual IR detection is jeopardized since its strongest infrared bands at ~10 μm overlap the Si−O silicate band (Bernstein et al. 1994, 1995). Its detection on comets from remote sensing has the same difficulties. Bernstein et al. (1995) suggested that the degradation of HMT on cometary grains ejected from the nucleus could possibly be responsible for the extended source of the CN radical observed in comet Halley (Klavetter & A'Hearn 1994). This could be an interesting indirect detection of HMT. But Cottin et al. (2001) have tested this hypothesis regarding the photostability of HMT and its photodegradation products and concluded that the photolysis of HMT is very unlikely to account for the amount of extended CN in comets. Nevertheless, the idea of thermal degradation of HMT on very hot cometary grains remains to be investigated in the laboratory. Indeed, HMT is known to decompose into amines and nitriles at temperatures as low as 500 K (Iwakami, Takazono, & Tsuchiya 1968), a temperature that could easily be reached by small grains in cometary comae (Crifo 1988; Greenberg & Li 1998).

The coming in situ investigation of a cometary nucleus (46P/Wirtanen) with the ESA *Rosetta* mission will search for complex organics. The COSAC (COmetary Sampling And Composition) experiment (Rosenbauer et al. 2001) on board the *Rosetta* lander includes a gas chromatography system devoted to the analysis of the nucleus molecular composition (Szopa et al. 2000). One of the columns selected to be used in the experiment is an MXT-1, similar to the one we used for our laboratory analysis of HMT, with some differences: length = 10 m, internal diameter = 0.18 mm, and inner coating = 0.1 μm. If present on P/Wirtanen in sufficient amounts, HMT should then be detected, as shown in Figure 3.
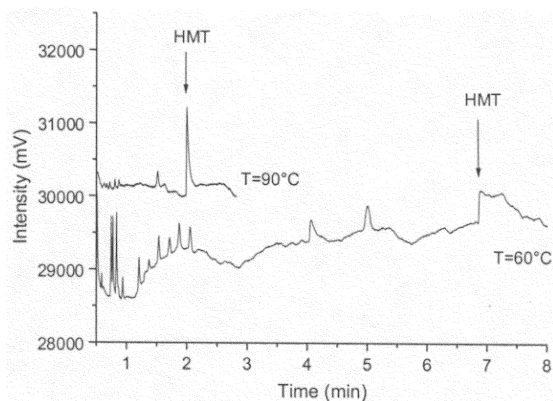
Fig. 3.—HMT injected along with other organic compounds expected to be present on a cometary nucleus (including benzene, toluene, pyridine, octane, nonane, decane, pentanol, xylene, naphtalene, indene, and trioxane). The top chromatogram was collected at $T = 90°C$ and the bottom one at 60°C, on the same MXT-1 column as the one selected to be part of the COSAC experiment on board the *Rosetta* lander. Length = 10 m, internal diameter = 0.18 mm, and inner coating = 0.1 μm. The analysis has been performed within the spatial requirement of the mission (T between 30°C and 90°C).

If not, a compound such as HMT, likely to be synthesized by proton and UV irradiations in the interstellar medium, might have been destroyed during the collapse of the presolar cloud or in the early turbulent nebula. Indeed, temperatures above 800 K are necessary to produce the crystalline phase silicates observed in comet Hale-Bopp (Crovisier et al. 1997). Temperature $T > 800$ K is consistent with estimations of conditions in the inner presolar nebula (Mousis et al. 2000). They are sufficient to destroy HMT (Iwakami et al. 1968). The nondetection of HMT could therefore be an indication that most of the interstellar material has been reprocessed at high temperature before the accretion of the comet and that mainly thermal processes dominated comet P/Wirtanen ices history.

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