New experimental results on the degradation of polyoxymethylene. Application to the origin of the formaldehyde extended source in comets.

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Abstract

The formaldehyde (H$_2$CO) observed in cometary atmospheres presents a so-called “extended source”. It means that its distribution in coma cannot be explained by sublimation from the nucleus alone, but a production inside the coma has to be included. Polyoxymethylene [formaldehyde polymers: (-CH$_2$-O-)$_n$ also called POM] is sometime evoked as a parent molecule for this extended source. This solid polymer on cometary grains could release gaseous formaldehyde through thermal and photolytic degradation.

We have developed an experimental program in order to study the chemical reactions of degradation of POM by UV photolysis and heating. It provides identification of the degradation products and the determination of the photo degradation quantum yields or the thermal degradation kinetics. In this paper, we present the improvements of our experimental setup and new measurements on the kinetics of gaseous formaldehyde production by thermal degradation of two types of commercial POM on a greater temperature range than the previous ones.

These new data are then included into a model of the outer coma in order to interpret observations. This model takes into account the production of gaseous molecules from solid material present on grains and leads to a very good agreement with Giotto observations of comet 1P/Halley, if we assume that the cometary grains contain 1-16% of POM by mass. Thus, without being a final evidence of this polymer presence on comets, we conclude that the degradation of solid POM-like polymers state on cometary grains is to date the best explanation of the H$_2$CO extended source.
1. Introduction

Most of the molecules observed in the cometary environment are directly produced by sublimation from the nucleus or by the sublimation of ice coating grains within the first few kilometers after they are ejected from the nucleus. However, the radial distribution of some molecules (CO, H$_2$CO, HNC….) cannot be totally explained with such simple processes. These molecules present a so called extended source, i.e. a production throughout coma and not only at or near the surface nucleus. This phenomenon prevents the direct extrapolation from the abundance of these gaseous molecules in the coma to their abundance in the nucleus. Nevertheless, the study of the extended source phenomenon could constrain the chemical composition of solid organics present on cometary grains.

In this paper, we study the origin of the formaldehyde (H$_2$CO) extended source. Its density profile has been derived in comet 1P/Halley from the *Giotto* Neutral Mass Spectrometer (NMS) measurements [Meier et al., 1993]. This observation demonstrates that H$_2$CO is not produced only by nucleus sublimation. Moreover, it has been confirmed that H$_2$CO is produced by an extended source in comet Hyakutake [Lis et al., 1997; Biver et al., 1999] and also in comet Hale-Bopp [Wink et al., 1999].

As H$_2$CO cannot be produced by photodissociation of another gaseous molecule, polyoxymethylene [formaldehyde polymer: (-CH$_2$-O-)$_n$, also called POM] has been proposed to interpret the H$_2$CO extended source [Meier et al., 1993; Eberhardt, 1999]. Indeed if POM is present on cometary grains, it may produce gaseous H$_2$CO by UV photolysis or thermal processing. This polymer of H$_2$CO has been tentatively detected on the grains of comet Halley by the PICCA mass spectrometer [Huebner, 1987]. Nevertheless, this detection is controversial since it has been shown that the feature attributed to POM in the PICCA mass spectrum could be merely the signature of the presence of organic material [Mitchell et al., 1992]. But POM has been surely detected in laboratory analogs of interstellar or cometary ices. It is synthesized by thermal processing of ices containing H$_2$O, H$_2$CO, NH$_3$ [Schutte et al., 1993] or during UV photolysis of ices containing H$_2$O, CH$_3$OH, CO and NH$_3$ [Bernstein et al., 1995]. Thus, the presence of POM in cometary ices is possible.

Recently, we have performed an experimental study of the POM degradation by UV photolysis and thermal processing [Cottin et al., 2000, 2001b]. Cottin et al. [2000] have shown that several oxygenated compounds (H$_2$CO, HCOOH, CO, CO$_2$ and CH$_3$OH) are produced by UV photolysis of POM at 122, 147 and 193 nm. The quantum yield of H$_2$CO production is roughly 1 up to 180 nm but decreases at longer wavelengths. On heating, POM produces only gaseous H$_2$CO since the polymer is in equilibrium with gaseous formaldehyde (POM $\leftrightarrow$ n H$_2$CO) [Dainion et al., 1959]. The production of gaseous molecules has been measured at several temperatures between 278 and 300 K by Cottin et al. [2001b]. The H$_2$CO kinetics has been shown to follow the Arrhenius law according to:

$$\frac{dH_2CO}{dt} = k(T).m_{POM} \quad \text{where} \quad k(T) = A.e^{-Ea/k_bT} \quad (1)$$

$k(T)$ is the number of gaseous formaldehyde molecules which are produced per gram of POM and per second, $A$ is the frequency factor in molecule.g$^{-1}$.s$^{-1}$ and $Ea$ is the activation barrier in Joule.molecule$^{-1}$. These experimental data have been included in a model of the coma [Cottin et al., 2001a and in press]. The required fraction of POM on cometary grains in order to reproduce the observed density profile of H$_2$CO has been determined. A last version of the model [Cottin et al., in press] has been built more recently taking into account of the whole distribution size of cometary grains. Measurements of the Giotto spacecraft are very well reproduced, if we suppose that the cometary grains contain less than 10% of POM by mass [Cottin et al., 2001a, in press]. A second issue of this study is that the production of gaseous
H$_2$CO by thermal degradation of POM is predominant over photo degradation when the comet Halley is at 0.9 AU from the Sun.

The chemical parameters used to model the thermal degradation of POM were very uncertain as the measurements were performed only on a small range of temperature (between 273 and 298 K), whereas the temperature of cometary grains at 1 AU is approximately ranging from 300 to 700 K [Greenberg and Li, 1998]. Moreover, when the comet is close to the Sun, thermal processing is predominant over the photolysis. Therefore, in order to improve the theoretical description of the thermal degradation of POM, we have performed a new experimental study with a new experimental setup allowing a more accurate determination of the H$_2$CO production kinetics from POM and over a greater temperature range (from 255 to 325 K). Moreover, two commercial types of POM have been studied to test the influence of different polymers on the thermal degradation kinetics. All new results are presented in this paper.
2. Experimental study

Thermal degradation of two commercial polyoxymethylenes (>99.5%, Prolabo and >95%, Aldrich) has been studied in a Pyrex reactor (Figure 1) with a double wall allowing the circulation of a thermostated fluid necessary to operate at a constant temperature. The temperature is measured with a K-type thermocouple on the wall of the reactor and is recorded during the whole time duration of the experiment with a digital thermometer. The reactor is equipped with a vacuum stopcock leading to the analysis system and another connection to a secondary vacuum pump which allows it to reach a vacuum better than 10^-6 mbars. A cryothermostat (LAUDA, RUL 80) filled with silicon oil (polydimethylsiloxane) allowing a thermal regulation between 210 and 350 K is used. The pressure inside the reactor is measured with a Baratron gauge (range 10^-4 -1 mbars) and the pressure is recorded with a time scale of one second.

The polymer is deposited at the bottom of the reactor. Then the temperature of the thermostated fluid is set at its minimal value. Several days are necessary to get rid of residual gas trapped between POM grains. After this step, the temperature was increased up to the required value.

First, we have verified using infrared spectroscopy that formaldehyde (H₂CO) is the single product of thermal degradation for both types of POM. In this case, the kinetics of H₂CO production is directly related to the pressure increase. Figure 2 represents the pressure as a function of time during an experiment at 278 K. The pressure increases and tends towards the equilibrium pressure [Dainton et al., 1959]. Thus, the production of gaseous formaldehyde under vacuum is proportional to the pressure increase measured on the 20 first seconds (which can be accurately fitted by a straight line in all the experiments (Figure 2)). Assuming the Ideal Gas Law, the kinetics of formaldehyde production (in number of molecules per second) is directly proportional to the pressure increase. Moreover, if we suppose that this production is proportional to the mass sample, the production of H₂CO in number of molecules per second and per gram of polymer is:

\[
k(T) = \frac{dn}{dt} \cdot \frac{1}{m_{\text{POM}}} = \frac{dP}{dt} \cdot \frac{V_{\text{reactor}}}{k_B \cdot T \cdot m_{\text{POM}}}
\]

where \(V_{\text{reactor}}\) is the total volume of the reactor including the volume of the connection of the pressure captor \(V_{\text{reactor}} = 195 \pm 1 \text{ cm}^3\) and \(k_B\) the Boltzmann constant.

In order to check that the production of formaldehyde is proportional to the mass sample, we have studied the pressure increase as a function of the mass of POM in the reactor at 289 K. As shown in figure 3, the pressure increase is proportional to the mass sample. Thus equation (2) can be used to determine the kinetics of formaldehyde production from the pressure increase. Moreover, the linear relationship shows that the thermal degradation of POM takes place in the whole volume of the sample, and not only at the surface like for the UV photolysis. This result has important implications for the modeling in the cometary grains. We also note that the “Prolabo POM” is more productive than the “Aldrich POM” at a temperature of 289 K.

We have measured H₂CO production for both kinds of POM between 250 and 330 K. The results are presented in figure 4. The errors bars on each point take into account the uncertainties of the slope of pressure increase, on the mass sample and of the total volume of the reactor. These measurements are well fitted by the Arrhenius law (see eq. (1)). These fits allow us to determine \(E_a\), the activation barrier and \(A\) the frequency factor:

- \(E_a = 81 \times 10^3 \pm 0.76\% \text{ J.mole}^{-1}\) and \(A = 1.2 \times 10^{30} \pm 28\% \text{ molecules.g}^{-1} \text{s}^{-1}\) for the “Prolabo POM”
- \( E_a = 99 \times 10^3 \pm 2.3\% \) J.mole\(^{-1}\) and \( A = 7.2 \times 10^{32} \pm 140\% \) molecules.g\(^{-1}\).s\(^{-1}\) for the “Aldrich POM”.

The non symmetric errors bars on \( A \) are due to the logarithm function (\( \ln A \) is calculated with a symmetric error bar). The value of the activation barrier is quite important; it shows that the production of \( \text{H}_2\text{CO} \) from POM is highly sensitive to the temperature. But, the kinetics of formaldehyde production is different for the two kinds of POM. In order to understand the origin of this discrepancy, we have performed infrared spectroscopy of both types of POM in KBr pellets. These spectra are displayed in Figure 5 (the resolution is 4 cm\(^{-1}\)). The minor difference in the spectra at 668 and around 2350 cm\(^{-1}\) are due to the presence of \( \text{CO}_2 \) (due to incomplete purge of the spectrometer) and the one around 1630 cm\(^{-1}\) to \( \text{H}_2\text{O} \). However, these spectra are roughly identical. It suggests that the POM structures are very similar so that the difference in the kinetics of thermal degradation could rather be due to the length of the chain of polymers or the impurities in the sample. Work focused on the differences between different kinds of POMs is currently in progress.

In conclusion, we have determined new values of the activation barrier \( E_a \) and the frequency factor \( A \) that differ from \([\text{Cottin et al.,2001b}]\) ones (\( E_a = 74.2 \times 10^3 \pm 10\% \) J.mole\(^{-1}\) and \( A = 8.7 \times 10^{27} \pm 120\% \) molecules.g\(^{-1}\).s\(^{-1}\) ) which were obtained on “Prolabo POM” between 273 and 298 K. These new results are considered to be more reliable as they have been retrieved with an optimized experimental setup. Indeed we are now able to record the pressure inside the reactor with a time scale of one second whereas previously it was manually recorded. Then we are now able to derive the pressure increase from the first 20 second of the experiments (see Figure 2) and therefore we are not affected by the equilibrium between gaseous \( \text{H}_2\text{CO} \) and POM. These new results are then more reliable than the previous ones.
3. Modeling of the cometary environment

We [Cottin et al., 2001a and in press] have derived new equations assuming the hypotheses of Haser [1957] (spherical symmetry of the coma, steady state in the production of gas and dust…) in order to model the production of gaseous molecules from solid materials present on grains. This model takes into account the photo and thermal processes in order to reproduce the production of gaseous formaldehyde by an extended source but it takes also account of the possible production of formaldehyde by sublimation from nucleus. It allows us to fit the formaldehyde density profiles which have been obtained from Giotto NMS measurements [Meier et al., 1993]. For the present study, we have used the last version of the model [Cottin et al., in press] which takes into account a grain size distribution. The free parameters of this model are the percentage of POM by mass percent in grains (Q_{POM}) and the production rate of parent formaldehyde (i.e. the formaldehyde produced directly at the nucleus surface, Q_{H_2CO}). Other important parameters of this model are the temperature, the velocity and the size distribution of the grains. The grain temperature is calculated at 0.9 AU from the Sun using Mie theory considering spherical grains made of a mixture of amorphous carbon and olivine. Amorphous carbon is representative of black matter, and stands as an upper limit for a strongly absorbing organic component of grains. Olivine stands for the silicate component of grains with a very low absorption in the visible. Then pure grains of amorphous carbon stand for an upper limit of grain temperature whereas pure grains of olivine represent a lower limit. The grain temperature as a function of their radius for different composition is presented in figure 6. A similar figure has already been presented in Cottin et al. [in press]. The velocity of each grain is calculated as a function of the grain size using the formula given in Crifo [1995]. We have used the grains distribution which is presented in Crifo and Rodionov [1997] (Figure 7). It is derived from in situ measurements presented in McDonnell et al. [1991]. Nevertheless, it must be noted that data for grains up to 1 mg are direct in-situ measurements, whereas higher values are extrapolation.

The temperature of grains as well as the mass of the bigger ones which can be lifted by the nucleus are not well constrained. Therefore we have performed several fits with grains containing 30 or 50% of amorphous carbon to simulate different temperatures and for different mass of the bigger grains. This mass of the bigger grains is arbitrary set at $10^{-2}$, 1, $10^{-2}$ or $10^{+2}$ g. For comparison, the grains distribution leading to the best fit in Cottin et al. [in press] corresponds to the same size distribution and a cut off at 1 g. Moreover, we have used both kinetics data derived from “POM Prolabo” and “POM Aldrich”. Results are presented in Table 1a and 1b which are displaying both free parameters (Q_{POM} and Q_{H_2CO}/Q_{H_2O}) and $\sigma$ which is the standard deviation of the fit. Two examples of fits are presented in Figure 8a and 8b.

As it has already been shown in Cottin et al. [in press, 2001a], we find that, at the heliocentric distance of the Giotto encounter with comet Halley, the thermal degradation of POM is predominant over the photo degradation. The required fraction of POM is from 1.2 to 1.7 times higher if we consider the kinetic data of the “Aldrich POM” rather than the ones of “Prolabo POM” (see Table 1a and 1b). Indeed most of the gaseous formaldehyde are produced by the bigger grains [Cottin et al., in press] for which the temperature is about 320 K. At this temperature, the kinetic of gaseous formaldehyde production is roughly 1.4 times higher for the “Prolabo POM” than for the “Aldrich POM”. Thus the required fraction of POM in cometary grains is directly related to the kinetics data which are used.

For some fits, the standard deviation is relatively high. Indeed, no relevant results are obtained with a mass of the bigger grains equal to $10^{-2}$ gram. In this case, the grains are not abundant enough to fit measurements. Nor are relevant results obtained if we consider high
temperature grain (grains containing 50% of amorphous carbon) with a mass of the bigger grains equal to 10 grams. In this case, too much gaseous formaldehyde is produced from POM degradation. If we exclude these extreme cases, the best fits are obtained with a standard deviation ranging from 6 to 7%. For all these adjustments, the production of parent formaldehyde from the nucleus is ranging from 0 to and 0.8%, and the fraction of POM by mass from 1.3 to 15.5%.

Greenberg [1998] has estimated that complex organic molecules dominated by carbon represent about 47% of the mass of the refractory materials present in cometary nucleus. Moreover, Bernstein et al. [1995] has measured that POM-related compounds represent 20% by mass of the organic material remaining after photolysis and heating at room temperature of laboratory ice analogs. We can derive from these data that values up to 9% in mass of POM-like polymers can be reached in comets. Thus, the required fraction of POM to fit the H$_2$CO density profile is consistent with this latter value. Moreover, this result is not dependent on the type of POM used in the model. Therefore, the production of gaseous formaldehyde from POM degradation is a quantitative explanation of the formaldehyde extended source and the presence of POM-like polymers in cometary nucleus is highly probable.
4. Conclusion.

It has been shown that the degradation by UV photolysis or heating of POM could explain the \( \text{H}_2\text{CO} \) extended source [Cottin et al, in press, 2001a]. We have presented in this paper new experimental measurements of the thermal degradation of this polymer on a greater temperature range than the previous ones. The kinetics of gaseous formaldehyde production has been derived for two types of POM. The results are quite different. This discrepancy is not completely understood so far, but it could be due difference of the length of the chains of the polymers. New studies are in progress to understand the origin of this difference.

Nevertheless, these kinetics data have been included into a model of the coma, which takes into account the production of gaseous molecules from solid materials present on cometary grains. The data on both type of POM allow us to reproduce with a good accuracy the measurements of the \( \text{H}_2\text{CO} \) density acquired by the Giotto spacecraft inside the coma of comet Halley, and are leading to similar results at this heliocentric distance. Since the production of gaseous \( \text{H}_2\text{CO} \) depends of the type of polymer that we consider, we are now currently studying the \( \text{H}_2\text{CO} \) extended source as a function of the heliocentric distance in comet C/1995 O1 (Hale-Bopp) to test the influence of a variation of grain temperature.

The required fraction of POM by mass on grains in order to fit the Giotto observations has been found to range from 1.3 to 15.5% for different parameters of grains. Theses values are quite consistent with previous estimates based on observations and laboratory works. Thus, without being a final evidence of the presence of the polymer on comets, we conclude that POM-like polymers in the solid state on cometary grains are to date the best interpretation of the \( \text{H}_2\text{CO} \) extended source.
References


Cottin, H., Y. Benilam, M.-C. Gazeau, and F. Raulin, Origin of cometary extended sources from degradation of refractory organics on grain: polyoxymethylene as formaldehyde parent molecule, Icarus, in press.


**Figure captions**

**Figure 1:** Experimental Setup. The Pyrex reactor has a double wall for circulation of a thermostated liquid. The temperature is measured with a K-type thermocouple on the wall of the reactor. It is equipped with a vacuum stopcock leading to the analysis system and another connection to a vacuum pump.

**Figure 2:** Pressure in the reactor as a function of time in an experiment at 274 K. The black line represents the pressure measurements, whereas the gray line is a fit on the 20 first seconds of the pressure measurements as shown in the zoom.

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**Figure 4:** log of the formaldehyde production rates as a function of the inverse of the temperature. The black squares represent the measurement on the “Prolabo POM” and the grey circles on the “Aldrich POM”. The black and grey lines are fits on the measurements. They allow us to determine $E_a$ (the activation barrier) and $A$ (the frequency factor).

**Figure 5:** Infrared spectra of solid POMs in KBr pellets. The resolution is 4 cm$^{-1}$. The spectrum of “POM Aldrich” has been shifted.

**Figure 6:** Grain temperature as a function of their radius and composition at 0.9 AU from the Sun. The grey circles and triangles are for pure grains of amorphous carbon and olivine. They represent the upper and lower limit for the grain temperature. The black squares are for grains made of a mixture made of 30% of amorphous carbon and 70% of olivine. The black circles are for grains made of a mixture of 50% of amorphous carbon and 50% of olivine.

**Figure 7:** Dust grain production from comet Halley nucleus as a function of the grain mass. This distribution has been presented in Crifo and Rodionov [1997] and is derived from in situ measurements. The data for grains up to 1 mg are direct in situ measurements, whereas higher values are extrapolation. The dashed lines represent the cut offs which have been used in the modeling ($10^{-2}$, 1, $10^{-2}$ or $10^{-4}$g).

**Figure 8a:** H$_2$CO density as a function of the distance from the nucleus. The solid line represents the fit obtained with our model, whereas the dotted line is the fit obtained with a simple Haser model (production only at the nucleus surface). This fit has been obtained with the kinetics data of the « Prolabo POM », with grains made of 30% of amorphous carbon and of 70% of olivine. The mass of the bigger grains is 100 g.

**Figure 8b:** H$_2$CO density as a function of the distance from the nucleus. The solid line represents the fit obtained with our model, whereas the dotted line is the fit obtained with a simple Haser model (production only at the nucleus surface). This fit has been obtained with the kinetics data of the « Aldrich POM », with grains made of 50% of amorphous carbon and of 50% of olivine. The mass of the bigger grains is 1 g.
Grains made of 30% of amorphous carbon and 70% of olivine  
Grains made of 50% of amorphous carbon and of 50% olivine

<table>
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<th>Mass of the bigger grains (g)</th>
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<tr>
<td>QPOM (%)</td>
<td>20 15.5 4 1.5</td>
<td>20 6.2 2.3 1</td>
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<td>QH2CO / QH2O (%)</td>
<td>1.8 0.8 0.7 0.35</td>
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**Table 1a:** Results of the fits performed with the kinetics data acquired on “POM Aldrich”.  
QPOM (%) is the percentage of POM by mass present in grains, QH2CO is the production rate of formaldehyde produced by the nucleus sublimation (in molecules.s⁻¹) and QH2O is the production rate of water (in molecules.s⁻¹) which has been taken equal to 6 10²⁹ molecules.s⁻¹ [Fink and DiSanti, 1990]. σ is the standard deviation of the fit.

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<td>QPOM (%)</td>
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<td>σ (%)</td>
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<td>6.8 6.3 6.3 14.1</td>
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**Table 1b:** Results of the fits performed with the kinetics data acquired on “POM Prolabo”.  
QPOM (%) is the percentage of POM by mass present in grains, QH2CO is the production rate of formaldehyde produced by the nucleus sublimation (in molecules.s⁻¹) and QH2O is the production rate of water (in molecules.s⁻¹) which has been taken equal to 6 10²⁹ molecules.s⁻¹ [Fink and DiSanti, 1990]. σ is the standard deviation of the fit.
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