

POLYOXYMETHYLENE AS PARENT MOLECULE FOR THE FORMALDEHYDE EXTENDED SOURCE IN COMET HALLEY

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ABSTRACT

Among unsolved questions raised by observations of comets is the origin of extended sources, i.e., the distribution of molecules in the coma which cannot be explained by a direct sublimation from the nucleus. Polyoxymethylene [formaldehyde polymer: $(-\text{CH}_2\text{O}-)_n$, also called POM] is sometimes invoked as a potential parent compound, the degradation of which could produce the required amount of H_2CO across the coma, but no quantitative study has ever been undertaken with relevant parameters. From new experimental data, we are now able to consider multiphase chemistry: POM in the solid state on cometary grains slowly degrades by solar photons and heat and produces H_2CO in the gaseous phase. This is a new approach to cometary organic chemistry. We show, by considering simple assumptions about the cometary environment, that the hypothesis of POM on grains leads to a very good agreement with *Giotto* observations if we assume that the cometary grains are $\sim 7\%$ POM by mass at a temperature of 330 K.

Subject headings: comets: general — comets: individual (Halley) — molecular processes

1. INTRODUCTION

Formaldehyde density profiles in comet Halley have been derived from *Giotto* NMS (Neutral Mass Spectrometer) measurements between 1740 and 4400 km from the nucleus (Meier et al. 1993). It cannot be interpreted by a direct sublimation of H_2CO from the nucleus, and no interpretation relevant to cometary conditions has ever been proposed. Indeed, none of the gaseous parent molecules already detected have a lifetime compatible with formaldehyde observations (Biver et al. 1999). This is also the case for comets Hyakutake (Biver et al. 1999) and Hale-Bopp (Wink et al. 1999).

Polyoxymethylene has been tentatively detected in the coma of comet Halley by the Positive Ion Cluster Composition Analyzer (PICCA) mass spectrometer instrument onboard the *Giotto* spacecraft (Huebner 1987). This detection is very uncertain since it has been shown that the mass pattern attributed to POM in the PICCA mass spectrum is only a signature of the presence of complex organic material made of C, H, O, and N atoms (Mitchell et al. 1992). Nevertheless, POM has been detected after experimental simulations of energetic processes on cometary or interstellar ice analogs. It is synthesized in ices containing H_2O , H_2CO , CH_3OH , CO, and NH_3 , during UV photolysis or thermal processing (Bernstein et al. 1995; Schutte et al. 1993). The latter mechanism seems to be the more efficient; therefore, the presence of an important amount of POM in comets could be an indicator of an ice history dominated by thermal transformation rather than UV photolysis or energetic particle bombardment (Cottin et al. 1999). Thus, the presence of POM is still an open and important issue.

Recently, we have performed an experimental study that has provided physicochemical data that were missing to model the production of formaldehyde from solid polyoxymethylene: its production quantum yield from photolysis as a function of wavelength (Cottin et al. 2000) as well as its

thermal production rate as a function of temperature (Arrhenius constant and activation barrier) (Cottin et al. 2001). If formaldehyde is the one and only molecule produced by thermal degradation of POM, its photodegradation leads to the production of other molecules, mainly CO, CO_2 , HCOOH, CH_3OH , CH_3OCHO , already detected in comets (Bockelée-Morvan et al. 2000). We have developed a mathematical model describing the degradation of polyoxymethylene present in the solid state on grains. This model is applied to *Giotto* measurements in comet Halley. Our work differs from previous studies on this subject (Boice et al. 1990; Meier et al. 1993), where POM photochemistry was modeled in the gaseous phase with estimated rate coefficients and no parameters for H_2CO thermal production were included.

2. MODEL

We consider that polyoxymethylene is ejected from the nucleus as single spherical grains of pure POM. Discussions of our results show that our conclusions can be extended to a production from grains with heterogeneous compositions and sizes.

A decrease of the grain size (caused by loss of material by POM degradation) as a function of the distance from the nucleus is described by equations (1) and (2):

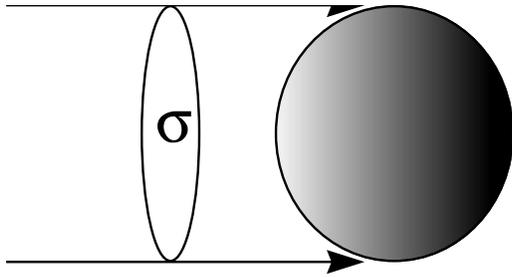
$$\frac{dm}{dr} = 4\mu\pi R^2 \frac{dR}{dr}, \quad (1)$$

where m is the grain mass, r the distance from nucleus, $\mu = 1.46 \times 10^3 \text{ kg m}^{-3}$ the density of POM, and R the radius of the grain:

$$\frac{dm}{dt} = -\sigma C - L_T. \quad (2)$$

The photodegradation of the grain is described by σC , with $\sigma = \pi R^2$, the effective absorbing surface (see Fig. 1), and C the grain mass loss by photodegradation per second

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$$\sigma = \pi R^2 \quad \text{Grain}$$

$$V = \frac{4}{3} \pi R^3$$

FIG. 1.—Spherical grain (radius = R) lit up by a parallel photon flux. Photons reaching the grain surface are in a σ section cylinder.

given by

$$C = \sum_X \left(m_X \int_{\lambda} f_{\lambda} \Phi_{\lambda}^X d\lambda \right). \quad (3)$$

The molecular mass of the main photodegradation products of POM is m_X ($X = \text{H}_2\text{CO}, \text{CO}, \text{CO}_2, \text{HCOOH}$), f_{λ} is the solar flux at the wavelength λ (Mount & Rottman 1981), and the production quantum yield profile as a function of wavelength proposed in Cottin et al. (2000) (i.e., for H_2CO , roughly 0.9 from 120 to 190 nm and 0 for higher wavelength) is adopted.

We consider that the grain rotates on itself, so that its mass loss by photodegradation is uniform over its surface, and calculate $C = 6.76 \times 10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$.

L_T describes the polymer's thermal degradation. We assume a homogeneous grain temperature and the fact that formaldehyde is not only produced from the grain surface but that the polymer is porous enough to allow a production and diffusion of H_2CO throughout its volume and thereby contribute to the extended source. Then $L_T = M_{\text{H}_2\text{CO}} k m$, with $M_{\text{H}_2\text{CO}}$ the molar mass of formaldehyde and k the kinetic constant for the thermal degradation reaction calculated from the Arrhenius law: $k = A \exp(-E_a/RT)$, where the Arrhenius constant $A = 8.7 \times 10^8 \text{ mol kg}^{-1} \text{ s}^{-1} \pm 60\%$; the activation barrier $E_a = 74.2 \text{ kJ mol}^{-1} \pm 10\%$; $R = 8.32 \text{ J mol}^{-1} \text{ K}^{-1}$, and T is the grain temperature (Cottin et al. 2001).

Equations (1) and (2) lead to an expression for the grain radius as a function of its distance from the nucleus:

$$R = -\frac{D}{B} + \left(R_0 + \frac{D}{B} \right) e^{-Br}, \quad (4)$$

with R_0 the initial radius of the grains, $B = k M_{\text{H}_2\text{CO}}/3v_p$ and $D = C/(4\mu v_p)$.

The grain velocity is v_p , calculated from Crifo (1995) using the initial radius for the grains, and assumed constant (the acceleration occurs in the first kilometers from nucleus, where $R = R_0$ can be assumed).

Since the dynamics of the coma are complex, we make simplifying assumptions in order to describe the density profile of a particle (gaseous molecule or solid grain) around the nucleus. We use Haser's model (Haser 1957), which

assumes the following points:

1. Spherical symmetry around the nucleus: uniform emission from the nucleus at surface, or the mixing of emitted particles within the first few kilometers,
2. Stationary state: the nuclear production is constant on the timescale of the modeled processes, and
3. Radial expansion occurs at a constant rate.

The formaldehyde density profile in the coma as a function of the distance r from the nucleus can be described, according to the Haser model, by the following equation of conservation (H_2CO production and loss is from POM degradation and H_2CO photochemistry, respectively):

$$\frac{v}{r^2} \frac{dnr^2}{dr} = \frac{dn}{dt} \Big|_g - Jn, \quad (5)$$

where v is the mean gas velocity in the studied region (780 m s^{-1} ; Meier et al. 1993), n is the formaldehyde density (m^{-3}), and J is the formaldehyde photodissociation rate ($2.00 \times 10^{-4} \text{ s}^{-1}$; Crovisier 1994).

The formaldehyde production rate by photo and thermal degradation of POM is

$$\frac{dn}{dt} \Big|_g = \frac{Q_p C'}{4v_p} \frac{R^2}{r^2} + \frac{Q_p N \mu k}{3v_p} \frac{R^3}{r^2}, \quad (6)$$

where Q_p is the grain production from nucleus, $C' = \int_{\lambda} f_{\lambda} \Phi_{\lambda}^{\text{H}_2\text{CO}} d\lambda = 5.07 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$ is the formaldehyde photoproduction calculated from Mount & Rottman (1981) and Cottin et al. (2000), and N is the Avogadro number (6.02×10^{23}).

The solution of former equations (4), (5), and (6) leads to

$$\begin{aligned} n_{\text{H}_2\text{CO}} = \frac{1}{r^2} \left\{ \right. & \left[\frac{MH}{(1/l) - 3B} (\exp^{-3Br} - \exp^{-r/l}) \right] \\ & + \left[\frac{EL - MI}{(1/l) - 2B} (\exp^{-2Br} - \exp^{-r/l}) \right] \\ & + \left[\frac{MJ - FL}{(1/l) - B} (\exp^{-Br} - \exp^{-r/l}) \right] \\ & + [(IG^2L - IG^3M) \cdot (1 - \exp^{-r/l})] \\ & \left. + \left(\frac{Q_{\text{H}_2\text{CO}}}{4\pi v} \exp^{-r/l} \right) \right\} \quad (7) \end{aligned}$$

with $Q_{\text{H}_2\text{CO}}$, the direct production rate of formaldehyde as a parent molecule from the nucleus (s^{-1}), l the formaldehyde scale length (v/J), $G = D/B$, $E = (G + R_0)^2$, $F = 2(G^2 + GR_0)$, $H = (G + R_0)^3$, $I = 3(G^3 + 2G^2R_0 + GR_0^2)$, $J = 3(G^3 + G^2R_0)$, $L = Q_p C'/4v_p v$, and $M = Q_p N \mu k/3v_p v$. $Q_{\text{H}_2\text{CO}}$, Q_p , R_0 , and T are the free parameters adjusted to fit the *Giotto* formaldehyde measurements within ranges relevant to known cometary environments.

3. RESULTS AND DISCUSSION

The best fit to *Giotto* NMS measurements with our model is presented in Figure 2. Such a result is obtained for $Q_{\text{H}_2\text{CO}} = 5 \times 10^{27} \text{ s}^{-1}$, $Q_p = 1.2 \times 10^{14} \text{ s}^{-1}$, $R_0 = 10 \text{ }\mu\text{m}$, $T = 330 \text{ K}$. Since $Q_{\text{H}_2\text{O}} = 3 \times 10^{29} \text{ s}^{-1}$, and the grain production from Halley near perihelion was $\sim 10^4 \text{ kg s}^{-1}$ (Arpigny 1994), we can conclude that the direct H_2CO production from the nucleus (i.e., as a monomer) is 1.7% relative to water and that POM grains with $R_0 = 10 \text{ }\mu\text{m}$ are

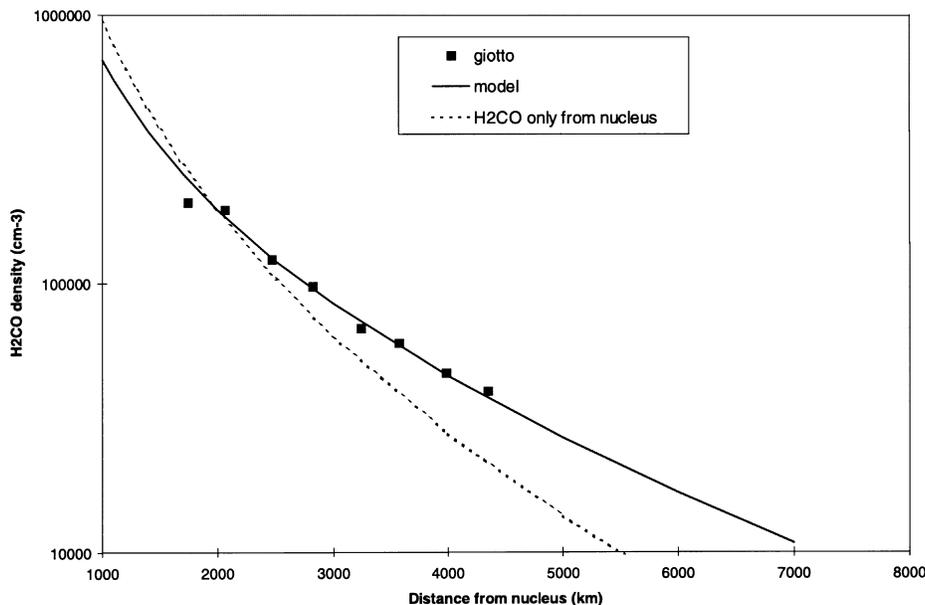


FIG. 2.—Formaldehyde density profile in comet Halley measured by *Giotto* (squares) and calculated with (continuous line) or without (dotted line) extended source production. The density profile without POM is calculated with $Q_{\text{H}_2\text{CO}} = 1.2 \times 10^{28}$ (i.e., $\sim 4\%$ relative to water production).

$\sim 7\%$ of the total dust mass. From equation (4), we can check that the grain lifetime is consistent with our results: at 330 K, an initial POM grain radius of 10 micrometers ($vp = 0.2 \text{ km s}^{-1}$ calculated from Crifo 1995) is reduced $\sim 30\%$ at 5000 km, thus grains can contribute to the extended source throughout all the studied part of the coma.

A good production can also be achieved without any photodegradation for 330 K grains with the same POM amount, whereas considering only photodegradation requires a POM grain production from the nucleus at a level more than 10 times above the total grain production. We conclude that the main process responsible for H_2CO production is the thermal degradation of POM.

Only the porosity, which is not parameterized here, is an important factor that could change our results because some H_2CO diffusing within the grain might be trapped. But if we assume that grain temperature is the only influential parameter controlling a H_2CO production rate proportional to the mass of POM, the geometry, composition, and size of grains would not influence our results, which can then be extended to heterogeneous grains made of refractory material, including a certain amount of POM-emitting formaldehyde throughout its volume as previously described in this paper.

Our model leads to the same fit for the same relative mass of POM ($\sim 7\%$) for any grain size between 0.1 and 10 micrometers with T ranging from 340 to 320 K. Concerning the other free parameters of our model, $Q_{\text{H}_2\text{CO}}$ can vary from 0% to 3% compensated by small variation of T ($\pm 10 \text{ K}$). Such a formaldehyde production is consistent with measurements in Halley ranging from 1.5% to 4.5% (Mumma & Reuter 1989; Snyder et al. 1989; Combes et al. 1988) but cannot be better constrained. We have presented here the best production for the most relevant conditions. Indeed, Greenberg (1998) has estimated from observations and laboratory investigations that a cometary nucleus is made (by mass) of 26% silicates, 23% refractory organic molecules, 9% polycyclic aromatic hydrocarbons, and a mixture of volatile molecules dominated by water as the

remainder. Thus, refractory organic molecules would represent 40% of the nonvolatile component of comets. On the other hand, a laboratory photolyzed $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3$ ice mixture (ratio 10:5:1:1) leads to the formation of a refractory material containing 20% ethers and POM-like polymers (Bernstein et al. 1995), i.e., 8% of the cometary nucleus and grains refractory component. Moreover, we already underlined that POM production is more efficient in ices containing H_2CO and NH_3 when they are submitted to a simple warming process (Schutte et al. 1993), which could result in a mass fraction higher than 8%. Good production can also be achieved for higher amounts of POM and lower T , but the more polymer that is required, the less realistic is the simulation. Thus, the POM abundance derived from our model is consistent with the observations and experimental investigations of comets. Nevertheless, this abundance is low enough to originate either from UV or thermal processing of the initial ice mixture; we cannot conclude which is the dominant process at this point.

The temperature of cometary grains is a parameter that is not well constrained in the literature because it depends mainly on the nature of refractory material, which is poorly known. However, 320–340 K are typical temperatures that can be reached by grains in comae (Crifo 1991; Greenberg & Li 1998). Further improvements of our model should allow us to physically constrain the temperature, which is here a free parameter.

Carbon monoxide is another molecule that presents an extended source in comets (Eberhardt et al. 1987; DiSanti et al. 1999). The total amount of CO (nucleus + extended) is 24% in Hale-Bopp: about one half is produced by an extended source and the other half is from nucleus (DiSanti et al. 1999). CO can be produced by POM photodegradation at about the same quantum yield as H_2CO (Cottin et al. 2000) but not by thermal degradation. This latter mechanism contributes more than 99.9% to the extended formaldehyde profile for 330 K grains. Thus, if extended CO in Hale-Bopp originated from POM photodegradation, then one should expect a formaldehyde pro-

duction at least a thousand times more elevated because of its thermal production. This would result in more H₂CO than CO in the coma. Bockelée-Morvan et al. (2000) have calculated a formaldehyde molecular abundance of 1% in the coma of Hale-Bopp, assuming an extended source. POM clearly cannot be the main precursor for carbon monoxide. An experimental study of CO release by photodegradation or thermal degradation of refractory material obtained after energetic processing of ice mixtures should be undertaken in order to determine if a CO extended source can also originate from the slow degradation in the coma of other high molecular weight molecules.

Clearly thermal degradation of polyoxymethylene is a very efficient way to produce formaldehyde in cometary comae, and our model shows for the first time a realistic interpretation of the *Giotto* measurements in comet Halley. Other molecules could also permit a good fit to observation, but to date none of those have been detected after experimental simulation on cometary ice analogs. Without being a final evidence of the polymer presence on comets, we conclude that POM-like polymers in the solid state on cometary grains is to date the best interpretation of observations that have remained puzzling for a long time. A next step toward POM identification, apart from an in situ

analysis during a space mission like *Rosetta*, would be to either directly detect its signature from near-infrared observation or to observe as extended sources its other photodegradation products: CO₂, HCOOH, CH₃OH, and CH₃OCHO. But, as we have shown, photodegradation is not the main degradation mechanism, and production efficiencies of those molecules are low compared to that for H₂CO. An extended source for methanol has already been reported by Womack et al. (1997) but with a signal-to-noise ratio so low that this detection remains very tentative. Achieving detection sensitivity and spatial resolution high enough to study such processes will be the future challenge.

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