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S.E.M.A.Ph.Or.E COMETAIRE, a Tool for the Study of the Photochemical decomposition of Probable Large Organic Molecules in Comets. First Application: Polyoxymethylene

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Abstract. This paper presents a current experimental program concerning the study of the photochemical evolution of the organic matter ejected from the cometary nucleus. The aim of the work is to better understand, using laboratory simulations, the mechanisms which are involved in the degradation of the high molecular weight organics in cometary ices and dust when they are submitted to the warming up and to the bombardment of photons in the surrounding area of the Sun. This experimental study will establish correlations between the nucleus and the molecular composition of the coma. Furthermore, experimental data will provide useful information to bring to a close the question of the origin of the extended sources of H_2CO and CO . Polyoxymethylene, suspected to be present in the cometary nucleus, is often mentioned as a possible parent molecule for the extended source of H_2CO . In order to test this hypothesis, irradiation of POM has been performed at 147 nm. The preliminary results show effectively H_2CO as one photodegradation product as well as CO , CO_2 and $HCOOH$. Tentative detections of CH_3OCH_3 , $CH_3OCH_2OCH_3$, CH_3OCHO and C_3H_6O , are also presented. © 1999 Elsevier Science Ltd. All rights reserved

1 Introduction

Comets are objects that should have kept a lot of key information about the formation of our Solar System. In the Oort's Cloud or the Kuiper Belt, they've been held in the furthest and coldest regions of the Solar System. Thus they may be composed of the most pristine material we can access. After collisions or gravitational perturbation they leave their original orbit, for a more eccentric trajectory that drives them closer to the Sun, where they are heated and develop a coma which splits into two tails.

Although more than twenty parent molecules have already

been detected in the gaseous phase (Crovisier, 1998), we note that there is no direct information on the chemical composition of the nucleus. In order to get further indications, experimental simulations on cometary ice analogs have been carried out. Most of them are based on Greenberg's model of cometary nuclei which suggest that comets are made of interstellar dust (Greenberg, 1984). Molecules formed in molecular clouds condense on silicate cores and are irradiated by UV and/or galactic cosmic rays in the interstellar medium. The laboratory experiments simulate these processes, which lead to the formation of a mantle of complex refractory organics, called "Yellow Stuff" (see for instance (Hagen et al., 1979) for one of the first publication on that topic). Afterwards, when the cloud collapses to form a new planetary system, the grains may accrete together with their organic mantle. Looking at the list of organic compounds which have been identified in the experimental simulations, one can expect that many more compounds than those already detected should also be present in cometary nuclei. Nevertheless, some of them, with high molecular weight, will never be detected in the gaseous phase because their vapor pressures are too low. Only degradation products of these molecules could be detected by remote observations.

The daughter molecules produced by reaction in the coma can present an extended source in the coma. This is the case of formaldehyde (H_2CO) in comet Halley (Meier et al., 1993), and in comet Hale-Bopp. Since Polyoxymethylene (POM), a polymer of H_2CO , has been tentatively detected by (Huebner et al., 1989) in comet Halley, it is often evoked as a parent molecule of formaldehyde to explain its extended source (Biver, 1997; Greenberg and Li, 1998; Meier et al., 1993).

In this paper, we will discuss in further detail the organic molecules detected in cometary atmospheres and those suspected to be present in the nucleus using experimental simulations. We will also present our experimental work, developed to study the link between solid and gaseous

molecules upon UV irradiation. The first results on POM photodegradation at 147 nm are presented.

2 Observations and Experimental Simulations

Reviews about cometary volatiles discuss observational constraints and uncertainties (Bockelée-Morvan, 1997; Crovisier, 1997). Table 1 presents all molecules detected in gaseous phase to date, including those detected in Hale-Bopp, and their abundance relative to water. The large array of values for some compounds are due to differences among comets and the use of different observational methods.

Compound	Abundance	Method
H ₂ O	100	IR, MS, OH(UV/Radio)
CO	2-30 *	UV, IR, NMS, Radio
CO ₂	2-10	IR, NMS, CO
H ₂ CO	0.03-4 *	IR, Radio, NMS, IMS
CH ₃ OH	1-7	IR, Radio, NMS, IMS
HCOOH	0.1	Radio
CH ₃ OCHO	0.15	Radio
CH ₄	0.7-2	IR, IMS
C ₂ H ₆	0.4	IR
C ₂ H ₂	0.2-0.9	IR
Phenanthrene	0.15	UV
NH ₃	0.1-1	NH, NH ₂ (UV / vis), IMS, NMS, Radio
HCN	0.05-0.2	IR, Radio, NMS, IMS
HNC	0.0096	Radio
CH ₃ CN	0.01	Radio
HC ₃ N	0.01	Radio
N ₂	0.02-0.2	N ₂ ⁺ (vis.)
NH ₂ CHO	0.1	Radio
H ₂ S	0.1-0.6	Radio, IMS, NMS
H ₂ CS	0.01	Radio
CS ₂	0.1	CS (UV)
S ₂	0.005-0.05	UV
OCS	0.1	IR, Radio
SO ₂	0.15	UV, Radio

Table 1. Molecular abundances in comets relative to water. NMS and IMS mean Neutral/Ion Mass Spectrometer and refer to in-situ measurement in comet Halley. When a molecule is indicated in the Method column it means that the detection is indirect from photodecomposition products. There is a * for molecules which present an extended source in comae. Table based on (Bockelée-Morvan, 1997; Crovisier, 1994), (Moreels *et al.*, 1994) for Phenanthrene, and updated for recent detections in comet Hale-Bopp (HCOOH: (Wink *et al.*, 1997), CH₃OCHO: (Colom *et al.*, 1997), HC₃N: (Lis *et al.*, 1997), NH₂CHO: (Mehring *et al.*, 1997), H₂CS: (Woodney *et al.*, 1997)).

To this list, one could add molecules detected by mass spectroscopy during Halley flyby by PICCA and PUMA instruments onboard Giotto and Vega spacecrafts in 1986. Polyoxymethylene has been inferred from a regular mass spectra pattern obtained with PICCA (Huebner, 1987; Huebner *et al.*, 1989). Other organic molecules such as Pyridine, Purine, Adenine, have been proposed as an interpretation of the complex mass spectra resulting from impact of dust particles on the PUMA's target (Kissel and Krueger, 1987). Nevertheless those detections are very uncertain: Mitchell *et al.* (1992) showed that the pattern

attributed to the presence of POM indicates nothing more than the presence of large CHON molecules, and according to Kissel and Krueger themselves (1987), their detections are very tentative.

This shows that observations are not yet accurate enough, thus one has to use experimental simulations to give a better insight of what could be the nucleus's chemical composition, especially concerning large organic molecules. The principle of such experiments is the following: a mixture of gases relevant to cometary majoritary ice composition (H₂O, CO, CH₃OH, H₂CO...) is condensed on a cold substrate. Ices formed that way are irradiated by UV or high energy particles. When the sample is warmed up for analysis, a refractory organic residue remains on the substrate while volatiles sublimate. The number and the diversity of organic compounds synthesized are remarkable but their identification is seldom exhaustive. Table 2 sums up all the organic molecules detected after these simulations.

We note that Polyoxymethylene has been detected by Schutte *et al.* (1993) after thermal processing of ices containing H₂CO. POM is not necessarily present in comets, but could be an important candidate as a parent molecule of formaldehyde. Therefore physico-chemical data such as the photodegradation rate of POM upon UV irradiation are needed. Those results will have to be incorporated in models of the coma and be compared to observations. This is the aim of our work.

Hydrocarbons : CH ₄ C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ C ₃ H ₈ , C ₄ H ₁₀ C ₆ H ₁₀ , C ₆ H ₁₂ C ₆ H ₁₂ , C ₆ H ₁₄ C ₇ H ₁₆	Aldehydes : H ₂ CO CH ₃ OCH ₂ CHO (t) Ketones : CH ₃ COCH ₃ HOCH ₂ COCH ₃ HOCH ₂ CH ₂ COCH ₃	Alcohols : CH ₃ OH CH ₃ CH ₂ OH HOCH ₂ CH ₂ OH HOCH ₂ CH(OH)CH ₂ OH C ₄ H ₈ (OH) ₂ C ₃ H ₇ OH (t) Esters : HCOOCH ₃ CH ₃ COOCH ₃ CH ₃ CH ₂ COOCH ₃
Amides : NH ₂ CHO CH ₃ CONH ₂ HOCH ₂ CONH ₂ NH ₂ (CO) ₂ NH ₂ HOCH ₂ CH(OH)CONH ₂	Amino Acids : NH ₂ CH ₂ COOH (Glycine) NH ₂ CH(CH ₃)COOH (Alanine) CH ₃ CH ₂ CH(NH ₂)COOH (α ABA) CH ₃ CH(NH ₂)CH ₂ COOH (β ABA) (CH ₂ NH ₂)(CH ₂)CHCOOH (AIBA)	
Carboxylic Acids : HCOOH CH ₃ COOH (t) HOCH ₂ COOH HOCH ₂ CH(OH)COOH HOCH ₂ CH ₂ COOH NH ₂ COCOOH	Amines : HOCH ₂ CH ₂ NH ₂ HCNH(NH ₂) Others : CO, CO ₂ , C ₃ O ₂ , H ₂ CO ₃ HNCO, NH ₂ CONH ₂ , NH ₂ CONHCONH ₂ (CH ₂) ₆ N ₄ : HMT, (-CH ₂ -O) _n : POM	Ethers : CH ₃ OCH ₂ OCH ₃ (t) C ₃ H ₈ O ₃ (Trioxane) (t)

Table 2. Molecules detected after irradiations (UV or High Energy Particles) of interstellar or cometary ices analogs. (t) refers to tentative detections. ABA is Aminobutyric Acid, AIBA is Aminoisobutyric Acid. This compilation is from: (Agarwal *et al.*, 1985; Allamandola *et al.*, 1988; Bernstein *et al.*, 1997; Bernstein *et al.*, 1995; Briggs *et al.*, 1992; Brucato *et al.*, 1997a; Brucato *et al.*, 1997b; Hagen *et al.*, 1979; Hudson and Moore, 1997; Kobayashi *et al.*, 1995; McDonald *et al.*, 1996; Moore *et al.*, 1996; Moore *et al.*, 1991; Schutte *et al.*, 1991; Schutte *et al.*, 1993).

3 Experimental

We have developed a reactor in which solid molecules can be irradiated, in the far UV and in pressure conditions close

to the cometary environment. Gaseous molecules produced are analyzed by different complementary methods. Our experimental setup (see Fig.1) is called S.E.M.A.Ph.Or.E. Cométaire (A french acronym : Simulation Experimentale et Modelisation Appliquées aux PHénomènes ORganiques dans l'Environnement Cométaire). We have started working on Polyoxymethylene, but we will also investigate other solid organic molecules such as Hexamethyltetramine (HMT), in the near future.

3.1 Ultraviolet irradiation

In the first experiments, a microwave powered Xenon Lamp, at a pressure of 0.3 mb, was used. The gas (Xenon, N45, Alphagaz, France) was excited by a microwave generator (Somelec, France) with a power of 200 W at 2450 MHz. Two titanium getters can be warmed up to purify the gas in the lamp. A MgF₂ window (diameter = 25 mm, thickness = 2 mm, Sorem, France) permits the transmission of the light to the reactor. In order to perform reproducible experiments, we adjust the microwave cavity electrodes so that the blue light source reaches the MgF₂ window (Bossard, 1979). Under these conditions, the flux of the lamp at 147 nm can be determined by N₂O or NH₃ actinometry measurements (Greiner, 1967; Groth and Rommel, 1965), and was found to be about $5 \cdot 10^{15}$ photons/sec. In the future, the use of a microwave-powered, flowing hydrogen discharge lamp is planned. This lamp has a flux which is dominated by Lyman α line (122 nm). The pressure inside the lamp is set at about 0.1 mb by maintaining a continuous controlled flow of hydrogen. Changing the wavelength of irradiation will allow the study of the sensibility of POM photodegradation to this parameter, which will be necessary for application to the solar spectrum.

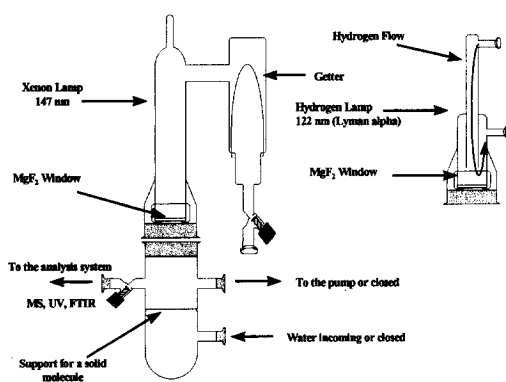


Fig.1. Schematic view of the photochemical reactor used for the irradiation of solid molecules. Two lamps (Xe or flowing H₂) can be adapted.

3.2 Simulation reactor

The reactor, made of Pyrex, is equipped with a vacuum stopcock leading to the analysis system. Two other openings allow connection to a secondary vacuum pump (Turbomolecular pump, Balzers), and a water vapor flow system that is not yet operational, but will permit the study of interactions between photodegradation products of solid molecules and the main constituent of the coma : H₂O. At about half the depth of the reactor, a stainless steel grid can be set as a support for the studied organic molecules. A vacuum better than 10⁻⁴ mb can be reached in the reactor. The irradiated Polyoxymethylene is supplied by Prolabo (France); its purity is greater than 95%.

3.3 Analysis system

Chemical analysis of the gaseous mixture resulting from the irradiation of the heavy organic molecules is carried out using a mass spectrometer (Leybold Inficon - Transpector). We have also used a 1 m³ atmospheric simulation chamber, here at LISA, usually devoted to the study of tropospheric chemistry. In this case, the gaseous photodegradation products are simply introduced to the chamber by diffusion and can be analyzed by two spectrometric techniques : long optical path UV-visible spectrometry (optical path length : 72 m, range : 250 to 650 nm, maximum resolution : 0.05 nm) and very long path FTIR spectrometry (optical path length : 672 m, range : 600 to 4000 cm⁻¹, resolution : from 64 to 0.003 cm⁻¹) (Doussin *et al.*, 1997). The simulation chamber is used as a high performance spectrometer.

Only MS and FTIR results will be presented in this paper. MS experiments have been performed at $5 \cdot 10^{-5}$ mb, between 1 and 200 AMU with a resolution of 1 AMU. This technique is very sensitive but as there is no separation of the different products before analysis, it can only give hints of the presence of a compound if one refers to the major ions detected and compare to reference spectra from the NIST (National Institute of Standards and Technology) library. Detections have then to be confirmed by infrared spectroscopy. Concerning the FTIR analysis one has to work in an inert atmosphere of 2 mb of He (Type C, Aga, France) in order to avoid desorption of molecules, previously adsorbed on the walls of the atmospheric simulation chamber. Identification and quantification of the different compounds are based on reference spectra from the EPA library (Daugherty *et al.*, 1995; Daugherty *et al.*, 1994). Detections are less sensitive than with the MS, but they are more certain and indeed quantitative. For the experiment presented in this paper the optical path was 96 m and the resolution 1 cm⁻¹.

4 First Results and Discussion

4.1 Infrared analysis

Figure 2 presents an infrared spectrum obtained in the atmospheric simulation chamber after a four-hour irradiation of POM. The major product is formaldehyde, clearly identified by its main signatures at 1746, 2765, 2801 and 2897 cm^{-1} . Its formation has been followed during the whole irradiation time, as shown in Figure 3a. From these results one can easily derive the production rate of formaldehyde from POM at 147 nm. As shown in Fig. 4, it is quite constant as a function of time. Since the thermal degradation of POM into H_2CO is very sensitive to temperature, we can conclude from this constant value that POM is not noticeably heated during the irradiation and that H_2CO production by thermal processes can be neglected. Because a large uncertainty remains in the Xenon Lamp flux it is not yet possible to calculate the quantum yield of formaldehyde production.

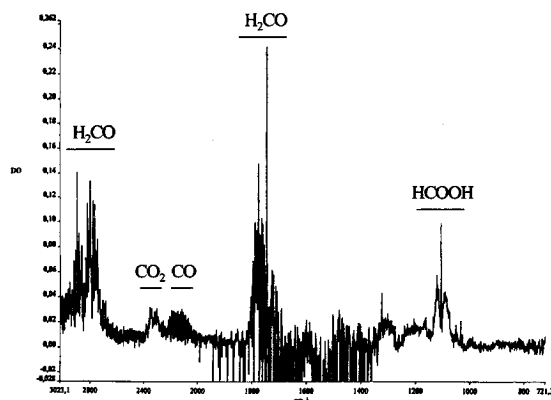


Fig.2. Infrared Spectra in the Atmospheric Simulation Chamber after a four-hour irradiation of POM. Optical Path Length : 96 m. Resolution : 1 cm^{-1}

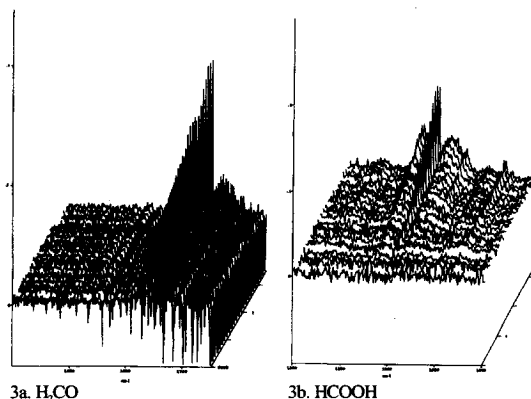


Fig.3a. and 3b. Evolution of absorbance of H_2CO (1745 cm^{-1}) and HCOOH (1105 cm^{-1}) as a function of time. Time is represented here in arbitrary units.

CO_2 and CO have also been detected. Some of the CO could be a secondary product resulting from the photochemistry of H_2CO in the reactor before it reaches the simulation chamber (see (Meier *et al.*, 1993) for the photochemistry of formaldehyde). Modelling work is necessary to resolve this point.

More unexpected is the detection of formic acid (HCOOH) with its PQR signature centered at 1105 cm^{-1} (Fig. 3b). It is less abundant than H_2CO by about a factor of ten.

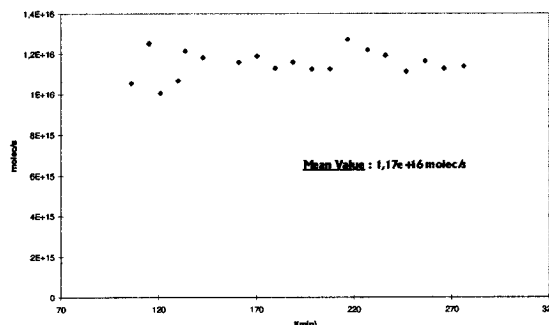


Fig.4. Production rate of H_2CO as a function of time.

4.2 Mass Spectroscopy results

Some other molecules have been tentatively detected by MS, but their identifications have not yet been confirmed by infrared spectroscopy because they are produced only in trace amounts. We will soon obtain better detection limits by increasing the IR optical path length of infrared in the simulation chamber.

According to reference spectra of the NIST library, to date, in addition to the molecules already mentioned above, we have detected characteristic ions of the following molecules in the mass spectra : CH_3OCH_3 (Mass 45), CH_3OCHO (Mass 60), $\text{CH}_3\text{OCH}_2\text{OCH}_3$ (Mass 75), and $\text{C}_3\text{H}_6\text{O}_3$ (Mass 89 - a trimer of H_2CO , either cyclic : Trioxane, or linear : $\text{CH}_3\text{OCH}_2\text{OCHO}$). Figure 5 shows the evolution of those four masses before, during and after irradiation of POM (the fifth one corresponds to a typical signal of a mass that is not detected). These detections, even if they still have to be confirmed, are not surprising. Indeed CH_3OCHO , $\text{CH}_3\text{OCH}_2\text{OCH}_3$ and $\text{CH}_3\text{OCH}_2\text{OCHO}$ have already been identified as degradation products of POM under high energy particle irradiations (Dole, 1973). Thus it seems that the UV degradation chemistry is quite similar.

Among the compounds detected, it is interesting to note that HCOOH and CH_3OCHO have recently been detected for the first time in comet Hale-Bopp (Colom *et al.*, 1997; Wink *et al.*, 1997), but no extended source has been proposed for them.

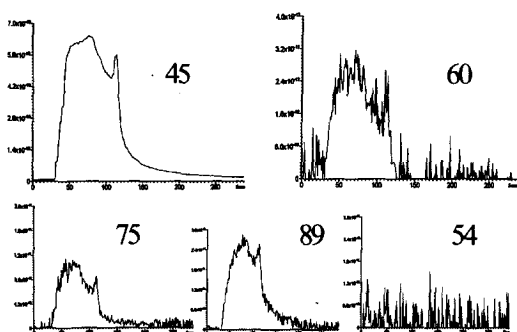


Fig.5. Evolution of the $m/z = 45, 60, 75, 89$ and 54 (as a reference for the noise aspect). The starting time of irradiation is scan 30 and the ending scan 114. Each scan represents a 5-second period. The bimodal aspect of the trends is due to variation in the lamp intensity. m/z ratio have been attributed to: CH_3OCH_3 (Mass 45), CH_3OCHO (Mass 60), $\text{CH}_3\text{OCH}_2\text{OCH}_3$ (Mass 75), and $\text{C}_2\text{H}_2\text{O}$ (Mass 89)

5 Conclusion

Laboratory experiments on the photochemical evolution of high molecular weight organic compounds suspected to be present in cometary nuclei contribute significantly to the knowledge of the chemistry of comets. We are planning a systematic study of many solid organic molecules to provide the necessary data to model observations and to establish correlations between the solid and the gaseous composition of comets. S.E.M.A.Ph.Or.E. Cométaire will have some direct implications for the preparation of the Rosetta mission and the interpretation of the data which will be obtained.

This work could represent one of the links between the observations of the nucleus by the lander and of the coma by orbiter instruments, concerning the evolution of the organic material.

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