JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 106, NO. E12, PAGES 33,325–33,332, DECEMBER 25, 2001

Experimental and theoretical studies on the gas/solid/gas transformation cycle in extraterrestrial environments

Hervé Cottin[1] and Marie-Claire Gazeau

Laboratoire Interuniversitaire des Systèmes Atmosphériques, Universités Paris VII-Paris XII, Créteil, France

Patrick Chaquin

Laboratoire de Chimie Théorique, Université Paris VI, Paris, France

François Raulin and Yves Bénilan

Laboratoire Interuniversitaire des Systèmes Atmosphériques, Universités Paris VII-Paris XII, Créteil, France

Abstract. The ubiquity of molecular material in the universe, from hydrogen to complex organic matter, is the result of intermixed physicochemical processes that have occurred throughout history. In particular, the gas/solid/gas phase transformation cycle plays a key role in chemical evolution of organic matter from the interstellar medium to planetary systems. This paper focuses on two examples that are representative of the diversity of environments where such transformations occur in the Solar System: (1) the photolytic evolution from gaseous to solid material in methane containing planetary atmospheres and (2) the degradation of high molecular weight compounds into gas phase molecules in comets. We are currently developing two programs which couple experimental and theoretical studies. The aim of this research is to provide data necessary to build models in order to better understand (1) the photochemical evolution of Titan's atmosphere, through a laboratory program to determine quantitative spectroscopic data on long carbon chain molecules (polyynes) obtained in the SCOOP program (French acronym for Spectroscopy of Organic Compounds Oriented for Planetology), and (2) the extended sources in comets, through a laboratory program of quantitative studies of photochemical and thermal degradation processes on relevant polymers (e.g., Polyoxymethylene) by the SEMAPhOrE Cometaire program (French acronym for Experimental Simulation and Modeling Applied to Organic Chemistry in Cometary Environment).

1. Introduction

A better knowledge of the organic chemistry involved in diverse environments such as the interstellar medium, planetary, and cometary atmospheres can be reached by combining observations, laboratory experiments, and theoretical modeling. However, reduction, analysis, and interpretation of pure observational results often require a large set of laboratory data. Many of these data are totally unknown, especially when one considers the extreme physical conditions of the corresponding environment. Furthermore, relevant laboratory simulations of extraterrestrial environments cannot easily be done. This implies a strong needs for realistic theoretical modeling. Improvement of our knowledge of processes occurring in the studied environment can be achieved by iteration between results of numerical models and observations. However, this methodology makes sense only if the theoretical descriptions of both physical and chemical phenomena are accurate. The aim of our work is to point out specific gaps in chemical schemes used in theoretical models to date and then do our best to measure part of the missing data. Indeed, by performing laboratory experiments, we should be able to reduce two major sources of uncertainty of theoretical models. The first one concerns laboratory determinations of the values of fundamental parameters: absorption cross sections, quantum yields, and rate constants. Many of those available are limited by great error bars or, even worse, have never been determined under appropriate temperature and pressure conditions. The second one is the possibility that models fail owing to systematic calculation errors when critical reaction pathways are not correctly described or are totally missing from the schemes.

In this paper, we present two programs developed at the Laboratoire Interuniversitaire des Systèmes Atmospheriques (LISA) at Créteil, near Paris: SCOOP (French acronym for Spectroscopy of Organic Compounds Oriented for Planetology) and SEMAPhOrE Cometaire (French acronym for Experimental Simulation and Modeling Applied to Organic Chemistry in Cometary Environment), which are dedicated studying particular species or processes in order to highlight their contribution to the gas/solid/gas transformation cycle in different Solar System environments.

The SCOOP program is establishing a spectroscopic data bank (both in the infrared and in the ultraviolet spectral range)

---

[1] Now at Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, USA

Paper number 2000JE001319.
0148-0227/01/2000JE001319$09.00

of molecules under adequate physical conditions of the studied environments (mainly low temperatures). In this paper we report on studies of polyynes (linear molecules with conjugated triple bonds with the general formula $C_{2n}H_2$), and explain how, using experimental and theoretical approaches, we plan to predict the spectral characteristics of longer carbon chain compounds which are unstable under the laboratory conditions. Studying those compounds is of prime importance because very recently polyynes (C_4H_2 and C_6H_2) have been observed in the circumstellar medium [*Cernicharo*, 2000] where they may be key molecules in the formation of higher molecular weight compounds like PAHs. Furthermore, C_4H_2 has been observed in planetary atmospheres and is thought to lead, via a complex photochemistry starting from methane, to the formation of solid particles (called "tholins" in experiments simulating the evolution of planetary atmospheres). The S.C.O.O.P. program coupling experimental and theoretical studies will determine the spectroscopic data of those compounds strongly needed to interpret observations and to develop photochemical models to explain the transformation of gases into complex organics.

In turn, through different processes, such as thermal- and photo-degradation, high-molecular weight molecules in the solid phase can release volatile products, which may be different than their original precursors and thus act as parent molecules for various compounds in the solar system and as new pathways for the production of interstellar species. Our interest focuses on the study of such processes in the cometary environment; these processes could be responsible for the extended source phenomenon. On the basis of their density profile in the coma as a function of the nucleus distance, some molecules (H_2CO [*Biver et al.*, 1999; *Meier et al.*, 1993], CO [*DiSanti et al.*, 1999]) are thought to have an origin other than direct sublimation from the nucleus. It could be the degradation of a parent molecule present on grains in the coma. The SEMAPhOrE Cometaire program consists specifically of the study of the degradation of high-molecular weight compounds (in the solid phase) leading to the formation of smaller gaseous compounds. The aim of this program is to bring a better understanding of the chemical mechanisms involved during those transformations and to provide physicochemical data such as the production quantum yield of gaseous molecules from the solid parent molecule as a function of the UV wavelength or the kinetics of its thermal degradation. Such data are not available for the interpretation and modeling of observations. We report here the results of studies on polyoxymethylene [POM: $(\text{-CH}_2\text{-O-})_n$] degradation processes to determine if the presence of POM is relevant as an explanation for the formaldehyde extended sources observed in several comets.

2. SCOOP Program: From Volatile to Complex Molecules

2.1. Organic Matter in Methane Containing Atmospheres

Titan's atmosphere is mainly composed of molecular nitrogen with methane as the second major constituent having an abundance of a few percent. Several higher hydrocarbons (C2-C4) have also been detected during the Voyager fly-by [*Hanel et al.*, 1981; *Kunde et al.*, 1981] and more recently from Infrared Space Observatory (ISO) observations [*Coustenis et al.*, 1998]. Their mixing ratios range from a few ppm (C_2H_6, C_2H_2, C_3H_8) to a few ppb (C_2H_4, C_3H_4, C_4H_2) [*Coustenis and Bézard*, 1995]. The recent detection of butadiyne (also called diacetylene, C_4H_2), also in Saturn's atmosphere using ISO [*de Graauw et al.*, 1997], confirmed the predicted production of polyynes in methane containing atmospheres [*Yung et al.*, 1984]. The general mechanism invoked for the production of polyynes is:

$$C_{2n}H_2 \xrightarrow{h\nu} C_{2n}H + H$$

$$\underline{C_{2n}H + C_2H_2 \longrightarrow C_{2n+2}H_2 + H}$$

$$\text{net}: C_{2n}H_2 + C_2H_2 \longrightarrow C_{2n+2}H_2 + 2H.$$

This chemical scheme for the production of long carbon chains has a special importance in the photochemical models of Titan's atmosphere since long chain molecules are supposed to be the main link between the gas phase and the solid phase particulates visible as haze at high altitude. Furthermore, acetylene and higher polyynes are supposed to control the abundance of atomic hydrogen by the competitive mechanism of molecular hydrogen dissociation and H recombination [*Gladstone et al.*,1996]. Polyynes are also involved in the methane catalytic dissociation via the radicals formed by their photolysis in the stratosphere [*Yung et al.*, 1984].

2.2. The SCOOP Program: From Volatile to Complex Molecules

One needs the absorption coefficient of a molecule, measured under physical conditions as close as possible to those of the extraterrestrial environment, to calculate its dissociation coefficient. Since the solar flux decreases rapidly with decreasing wavelength in the ultraviolet and apart from the Ly α (1216 Å) which does not penetrate below 600 km on Titan, the midultraviolet (mid-UV) wavelength range (λ>180 nm) is the most important for the determination of dissociation coefficients. Furthermore, the mid-UV range is also the most important wavelength range for observations since atmospheric opacity increases with decreasing wavelength.

For the detection and abundance determination of molecules present in the atmosphere by remote observations, the infrared wavelength range is complementary to the ultraviolet range. Indeed, they probe a different level in the atmosphere: IR radiation comes from thermal emission by the troposphere and lower stratosphere; observed UV radiation results from solar UV photons backscattered by the major gases and aerosols in the high stratosphere.

Band positions and absolute intensities of polyynes are required to be able to analyze observational data. Unfortunately, spectroscopic laboratory data are only partially available in the literature for polyynes. Thus we have started a specific program in the midultraviolet and infrared range to determine quantitative spectra of polyynes.

The description of the experimental setup for the determination of infrared and midultraviolet absorption coefficients is only briefly mentioned here. The ultraviolet absorption coefficient is presented for each molecule. Infrared results are also presented and compared with ab initio calculations.

2.3. Experimental Results

2.3.1. Ultraviolet spectra. Spectra in the 185-300 nm range were obtained with the SCOOP experimental setup

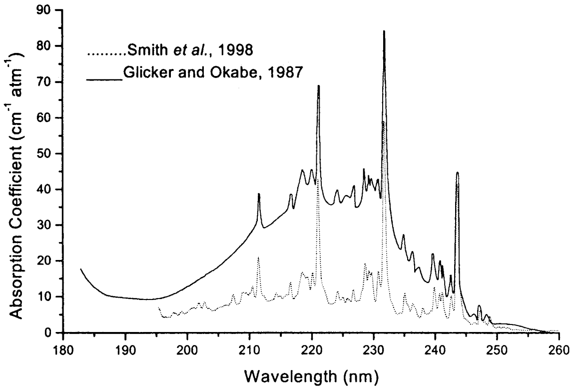

Figure 1. Comparison between the absorption spectrum obtained with our apparatus [*Smith et al.*, 1998] and that previously available in the literature for C_4H_2 [*Glicker and Okabe*, 1987]. The difference indicates the presence of impurity C_4H_3Cl, used in preparing C_4H_2.

[*Bruston et al.*, 1991; *Bénilan et al.*, 1994]. For spectra recorded below 200 nm, the monochromater was flushed with dry N_2 to remove, as much as possible, absorptions due to H_2O and O_2. The pressure regulation system, which used the sample vapor pressure, allows us to check the purity of the sample and detect the possible presence of trace impurities. As an example, we present in Figure 1 a comparison between our C_4H_2 spectrum and that obtained by *Glicker and Okabe* [1987]. The difference between the two seen as a continuum shift corresponds to absorption due to C_4H_3Cl, a by-product in the synthesis of C_4H_2 [*Smith et al.*, 1998]. The same kind of impurity was also observed in C_6H_2 samples [*Benilan et al.*, 1995].

A compilation of the polyyne spectra (n= 1 to 4) measured at room temperature, together with spectra available from the literature for wavelengths below 185 nm, is presented in Figure 2 from 150 to 300 nm. The C_8H_2 absolute absorption coefficient is presented for the first time. It was obtained at vapor pressure of a few 10^{-3} mb. The uncertainty associated with this measurement is around 20%, mainly owing to uncertainties in sample purity. In the 150-300 nm region, polyyne absorption can vary over 5 orders of magnitude. This results from the fact that allowed and forbidden transitions both occur in this wavelength range. For C_8H_2, the absorption coefficient corresponding to the forbidden transition cannot be measured because it requires study at high pressures where the sample starts to polymerize. It is clear, looking at figure 2 that polyyne absorption shifts to longer wavelengths as the length of the carbon chain increases. These results are in good agreement with previous measurements [*Kloster-Jensen et al.*, 1974]. However, we also find that the allowed transition oscillator strength, proportional to the integrated absorption coefficient, increases with the number of triple bonds. This has several important consequences for chemical evolution and for the possible detection of polyynes in planetary atmospheres as discussed in section 2.4.

2.3.2. Infrared spectra. IR spectra were obtained on a Perkin-Elmer 1710 FTIR spectrometer. Spectra were recorded at 4 cm^{-1} resolution between 250 and 4300 cm^{-1}. Typically, 50 scans were coadded to give a 0.3% noise in transmission. The gas was contained in a 10 cm path length cell equipped with CsI windows. Spectra were recorded at several pressures. N_2 gas at an approximate partial pressure of 700 mb was added to the cell to broaden the bands. All spectra were recorded at room temperature. The entire optical path in the spectrometer was flushed with dry N_2 to remove, as much as possible, absorptions due to H_2O and CO_2.

Infrared spectra were measured for polyynes with n=2, 3, and 4. However, absolute intensities have been obtained only for the first two molecules [*Khlifi et al.*, 1995; *Delpech et al.*, 1994] because of the small cell size which limits measurements to pressures ranging over only a few to tenths of millibars. For C_8H_2, as soon as the pressure increases to the millibar level, it spontaneously polymerizes onto the wall of the cell. Great caution has to be taken with this compound, since when the cold solid sample is allowed to warm up to room temperature, it quickly polymerizes and explodes violently.

For the study of cold planetary atmospheres, the region below 700 cm^{-1} is of particular interest. This is where the thermal emission flux is significant, being maximum at 300 cm^{-1} for a radiating black body at 150 K. However, many of the lower energy vibrational bands are out of our scope since our spectrometer is limited to 250 cm^{-1}. Thus we will concentrate here on the CCH bending mode of polyynes, which occurs in the 650-600 cm^{-1} range.

In Figure 3 we present spectra of this CCH band at 4 cm^{-1} resolution, with the absorbance normalized to the maximum value, for the three polyynes: C_4H_2, C_6H_2, and C_8H_2. As one can see, the band position shifts to lower energy as the length of the carbon chain increases. The intense Q branch starts to be less and less separated from R and P branches for higher polyynes. Since the moment of inertia increases with the length of the molecule, the separation between the P and R branches will decrease for higher polyynes because the separation varies as the square root of the rotational constant, itself proportional to the inverse of the moment of inertia.

A plot of the band position verses the number of triple bonds for each molecule is illustrated by Figure 4. The variation of the band position can be modeled by an empirical law varying as $1/n^4$, where n is the number of triple bonds in the molecule. This leads to an extrapolated position of 621 cm^{-1} for an infinite length polyyne. The convergence observed experimentally has been tested against ab initio calculations. Details of those calculations will be published elsewhere. The

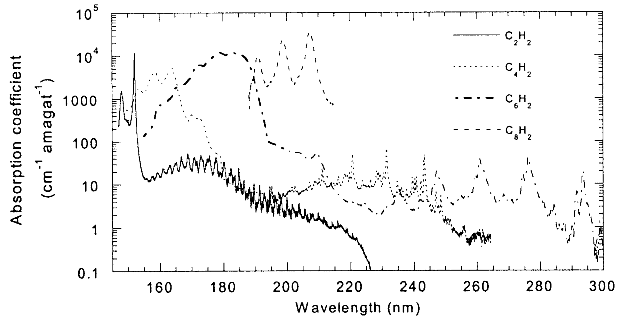

Figure 2. Absorption coefficient at ambiant temperature (T=293 K) of acetylene and polyynes ($C_{2n}H_2$, n=2-4) between 150 and 300 nm. Values below 185 nm are from the literature. C_2H_2 is from *Smith et al.* [1991]; C_4H_2 is from *Fahr and Nayak* [1994]; C_6H_2 is from *Kloster-Jensen et al.* [1974] normalized by *Benilan et al.* [1995], and C_8H_2 is from this work.

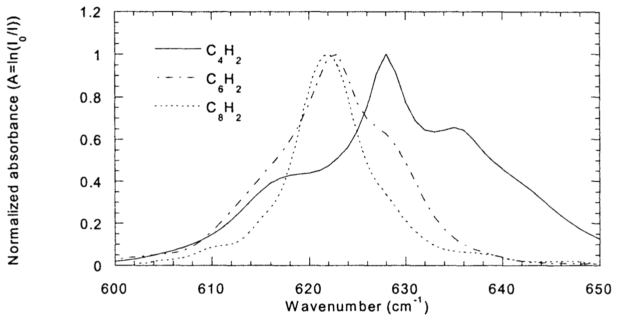

Figure 3. Spectra at 4 cm^{-1} resolution, broadened with 700 mb of N_2, of C_4H_2, C_6H_2, and C_8H_2, in the CCH bending region 600-650 cm^{-1}.

main result is that a theoretical approach leads to the same conclusions concerning the convergence of the band position as a function of the length of the molecule. Nevertheless, the theoretical data had to be scaled by a factor 1.05, which is the mean value of the ratio between experimental and theoretical results for 2-4 triple bond molecules. A discrepancy can still be observed since the theoretical positions converge less rapidly ($1/n^{2.5}$) than the experimental values.

2.4. Implications for Models and Observations of Planetary Atmospheres

We have reviewed the absolute absorption coefficient of polyynes in the 150-300 nm range. These results are essential for the development of photochemical models and for the interpretation of mid-UV spectra of planetary atmospheres in which these compounds are likely to be present. The wavelength shift of the allowed transitions of polyynes in the 150-220 nm wavelength range is almost linear with conjugated triple bonds. This agrees with measurements performed on higher polyynes trapped in a rare gas matrix [*Grutter et al*, 1998]. However, we also found that the intensity of the allowed transition increases almost linearly with the length of the molecule as well. Since the solar flux is also increasing with wavelength in the ultraviolet region, the dissociation coefficient of polyynes, proportional to the integrated product over wavelength of the solar flux times the absorption cross section, will increase very quickly with the size of the molecule. This leads to the conclusion that solar radiation could quickly polymerize the polyynes into solid material as inferred by the chemical mechanism if the second step of the chemical scheme is efficient. An important implication would be that these polyyne molecules (especially the longer ones) should not be observable in the atmosphere. Unfortunately, the recombinaizon of $C_{2n}H$ radicals with acetylene is largely unknown and experimentally difficult to measure. Ab initio calculations are underway to study those reactions. Nevertheless, a second conclusion can be drawn from our ultraviolet studies: higher polyynes might be more easily detectable from UV observations than lighter ones since the allowed transition shifts to longer wavelength as the size of the molecule increases. This is especially true in Titan's atmosphere for C_8H_2 as compared to C_6H_2 because the photon flux drops very quickly below 200 nm due to both the decrease of solar photons and the increase of opacity.

Infrared results also have several implications concerning the possible observation of polyynes in methane containing planetary atmospheres. First, since the position of the CCH bending mode converges to a fixed value for the higher polyynes, very high-resolution observations able to resolve rotational band structure would be needed to identify the different compounds. This is not expected in the near future. Composite Infrared Spectrometer (CIRS) onboard the Cassini mission will observed Jupiter in December 2000 and will be in orbit around Saturn in 2004. This will have a maximum apodized resolution of 0.5 cm^{-1}, insufficient for this purpose. Thus polyynes will have to be preferentially searched for in the far-IR using their emission bands below 250 cm^{-1}, corresponding to their CCC bending modes. Second, since the absolute intensity of the infrared band studied here is predicted to be almost constant for all polyynes, the upper limit that could be determined around 621 cm^{-1} will be characteristic of C_6H_2 and C_8H_2 because the emission from higher polyynes would be negligible if their abundance decreases rapidly as stated above. This leads again to the conclusion that infrared observations will have to concentrate on the low energy part of the spectrum to derive information on the amount of polyynes in the atmosphere of Jupiter, Saturn, and Titan.

3. The SEMAPhOrE Cometaire Program: From Complex Molecules to Volatiles

3.1. Cometary Investigations, Review of Previous Work

Our current knowledge about the cometary environment comes from (1) remote sensing through spectroscopic techniques from the UV to the submillimeter range, (2) in situ measurements using mainly mass spectrometry during the Halley encounter by Vega and Giotto spacecraft in 1986, and (3) laboratory simulation experiments [see *Cottin et al.*, 1999, and references therein]. The knowledge of the molecular composition of comets is of prime importance since these objects are generally considered to be accreted during the birth of our planetary system: they have been held in a cold environment and may have been unaltered by chemical evolution. Thus comets may have kept the primordial solar system chemical composition, offering a unique link to the interstellar medium. Comets are composed of a mixture of silicate minerals, ices, and complex refractory organic molecules. Until now, only the coma's composition has been analyzed by in situ measurements or remote observations, which has led to the detection of ~ 25 stable small molecules. Among them, formaldehyde (H_2CO) [*Biver et al.*, 1999; *Meier*

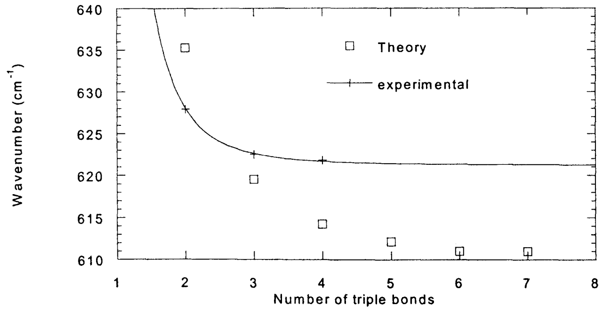

Figure 4. Comparison of the measured IR band position of the CCH bending mode of polyynes with ab initio calculations. The solid curve fits the experimental data with the equation: $\nu=621.2+107.9/n^4$.

et al., 1993] and carbon monoxide (CO) [*DiSanti et al.*, 1999] present an extended source which could be due to the degradation of a refractory parent molecule in the coma. However, there is no direct information about the molecular composition of the nucleus. Indeed, the abundance of compounds detected in the coma may not be directly representative of the molecular composition of the cometary nucleus because thermal differentiation processes may occur in the nucleus, and many products may have vapor pressures or abundances too low to be detected in the gaseous phase. This is the reason why experimental simulations have been carried out. The aim of these experiments is to understand the physical and chemical processes likely to occur in the interstellar medium or in comets, and to infer the organic composition of interstellar and cometary grains. These experiments consist of irradiating ices whose compositions are relevant to the interstellar medium or comets. After irradiating and subsequent warming to room temperature, a refractory mantle made of organic molecules remains. The resulting sample, supposed to mimic the interstellar or cometary organic refractory component, is analyzed by different techniques. A review of those experiments and their results are given in *Cottin et al.*, [1999]. Laboratory simulations on ice analogs can be classified into three different groups considering the source of energy deposition: ice analogs can be processed (1) thermally [*Schutte et al.*, 1993], (2) by UV lamps, specifically hydrogen discharge lamp (Leiden's observatory, Netherland: [*Briggs et al.*, 1992; *Gerakines et al.*, 1996]; NASA-Ames Research Center, Moffett Field, California, [*Bernstein et al.*, 1995]) or (3) by high energy particles (1-1000 keV): H, He ions and heavier nuclei generated by a Van de Graff accelerator (Catania, Italy: [*Strazzulla et al.*, 1991]; Yokohama, Japan, [*Kobayashi et al.*, 1995]; NASA-Goddard Space Flight Center, Maryland, [*Moore and Hudson*, 1998]). Generally, these experiments have been carried out at 10 K, representative of the interstellar medium or of the cometary environment in the outer solar system. These laboratory studies strongly suggest that many more compounds exist in the cometary environment than those that have been firmly detected by remote sensing up to now. Indeed, more than 100 compounds belonging to a wide range of chemical families, from the simplest hydrocarbons to amino acids or even more complex molecules such as HMT (hexamethylenetetramine, $C_6H_{12}N_4$) or POM (polyoxymethylene, $(\text{-}CH_2\text{-}O\text{-})_n$) have been found in laboratory simulation experiments on processed ices. One has to note that the resulting information is often qualitative and few quantitative data have been obtained so far.

3.2. A Complementary Approach: The SEMAPhOrE Cometaire Program

The contribution of our team to the study of cometary chemistry concerns the processes that can be responsible for the evolution of material in a cometary environment, and in particular, the chemical mechanism involved in transformation from the solid to gaseous phase. Our interest focuses on the study of photo- and thermo-degradation of solid molecules present on grains ejected from the nucleus. Such mechanisms could be responsible of the observed extended sources. The SEMAPhOrE Cometaire experimental program has started with the test of the hypothesis that POM is a possible parent molecule for the formaldehyde extended source. This polymer has been tentatively detected in comet Halley by *Huebner*, [1987], and has been identified in simulation experiments [*Bernstein et al.*, 1995; *Schutte et al.*, 1993]. Abundances, rate, and quantum yields of formation of the dominant products resulting from POM degradation can be derived from our experiments. Kinetic parameters of its thermal degradation are also determined. Providing such fundamental data is necessary to model the cometary environment and to determine if POM may be a parent molecule of H_2CO or not.

Quantitative analysis of the molecular composition of the resulting gaseous phase gives the "signature" of any high molecular weight compound. In other words, the purpose of this experiment is to determine to what extent the refractory organic component of comets could contribute to the gaseous phase.

3.3. Experiment

The experimental set up has already been described by *Cottin* [1999] and *Cottin et al.* [2000]. The reactor, made of Pyrex, allows a thermal regulation of the sample that is necessary to discriminate thermal from irradiation effects. The compound is simply deposited at the bottom of the reactor, whose temperature is set at a level allowing to neglect thermal degradation compare to photodegradation (typically 10 C). POM is irradiated with UV photons. The lamp is filled with an appropriate gas or gas mixture depending on the desired wavelength for processing: 5.5 mb H_2 (2%) in He (> 99.99% - Linde - France) for a 122 nm emission (Lyman α), 0.3 mb Xe (99.99% - Linde - France) for 147 nm, and 0.5 mb CH_4 (1%) in He (> 99.99% - Linde - France) for 193 nm. Discharge in the lamp is initiated with a Tesla coil, and the gas is excited by a microwave generator (Somelec - France) with a power of 200 W at 2450 MHz. The pressure of the gas in the lamp is set at a level allowing maintaining a stable discharge. Window of MgF_2 transmits 122 and 147 nm UV, and SiO_2 transmits 193 nm (both thickness, 2 mm; Φ, 25 mm; Sorem; France). The SiO_2 window absorbs UV below 170 nm and thus filters the other atomic lines of C atom at 166 and 156 nm [*Okabe*, 1978]. For each wavelength, the UV lamp flux is measured by chemical actinometry. Actinometers have been chosen to be relevant for the irradiation conditions, each has a significant cross section at the studied wavelength and a simple photochemistry.

The reactor can be directly connected to an IR spectrometer (optical length settled at 96 or 288 m, resolution 0.5 cm^{-1}). Then, as the gaseous photodegradation products diffuse into the chamber, they are continuously analyzed. Analysis has also included direct mass spectrometry or gas chromatography coupled with mass spectrometry (GC-MS).

Concerning thermal degradation, the polymer is set at a constant temperature in the reactor and its H_2CO production is measured through the pressure augmentation as H_2CO which is the only thermal degradation product of POM. In this paper, we summarize results that have been presented in more detail by *Cottin et al.* [2000] for the photodegradation of POM and focus on results of interest for the planetary community. Thermal degradation results for POM are presented here for the first time.

3.4. Results

3.4.1. Photodegradation. The infrared spectrum of the gas phase products resulting from 7 hours of POM irradiation at

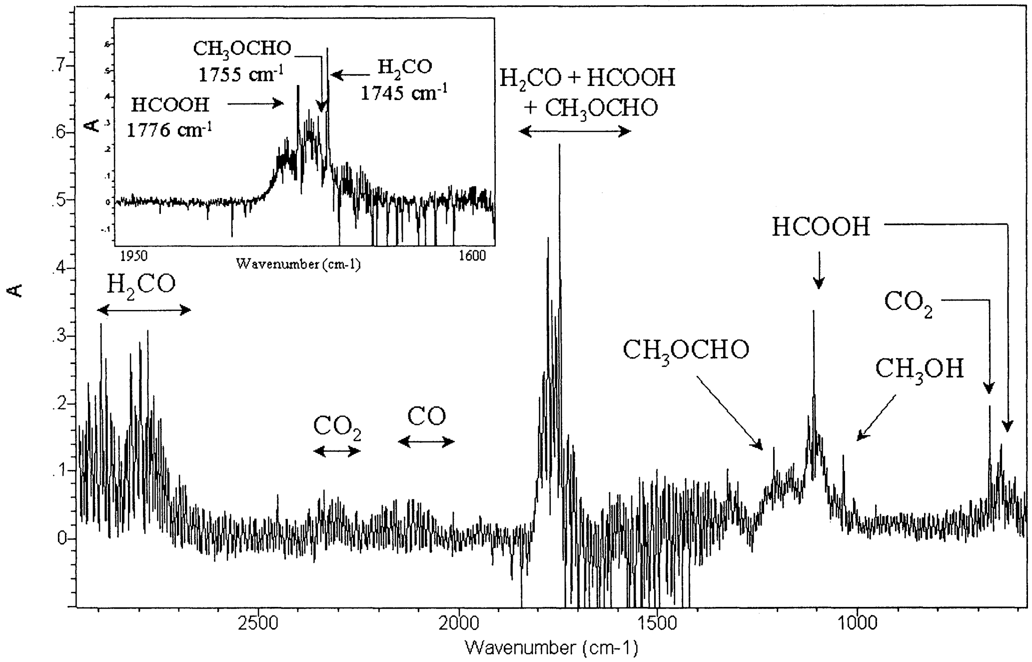

Figure 5. Infrared spectrum of the gas produced after 7 hours of POM irradiation at 122 nm. Optical path, 288 m; Resolution, 0.5 cm^{-1}; Polymer temperature, 288 K.

122 nm is presented in Figure 5. Calculation of the time required for molecules to diffuse from the photolysis reactor to the infrared cell, where they are no longer exposed to the UV flux, are reported by *Cottin et al.* [2000]. It shows that detected molecules are primary photodegradation products and that gaseous phase photochemistry during transport to the analysis system yields only a small amount of secondary products, which have been taken into account for quantum yields determination. Formaldehyde is the major product, clearly identified by its signatures at 1746, 2765, 2801, and 2897 cm^{-1}. Other molecules detected are CO, CO_2, HCOOH, CH_3OH, CH_3OCHO. These molecules have already been detected in comets. Knowing the lamp's flux, the production quantum yield as a function of the wavelength has been derived for H_2CO, HCOOH, CO, CO_2, and CH_3OH.

Quantum yields measured in this study are the result of a complex competition between initiation, production, and termination reactions, rather than a simple reaction such as one photon produces one molecule [*Rabek*, 1995]. The quantum yields of products as a function of the irradiating wavelength are reported in Table 1. We propose to interpolate those data for H_2CO and HCOOH and adopt the production profiles presented in Figure 6.

The analysis by GC-MS has led to the detection of other molecules, dimethoxymethane ($CH_3OCH_2OCH_3$) and trioxane (cyclic derivative compound of formaldehyde, $C_3H_6O_3$). Neither of these molecules has been detected in comets.

Table 1. Production Quantum Yield from POM Measured as a Function of Irradiation Wavelength.

Molecule/λ, nm	122	147	193
H_2CO	0.75±0.21	0.96±0.19	<0.16
HCOOH	0.13±0.05	0.26±0.10	ε
CO	not estimated	~1	ε
CO_2	not estimated	~0.3	ε
CH_3OH	~0.05	~0.05	ε

ε: below detection limit

3.4.2. Thermodegradation. The thermal degradation of POM has also to be considered. Indeed, the polymer is in equilibrium with formaldehyde (POM ⇔ n H_2CO) [*Dainton et al.*, 1959]. We have studied the reaction at different temperatures (278, 283, 288, 293, and 295.5 K):

$$\mathrm{POM_{solid}} \xrightarrow{\Delta} \mathrm{H_2CO_{gas}}.$$

The production rate of formaldehyde is a function of the amount of polymer. During an experiment, the mass loss of the polymer is negligible, thus we can consider a pseudo zero-order reaction and write its kinetics as

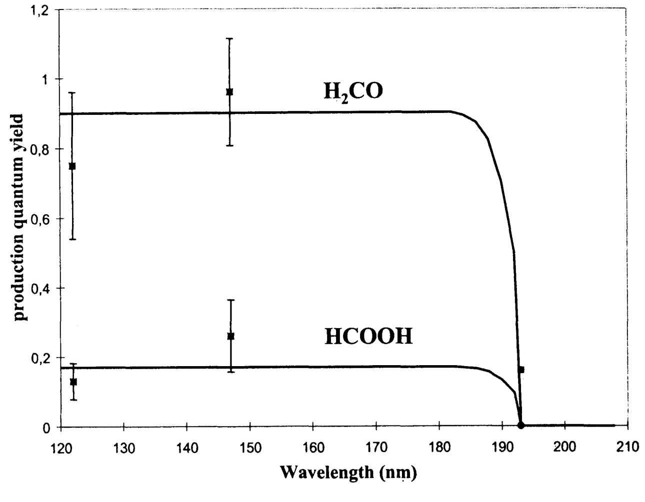

Figure 6. Quantum yield profiles as a function of irradiation wavelength for H_2CO and HCOOH under experimental conditions.

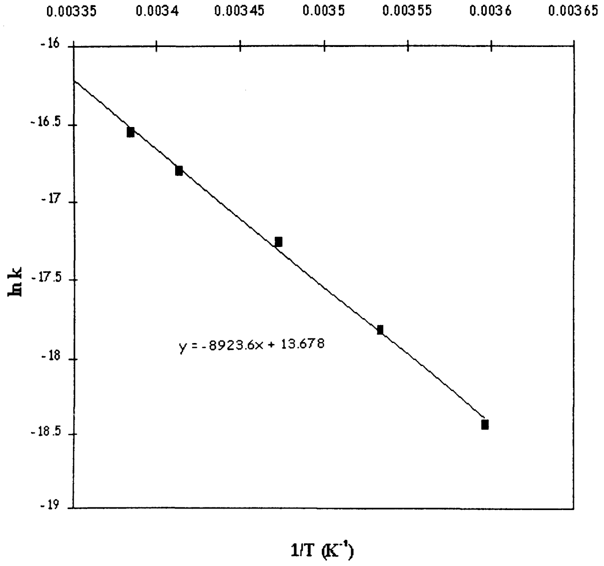

Figure 7. Arrhenius law for the production rate of formaldehyde from POM as a function of $1/T$.

$$\frac{dH_2CO}{dt} = km_{\text{POM}} = K$$

From Arrhenius law, we write $k = A\,e^{-Ea/RT}$. Ea is the activation barrier, and A is the frequency factor. This law can also be written

$$\ln k = -\frac{Ea}{RT} + \ln A.$$

Figure 7 presents ln k as a function of $1/T$.

From those results, using a linear least-square regression fit, we derive $Ea = 74.2$ kJ mole^{-1} ± 10 % and $A = 8.71\ 10^5$ mole g^{-1} s^{-1} (the $\pm^{120\%}_{60\%}$ estimated uncertainty for ln A is 20% but is amplified in a nonsymmetric way due to the ln function). The relative uncertainty of these results applied to a typical cometary grain temperature of 300 K is ~20%. The Ea value is quite important and means that the production of H_2CO from POM is highly sensitive to temperature.

3.5. Discussion

SEMAPhOrE Cometaire is an experimental set up dedicated to the study of the degradation of high-molecular weight species likely to be present in the cometary nucleus. The first quantitative study of the photodegradation products of POM has been carried out. We have measured the quantum yield of formation of the different photoproducts as a function of wavelength and the kinetic parameters to calculate the thermal production of formaldehyde as a function of temperature. Using different sensitive analytical methods, we have been able to detect many products from POM irradiation. These are quite important results since most of these compounds have already been detected in comets with two exceptions, dimethoxymethane and trioxane. Thus observational programs should look for these molecules since their detection could be an indication of the presence of polyoxymethylene on the cometary nucleus. Both photo- and thermo-degradation mechanisms are quite efficient and could be responsible for formaldehyde in cometary comae. Moreover CO, which is a photodegradation product of POM, presents an extended source in several comets. Thus polyoxymethylene could also be involved in its production. We have provided here new quantitative data for understanding the origin of extended sources. The next step of this work will be to introduce these data into numerical models to interpret observations. This work is in progress [*Cottin et al.*, 2001].

Another experimental complement will be to repeat our experiments in the presence of water vapor in order to study the interaction of water photofragments with those from solid POM. Similar processes may occur in the inner coma.

To conclude, this experiment brings new insight into the chemistry of possible cometary environments. It appears that solid phase molecules can contribute directly to gas phase species, and thus these contributions have to be taken into account when one studies the chemical evolution of the coma.

4. Conclusion

The aim of both programs is to provide accurate experimental data (1) for models built in order to describe the photochemical evolution of Titan's atmosphere and other methane containing atmospheres and the extended source phenomenon in the cometary environment and (2) for the interpretation of observation.

In the highly complex chemical evolution of the studied planetary objects, there is a competition between formation of solid material starting from gases and degradation of solids leading to the production of gases. In order to study these transformations, both the SEMAPhOrE Cometaire and SCOOP programs are using the same methodological approach. It consists of complementary theoretical and experimental studies and proceeds step-by-step with an increasing complexity of the studied compounds or mechanisms.

The SCOOP program will continue to study long carbon chain molecules. Cyanopolyynes are of special interest since (1) HC_3N has already been observed by Voyager in Titan's atmosphere and (2) HC_5N has recently been observed in simulation experiments [*de Vanssay et al.*, 1995]. These compounds might be a new route to the formation of solids in the atmosphere. It can be noted that these compounds have also been observed for a long time in the interstellar medium. Dicyanopolyynes are also good candidates since C_2N_2 and C_4N_2 have been observed during the Voyager fly-by of Titan's atmosphere. C_4N_2 was observed in solid phase, which implies that other polyyne-like compounds could also be observed as ices. Future experimental efforts should include these species.

The SEMAPhOrE Cometaire program will be extended to other molecules. Studies on hexamethylenetetramine ($C_6H_{12}N_4$), HCN polymer, tholins, PAHs, and amino acids are in progress or planned. Investigation of the interaction mechanism between those molecules and water photofragments may also have implications on our knowledge of the chemistry of comets. Moreover, photo- and thermo-degradation of refractory organic material could also play an important role in interstellar clouds. Such mechanisms could be an efficient complementary pathway for the production of small compounds. From our point of view, generalizations of our results will allow us to clarify many aspects of the gas/solid/gas transformation cycle occurring in other extraterrestrial environments.

Acknowledgments. The authors are very grateful to the referees for their careful reading, comments, and English corrections, which were helpful in improving the manuscript. We thank Souleyman Bachir and Rodolphe Mulette for their participation in the experimental part of the work. SEMAPhOrE Cometaire and SCOOP programs are supported by grants from CNES (Centre National d'Etudes Spatiales) and PNP (Programme National de Planétologie, Institut National des Sciences de l'Univers, CNRS).

References

Bénilan, Y., P. Bruston, F. Raulin, C. Cossart-Magos and J.-C. Guillemin, Mid-UV spectroscopy of propynenitrile at low temperature: Consequences on expected results from observations of Titan's atmosphere, *J. Geophys. Res. 99*, 17,069-17,074, 1994.

Bénilan Y., P. Bruston, F. Raulin, R. Courtin, and J.-C. Guillemin, Absolute absorption coefficient of C_6H_2 in the mid-UV range at low temperature: implications for the interpretation of Titan atmospheric spectra, *Planet. Space Sci.*, *43*, 83-89, 1995.

Bernstein, M.P., S.A. Sandford, L.J. Allamandola, S. Chang, and M.A. Scharberg, Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol, *Astrophys. J.*, *454*, 327-344, 1995.

Biver, N., et al., Spectroscopic monitoring of Comet C/1996 B2 (Hyakutake) with the JCMT and IRAM Radio Telescopes, *Astron. J.*, *118*(4), 1850-1872, 1999.

Briggs, R., G. Ertem, J.P. Ferris, J.M. Greenberg, P.J. McCain, C.X. Mendoza-Gomez, and W. Schutte, Comet Halley as an aggregate of interstellar dust and further evidence for the photochemical formation of organics in the interstellar medium, *Origins Life Evol. Biosphere*, *22*, 287-307, 1992.

Bruston, P., F. Raulin, and H. Poncet, A laboratory facility for mid-UV absorption spectroscopy of molecular compounds for planetary atmospheres, *J. Geophys. Res. 96*(17), 513-517, 1991.

Cernicharo, J., New molecular species discovered by ISO in the interstellar and circumstellar media, in *ISO beyond the Peaks: Proceedings of the Second ISO Workshop on Analytical Spectroscopy*, edited by A. Salama et al., Eur. Space Agency, Noordwijk, Netherland, 81-87, 2000.

Cottin, H., Chimie organique de l'environnement cométaire: Etude expérimentale de la contribution de la composante organique réfractaire à la phase gazeuse, Ph.D. thesis, Université Paris XII, Créteil, 1999. (Available as: http://www.lisa.univ-paris12.fr/GPCOS/Hc/H1t.htm)

Cottin, H., M.C. Gazeau, and F. Raulin, Cometary organic chemistry: a review from observations, numerical and experimental simulations, *Planet. Space Sci.*, *47*(8-9), 1141-1162, 1999.

Cottin, H., M.C. Gazeau, J.F. Doussin, and F. Raulin, An experimental study of the photodegradation of polyoxymethylene at 122, 147 and 193 nm, *J. Photochem. Photobiology*, Ser. A, *135*, 53-64, 2000.

Cottin H., M.C. Gazeau, Y. Bénilan, and F. Raulin, Polyoxymethylene as parent molecule for the formaldehyde extended source in comet Halley, *Astrophys. J.*, in press, 2001.

Coustenis, A., and B. Bezard, Titan's atmosphere from Voyager infrared observations, 4, Latitudinal variations of temperature and composition, *Icarus, 115*, 126-140, 1995.

Coustenis, A., et al., Titan's atmosphere from ISO observations: Temperature, composition and detection of water vapor, *Bull. Am. Astron. Soc.*, *30*(3), 1060, 1998.

Dainton, F.S., K.J. Ivin, and D.A.G. Walmsley, The equilibrium between gaseous formaldehyde and solid polyoxymethylene, *Trans. Faraday. Soc.*, *55*, 61-64, 1959.

de Graauw, T., et al., First results of ISO-SWS observations of Saturn: Detection of CO_2, CH_3C_2H, C_4H_2 and tropospheric H_2O, *Astron. Astrophys.*, *321*, L13-L16, 1997.

Delpech, C., J.C. Guillemin, P. Paillous, M. Khlifi, P. Bruston, and F. Raulin, Infrared spectra of triacetylene in the 4000-200 cm-1 region: absolute band intensity and implications for the atmosphere of Titan, *Spectrochim. Acta, 50A*(6), 1095-1100, 1994.

de Vanssay E., M.C. Gazeau, J.C. Guillemin, and F. Raulin Experimental simulation of Titan's organic chemistry at low temperature, *Planet. Space Sci.*, *43*, 25-31, 1995.

DiSanti, M.A., M.J. Mumma, N. DelloRusso, K. Magee-Sauer, R. Novak, and T.W. Rettig, Identification of two sources of carbon monoxide in comet Hale-Bopp, *Nature*, *399*, 662-665, 1999.

Fahr, A., and A.K. Nayak, Temperature dependent ultraviolet absorption cross sections of 1,3-butadiene and butadiyne, *Chem. Phys, 189*(3), 725-731, 1994.

Gerakines, P.A., W.A. Schutte, and P. Ehrenfreund, Ultraviolet processing of interstellar ice analogs. I. Pure ices, *Astron. Astrophys.*, *312*, 289-305, 1996.

Gladstone, G. R., M. Allen and Y.L. Yung, Hydrocarbon chemistry in the upper atmosphere of Jupiter, *Icarus, 119*, 1-52, 1996.

Glicker, S. and H. Okabe, Photochemistry of diacetylene, *J. Phys. Chem, 91*(2), 437-440, 1987.

Grutter, M., M. Wyss, J. Fulara, and J.P Maier, Electronic absorption spectra of the polyacetylene chains $HC_{2n}H$, $HC_{2n}H^-$, and $HC_{2n-1}N^-$ (n = 6-12) in Neon matrixes, *J. Phys. Chem. A, 102*, 9785-9790, 1998.

Hanel, R., et al., Infrared observation of the Saturnian system from Voyager 1, *Science, 212*, 192-200, 1981.

Huebner, W.F., First polymer in space identified in comet Halley, *Science*, *237*, 628-630, 1987.

Khlifi, M., P. Paillous, C. Delpech, M. Nishio, P. Bruston, and F. Raulin, Absolute IR band intensities of diacetylene in the 250-4300 cm-1 region: Implications for Titan's atmosphere, *J. Mol. Spectrosc.*, *174*, 116-122, 1995.

Kloster-Jensen, E., H-J. Haink, and H. Christen, The electronic spectra of unsubstitued mono- to penta-acetylene in the gas phase and in solution in the range 1100 to 4000 Å, *Helv. Chim. Acta, 57*, 1731-1744, 1974.

Kobayashi, K., T. Kasamatsu, T. Kaneko, J. Koike, T. Oshima, T. Saito, T. Yamamoto, and H. Yanagawa, Formation of amino acid precursors in cometary ice environments by cosmic radiation, *Adv. Space Res.*, *16*(2), 21-26, 1995.

Kunde, V.G., A.C. Ainkin, R.A. Hanel, D.E. Jennings, W.C. Maguire, and R.E. Samuelson, C_4H_2, HC_3N, C_2N_2 in Titan's atmosphere, *Nature*, *292*, 686-688, 1981.

Meier, R., P. Eberhardt, D. Krankowsky, and R.R. Hodges, The extended formaldehyde source in comet P/Halley, *Astron. Astrophys.*, *277*, 677-691, 1993.

Moore, M.R., and R.L. Hudson, Infrared Study of Ion-Irradiated Water-Ice Mixtures with Hydrocarbons Relevant to Comets, *Icarus*, *135*, 518-527, 1998.

Okabe, H., *Photochemistry of Small Molecules*, Wiley-Interscience, New York, 1978.

Rabek, J.F., *Polymer Photodegradation: Mechanisms and Experimental Methods*, Chapman & Hall, New York, 1995.

Schutte, W.A., L.J. Allamandola, and S.A. Sandford, An experimental study of the organic molecules produced in cometary and interstellar ice analogs by thermal formaldehyde reactions, *Icarus*, *104*, 118-137, 1993.

Smith N., Y. Bénilan, and P. Bruston. The temperature dependent absorption cross-sections of C_4H_2 at mid ultraviolet wavelengths, *Planet. Space Sci.*, *46*(9/10), 1215-1220, 1998.

Smith, P. L., K. Yoshino, W.H. Parkinson, K. Ito, and G. Stark, High resolution VUV (147-201nm) photoabsorption cross sections for C_2H_2 at 195 and 295K, *J. Geophys. Res., 96*, 17,529-17,533, 1991.

Strazzulla, G., G. Leto, G.A. Baratta, and F. Spinella, Ion irradiation experiment relevant to cometary physics, *J. Geophys. Res.*, *96*, 17,547-17,552, 1991.

Yung, Y. L., M. Allen, and J. P. Pinto, Photochemistry of the atmosphere of Titan: comparison between model and observations, *Astrophys. J. Suppl.*, *55*, 465-506, 1984.

Y. Bénilan, M.-C. Gazeau, and F. Raulin, Laboratoire Interuniversitaire des Systèmes Atmospheriques, UMR CNRS 7583, Universités Paris VII-Paris XII, 94010 Créteil Cedex, France. (Benilan@lisa.univ-paris12.fr, Gazeau@lisa.univ-paris12.fr, Raulin@lisa.univ-paris12.fr).

P. Chaquin, Laboratoire de Chimie Théorique, Université Paris VI, Place Jussieu, 75005 Paris, France.

H. Cottin, Astrochemistry Branch, Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20770, USA. (hcottin@lepvax.gsfc.nasa.gov).

(Received July 11, 2000; revised April 10, 2001;
accepted April 25, 2001.)