



## Experimental study of the degradation of polymers: Application to the origin of extended sources in cometary atmospheres

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**Abstract**—This paper presents some preliminary results concerning the degradation of refractory nitrogenated polymers, which could be responsible for the CN extended source in comets. We are studying hexamethylenetetramine (HMT) and HCN polymers. Both compounds have been irradiated or heated to simulate the degradation processes they undergo in the cometary atmosphere. We show that, even if both compounds are quite stable under photolysis, the heating leads to a much more efficient degradation with the formation of HCN, NH<sub>3</sub>, and other heavier compounds. Moreover, the thermal degradation of HCN polymers appears to be more efficient than that of HMT. Thus, the HCN polymers seem to be better candidates for the CN extended source. We are now developing a new reactor to quantify the production of gaseous molecules and to detect in situ CN radicals.

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### INTRODUCTION

Most of the gaseous material present in the coma of comets is directly released by the sublimation of the nucleus, and the main fraction of the observed radicals results from the photodissociation of gaseous “parent” molecules. However, some of these species have spatial distributions different from those expected for molecules directly ejected from the nucleus, which cannot be explained by these processes. They appear to arise from a “distributed source” or “extended source” in the coma, as observed for the spatial distribution of CO (Eberhardt et al. 1987) and H<sub>2</sub>CO (Meier et al. 1993) measured in situ by the Giotto neutral gas mass spectrometer (NMS). Other molecules (OCS [DelloRusso et al. 1998], HNC [Irvine et al. 1998]), as well as radicals (CN [Fray Forthcoming; Klavetter and A’Hearn 1994], C<sub>2</sub>, and C<sub>3</sub> radicals [Festou 1999]) also represent an extended source in different comets. The origin of these extended sources is not fully understood.

Knowledge of the physical and chemical processes involved in the origin of these extended sources is one of the challenging issues of cometary science because the study of these processes is a way to derive the molecular composition of the nucleus from the chemical composition observed in the coma. Several mechanisms have been proposed to explain these puzzling observations. Gaseous molecules may be released during the fragmentation of grains ejected from the nucleus. Another viable hypothesis is the degradation of high

molecular weight organics coating the grains. This degradation can be due to photolysis by solar UV and/or pyrolysis caused by solar heating of the grains as they are released from the nucleus. Unfortunately, the lack of both qualitative and quantitative experimental data makes it impossible to model gas production from grains in the cometary environment by any of these mechanisms. To address this problem, we are developing experimental methods to measure the chemical parameters necessary to model these solid-gas processes. We have begun to study the photo and thermal degradation of solid and macromolecular organic materials to determine the yields of gaseous products formed, the quantum yields for photolysis, and the kinetics of the thermal degradation.

Astronomical observations and laboratory simulations have shown that polyoxymethylene—a polymer of formaldehyde (–CH<sub>2</sub>–O–)<sub>n</sub>, also called POM—could be present on cometary grains (Huebner et al. 1988; Schutte et al. 1993). POM is often proposed to explain the formaldehyde (H<sub>2</sub>CO) extended source (Meier et al. 1993; Eberhardt et al. 1999) because solid POM is known to readily produce formaldehyde when heated as it is in equilibrium with gaseous formaldehyde (Dainton et al. 1959). We have measured the kinetic parameters of the POM degradation, and these new experimental data have been incorporated into a physico-chemical model of the coma. This model simulates the production of gaseous H<sub>2</sub>CO via multiphase chemistry—POM in the solid state on cometary grains is slowly degraded

by solar photons and heat to produce gaseous  $\text{H}_2\text{CO}$ —and is in good agreement with the Giotto spacecraft observations if we assume that the cometary grains contain a few percent POM by mass (Cottin et al. 2001a, 2004). The results indicate that thermal degradation of POM is a more important process than photodegradation at 0.9 AU from the sun. This study demonstrates that the production of gaseous molecules from the solid phase should be taken into account in coma models to fully understand the origin of extended sources.

We are now investigating the degradation of some nitrogen-containing compounds to explain the CN extended source. In this article, we present the preliminary qualitative results of this new study. The primary goal is to determine which solid compounds can be decomposed into smaller gaseous molecules and at what temperature. This information should help us better assess which compounds may be responsible for the CN extended source.

### THE TARGET MOLECULES

We are studying two nitrogen-containing materials, HCN polymer and hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ), as possible contributors to the CN extended source.

#### Hexamethylenetetramine (HMT)

Hexamethylenetetramine, or HMT (Fig. 1), has been detected (Bernstein et al. 1995) after an irradiation at 122 nm of interstellar ice analogues containing  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ , and  $\text{NH}_3$  at low temperatures. It was found that HMT represented up to 60% of the solid residue remaining after warming of the photolysis products to room temperature (Bernstein et al. 1995). Moreover, Cottin et al. (2001c) have shown that HMT can also be produced by proton irradiation of the same starting ice mixture composition. Although HMT has not been detected in the cometary environment so far, since it is present in interstellar ice analogues, its presence in comets seems reasonable. Because of this and its chemical structure, HMT was investigated as a possible candidate for an extended source parent of the CN radicals.

A few studies have already focused on the degradation of HMT by photolysis or heating. For example, Bernstein et al. (1994) have studied the photolysis of HMT in an argon matrix and in frozen water and detected  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and some methylamines ( $\text{R}_2\text{-N-CH}_3$ ), nitriles ( $\text{R-CN}$ ), and isonitriles ( $\text{R-NC}$ ). Iwakami et al. (1968) have studied the thermal degradation of HMT and have detected ammonia ( $\text{NH}_3$ ), methane ( $\text{CH}_4$ ), acetonitrile ( $\text{CH}_3\text{-CN}$ ), and some amines ( $\text{R-NH}_2$ ). Unfortunately, none of these experiments was designed to detect CN radicals.

#### HCN Polymer

The presence of HCN polymers in cometary nuclei was first suggested by Matthews and Ludicky (1986). Since then,

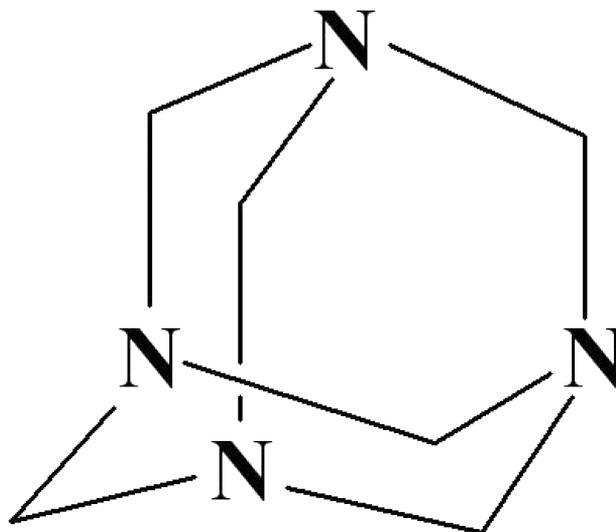


Fig. 1. Structure of hexamethylenetetramine.

a number of investigators have lent support to this idea. From the mass spectrum obtained with the PICCA instrument on the Giotto spacecraft, Huebner et al. (1989) proposed that HCN polymers could fit the observed data. Combes et al. (1988) have also reported the detection of a weak  $4.45 \mu\text{m}$  emission band in the infrared spectra of Halley acquired by IKS on Vega 1 and tentatively identified as a CN stretch. Cruikshank et al. (1991) inferred the presence of CN groups containing molecules on the dust of some comets through spectroscopic detection of the  $2.2 \mu\text{m}$  overtone of the CN stretching fundamental mode. Cruikshank et al. (1991) suggested that these  $2.2$  and  $4.45 \mu\text{m}$  bands were possibly due to HCN polymers. But if HCN polymers are present on cometary nuclei, a production process has to be found within the nucleus or precometary ices.

In the laboratory, liquid HCN polymerizes spontaneously in non-aqueous solvents or in water (Völker 1960). Hydrogen cyanide polymers—heterogeneous solids ranging in mass from the tetramer to macromolecules containing at least 30 HCN units and ranging in color from yellow to orange to brown to black—are readily hydrolyzed to yield  $\alpha$ -amino acids and nitrogen heterocycles, including purines and pyrimidines found in nucleic acids today. In spite of extensive efforts by Miller, Ferris, Matthews, Minard, and others, a complete structural understanding of HCN polymer eludes us. Several hypothetical models have been proposed (Minard et al 1998) but will not be given or discussed here. HCN polymer is also formed when methane and ammonia mixtures are converted to hydrogen cyanide by electric discharges (Matthews and Ludicky 1992). Thus, HCN polymers could be formed in cometary nuclei by interactions between hydrogen cyanide, methane, and ammonia with energetic particles and UV photons. Moreover, Rettig et al. (1992) have shown that HCN polymerization can be initiated in the cometary nucleus by HCN photoexcitation or heating. In spite of the fact that

there is no direct proof that HCN polymer is present on cometary nuclei, this hypothesis cannot be ruled out.

These polymers have indeed been proposed as a source for the observed CN, NH<sub>2</sub>, and C<sub>2</sub> jets (Huebner et al. 1989; Schulz and A'Hearn 1995). Calculations of the required energy for photodissociation have shown that the production of CN and NH<sub>2</sub> may be easier from these polymers than from HCN and NH<sub>3</sub> (Rettig et al. 1992). Similar to HMT, the HCN polymer appears to be a good candidate for the source of CN radicals in comets. To date, no study had been performed to investigate the decomposition of these compounds under cometary conditions.

Since HMT and HCN polymer could be readily formed under astrophysical conditions and can be easily degraded by photolysis or heating, we studied the degradation of these solids to better understand their possible contribution to the CN extended source phenomenon. Initial results are presented in this paper.

## DEGRADATION EXPERIMENTS

SEMPhOrE Cometaire (French acronym for Experimental Simulation and Modelling Applied to Organic Chemistry in Cometary Environments), a program developed in our laboratory, is dedicated to the study of photo and thermal degradation of polymers and, generally, of any kind of solid molecules under temperature and pressure conditions relevant to the cometary environment. In this section, we present our experimental setup protocol.

### Chemicals

We used commercial HMT (>99.5%, Fluka) for all experiments. R. Minard synthesized HCN polymer. HCN polymerization is catalyzed by traces of various bases such as ammonia or triethylamine and occurs in a variety of organic solvents, in water, or without solvent. The polymer used in the experiments was prepared by adding 50  $\mu$ L of triethylamine base catalyst to 1 g of neat liquid HCN (no solvent) to initiate polymerization, which occurred at room temperature over 2 to 3 days to give a black solid, (HCN)<sub>x</sub>. For both samples, the vapor pressure is negligible, and we detected no spontaneous degradation at ambient temperature.

### Photodegradation

The experimental setup for the photodegradation study consists of a UV lamp and a temperature-controlled photochemical reactor as shown in Fig. 2. The photochemical reactor, in which solid materials are irradiated, is equipped with two vacuum stopcocks: one leads to the analysis system, and the other one leads to a pumping system (TSH 065 D, Pfeiffer) consisting of a membrane pump (MZ 2T) and a turbomolecular pump (TMH 065). The reactor has a glass

jacket to allow temperature regulation. Generally, during an irradiation, the temperature is set at 300 K. The pressure inside the reactor is measured by a Baratron sensor (MKS 627A-01TDC) ranging from 10<sup>-4</sup> to 1 mbar. A vacuum better than 10<sup>-4</sup> mbar is achieved in the reactor after one night of pumping.

The UV lamp is filled with an appropriate gas or gas mixture according to the wavelength(s) desired (H<sub>2</sub>/He: 122 nm, Xe: 147 nm, and CH<sub>4</sub>/He: 193 nm). A microwave discharge inside the lamp is initiated with a Tesla coil. Titanium wires within the lamp can be heated to purify xenon during emission at 147 nm. The lamp could be equipped with two different windows (diameter of 19 mm): MgF<sub>2</sub> for transmission of 122 and 147 nm lines and SiO<sub>2</sub> for selective transmission of the 193 nm line of CH<sub>4</sub>. For each wavelength, the UV flux measured by chemical actinometries is given in Fig. 2.

The reactor is connected directly to an analysis system to detect the gaseous molecules produced during the irradiation, or to a liquid nitrogen cold trap to concentrate the resulting gas mixture before analysis, and to permit a more efficient detection of minor compounds.

### Thermodegradation

As HMT and HCN polymers are stable at room temperature, we have used a pyrolyser (SGE pyrojector II), which can reach 1000 °C (Fig. 3), to study their thermal degradation, rather than the experimental setup, which had been used for the study of POM (Cottin et al. 2001a, 2004). The solid sample is placed into a small quartz tube, which is attached at the end of an injection syringe. The syringe is attached to the injector, and the plunger is depressed to move the sample tube to a quartz-lined furnace. The temperature of the furnace is constant during an experiment, and it is measured with a thermocouple inside the furnace. The gaseous products of the pyrolysis are swept by nitrogen through a transfer tube and into the analysis system. The pressure of nitrogen inside the furnace is slightly higher than 1 bar to prevent contamination by the atmosphere. Unfortunately, the diffusion of the gaseous products inside the quartz tube appears to vary widely. So, at this point, we can only identify the nature of the degradation products and cannot determine the kinetics of the reaction. While rapid heating and high nitrogen pressures are undoubtedly not relevant to the cometary environment, the qualitative results we can derive from these experiments are a necessary step toward further investigations.

### Analysis

The degradation products are analysed with three different and complementary systems: a mass spectrometer (MS), a gas chromatograph coupled with a mass spectrometer (GC-MS), and a Fourier transform infrared spectrometer (FTIR).

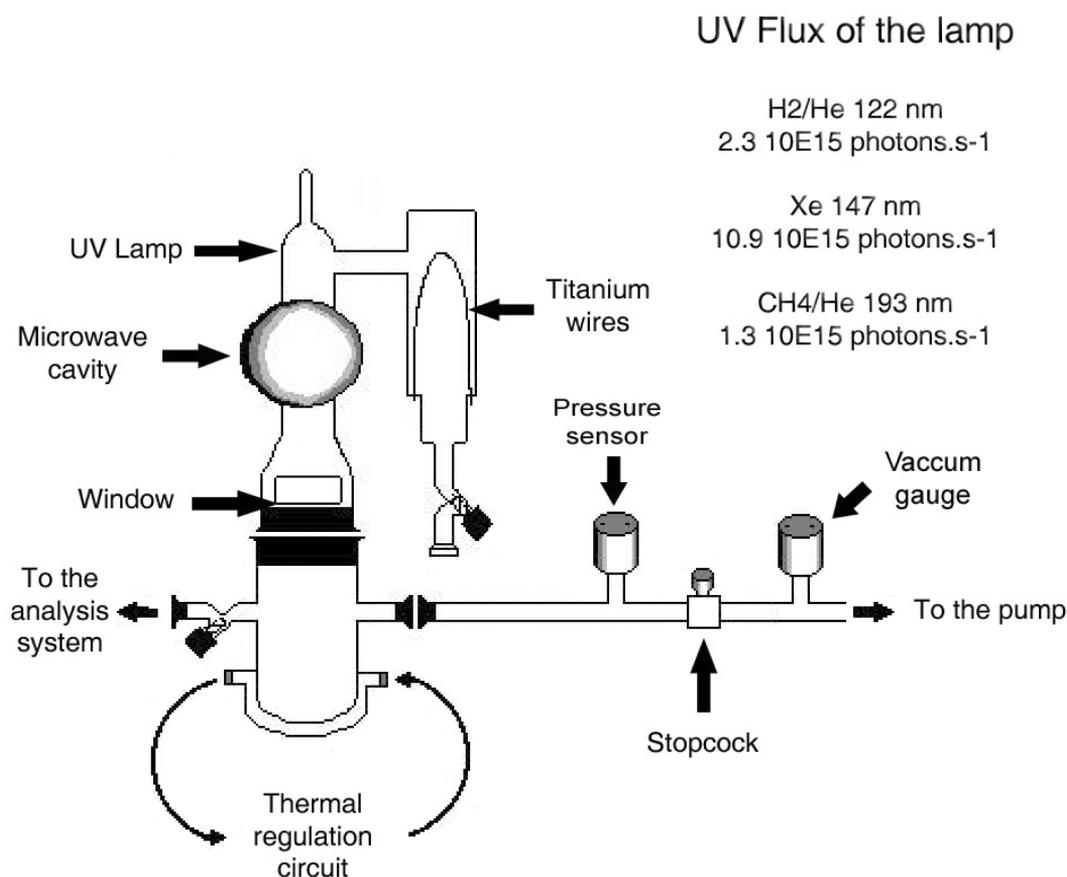


Fig. 2. Photodegradation experimental setup organization.

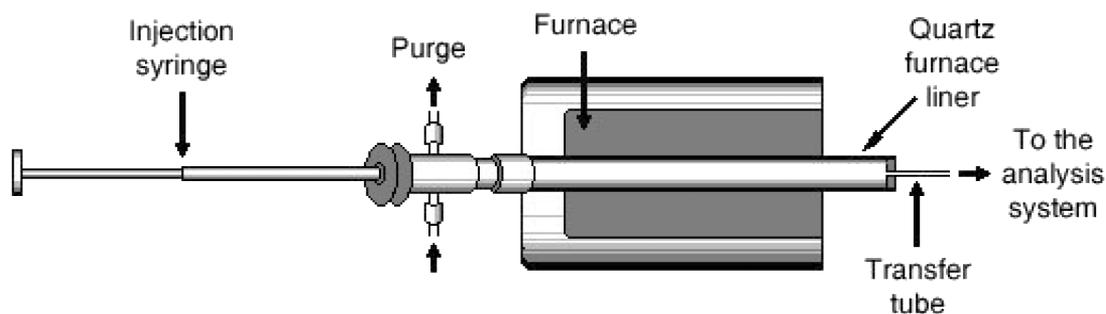


Fig. 3. The pyrolyser.

The mass spectrometer (Leybold, Transpector) has a mass range of  $m/z$  1 to 200 with a resolution of 1 amu and is directly connected to the reactor through a vacuum line. This technique is very sensitive, but since there is no separation of the different products before analysis, the presence of a product is inferred from the presence of key fragments observed that are somewhat unique to that product.

We have also used a GC (Varian 3400) equipped with an apolar column (MXT-1/Restek: 0.18 mm internal diameter;

30 m long; 0.6  $\mu\text{m}$  film thickness). The detector is an ion trap mass spectrometer (Finnigan-Varian) with a scan range of  $m/z$  1 to 650 at a resolution of 1 amu. The pyrolyser can be directly connected to this GC through a septum, but, in the case of irradiation experiments, concentration of the gaseous products in a cold trap is required. This kind of analysis allows us to identify all the degradation products but does not allow kinetics studies of the degradation process.

The infrared spectrometer is a Brüker Equinox 55 with a

wavenumber range of 350 to 7000  $\text{cm}^{-1}$  and a resolution of 0.5  $\text{cm}^{-1}$ . It is equipped with a multireflection cell (2.6 liters) with an optical path ranging from 2.1 to 10.6 m. The reactor and the pyrolyser can be directly connected to this cell.

## RESULTS

### HMT

HMT has been irradiated under vacuum at 122 and 147 nm at reactor pressures of less than  $10^{-4}$  mbars. During irradiation, no products were detected by directly coupled MS analysis. To reach a better detection limit, a liquid nitrogen cold trap was used to concentrate the products and produced a lower detection limit by FTIR spectrometry than by MS analysis. After two hours of irradiation performed at 147 nm, HCN is detected by FTIR analysis. Unfortunately, its amount is too low to be quantified (Cottin et al. 2002). At 122 nm, no products have been detected, probably because the lamp flux is lower at this wavelength than at 147 nm. These results are different from those obtained by Bernstein et al. (1994) in frozen water or argon matrix, which produced  $\text{CH}_4$ ,  $\text{NH}_3$ , and heavier compounds such as  $\text{CH}_3\text{NH}_2$ . When we performed irradiation at 147 nm with 0.1 mbar of water vapor for 6 hr, we detected HCN by its signature at 713  $\text{cm}^{-1}$  and  $\text{NH}_3$  by its signature at 967 and 929  $\text{cm}^{-1}$ . GC-MS analysis indicated some heavier compounds were produced, and one of these was tentatively identified as  $\text{CH}_3\text{CN}$  (Cottin et al. 2002).

In the pyrolysis of HMT, no products were detected by FTIR and GC-MS analysis at temperatures lower than 300 °C. At 350 °C, several compounds are identified by FTIR analysis: HCN,  $\text{NH}_3$ , and  $\text{CO}_2$  (Fig. 4).  $\text{CO}_2$  is not a degradation product of HMT. The  $\text{CO}_2$  could arise from the incomplete purge of the FTIR spectrometer or from desorption of this gas that had been adsorbed on the sample from the exposure to the atmosphere. A complex feature between 2300 and 2220  $\text{cm}^{-1}$  could not be readily interpreted, but it is probably attributable to a nitrile (R-CN) or isonitrile (R-NC). GC-MS analysis shows that some heavy compounds are produced by the heating of HMT at 350 °C (Fig. 5), and several components were identified from their mass spectra observed at a given retention time. The mass spectrum of the second chromatographic peak is presented in Fig. 6 and matches that of triazine ( $\text{C}_3\text{H}_3\text{N}_3$ ). The last peak has been attributed to HMT that was vaporized at this temperature.

### HCN Polymer

We have irradiated the HCN polymers at 147 and 193 nm. After eight hours of irradiation at 147 nm, HCN (by its signature at 713  $\text{cm}^{-1}$ ) and  $\text{C}_2\text{H}_2$  (by its signature at 730  $\text{cm}^{-1}$ ) are detected in very low amounts. No products are detected during an irradiation at 193 nm, either because the

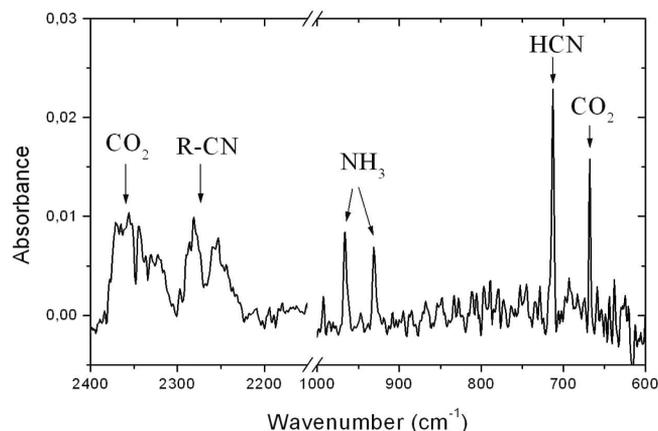


Fig. 4. FTIR spectrum of the thermal degradation products of the HMT at 350 °C. The resolution of the spectrum is 2  $\text{cm}^{-1}$ .

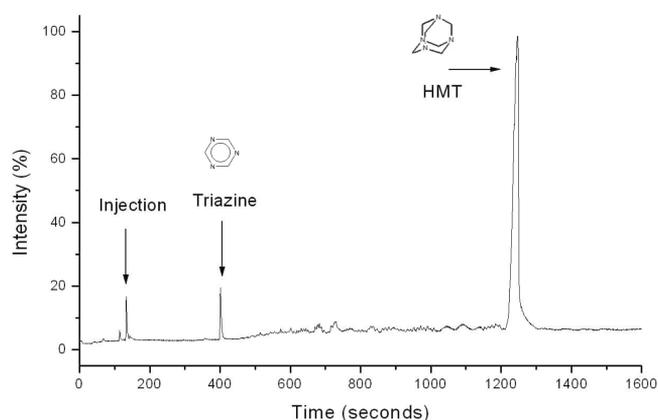


Fig. 5. Chromatogram of the thermal degradation products of HMT after pyrolysis at 350 °C.

lamp flux is significantly lower than for the 147 nm lamp or because the quantum yield decreases for longer wavelengths.

No product of HCN polymer thermal degradation is detected by FTIR or GC-MS analysis for temperatures lower than 200 °C. Above 200 °C, we observe the signature of several compounds: HCN,  $\text{NH}_3$ ,  $\text{CO}_2$ , and traces of triethylamine used as the base catalyst for the polymerization (Fig. 7). As mentioned earlier, the detected  $\text{CO}_2$  is certainly due either to an incomplete purge of the spectrometer or to desorption of this molecule previously adsorbed on the sample. Thus, HCN and  $\text{NH}_3$  seem to be the main products produced by the thermal degradation of HCN polymer.

### Discussion

These preliminary results show that hexamethylenetetramine and HCN polymers seem to be quite stable to direct photolysis since photodegradation products are detected at very low amounts. A comparison of the present

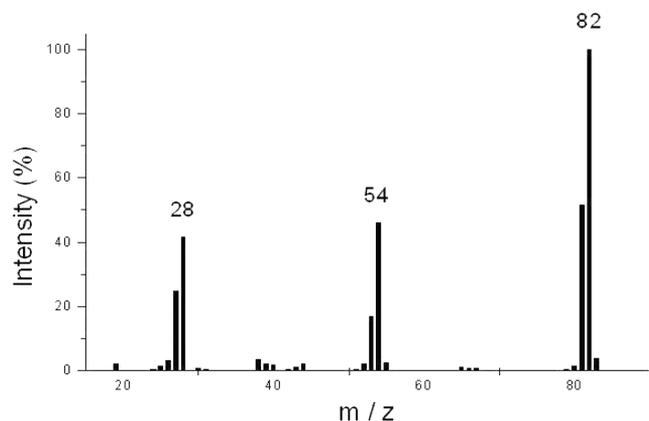


Fig. 6. Mass spectrum corresponding at the second peak of the chromatogram, triazine.

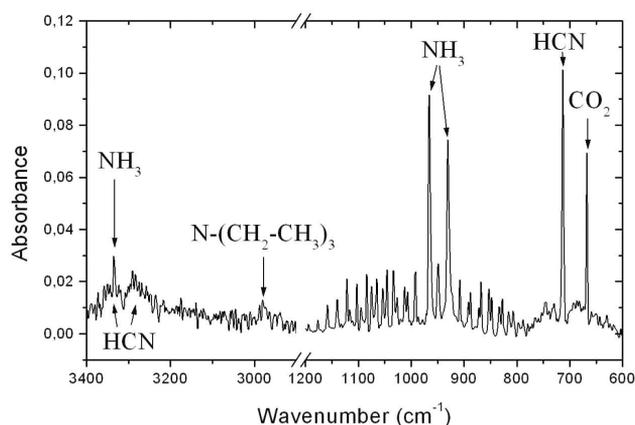


Fig. 7. FTIR spectrum of the degradation products of HCN polymers at 200 °C. The resolution of the spectrum is 2 cm<sup>-1</sup>.

study and the previous one performed on POM (Cottin et al. 2000) with the same apparatus leads to an estimate of the quantum yields for HCN and NH<sub>3</sub> production from HMT and HCN polymer being lower than 0.1. As in Bernstein et al. (1994), we detect nitriles and other N-bearing molecules. But, according to their results, photolysis of HMT should be more efficient than what we obtain. We think that the detection of most degradation products reported by Bernstein et al. (1995) when HMT is irradiated in an Argon matrix could be due to the trace amount of water evoked by the authors. Perhaps the degradation is enhanced by the presence of water ice or water vapor. HMT is more easily degraded by energetic H atoms or OH radicals produced from the photodissociation of water (Cottin et al. 2002).

The thermal degradation of HCN polymer seems to be more efficient than the one of HMT. Products are detected at lower temperature than for the HMT thermal degradation. Thus, HCN polymer seems to be a better candidate than HMT as the origin of the CN extended source in comets.

Although the temperature of degradation of these

compounds is high, it is relevant to the cometary environment since small grains, which are present in the coma, can reach temperatures higher than 300 °C at 1 AU from the sun (Lamy and Perrin 1988; Greenberg and Li 1998).

A question still remains: are HCN and NH<sub>3</sub> directly produced from HCN polymer and HMT or are these compounds a recombination of radicals we are not yet able to detect? This is a key question in the frame of the study of CN extended sources. We are currently developing a new reactor to be able to slowly heat solid compounds under a vacuum. Moreover, this reactor will be equipped with windows to be able to detect radicals in situ by LIF (laser induce fluorescence) or CRDS (cavity ring-down spectroscopy). It will also allow us to measure the kinetics of thermal degradation of solid compounds into gaseous molecules.

## CONCLUSION

In conclusion, just as previous studies have shown that thermal degradation of cometary grains containing a few percent POM can explain the extended source of H<sub>2</sub>CO, this preliminary study has shown that thermal degradation of nitrogen-containing organic molecules or macromolecules has to be considered to understand the origin of extended CN sources.

Initial results indicate that HMT and HCN polymer are quite resistant to direct photolysis and that thermal degradation seems to be more efficient. Moreover, it appears that the degradation of HCN polymer is easier than that of HMT. Thus, HCN polymer seems to be a better candidate as a parent molecule for CN extended sources.

Due to a range of temperatures different than those used to study POM degradation, our present experimental setup does not allow us to quantify the production of gaseous products of thermal degradation. Moreover, to relate our experimental results to the cometary environment, it would be desirable to detect CN radicals. Thus, we are now developing a new reactor that will be dedicated to the study of thermal degradation of solid compounds at high temperature and be able to detect in situ the CN radical by LIF (laser induce fluorescence) or CRDS (cavity ring-down spectroscopy). This should provide the quantitative kinetic and product distribution data required to model the production of the CN extended sources from the degradation of HMT and/or HCN polymer.

*Editorial Handling*—Dr. Scott Sandford

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