Heliocentric evolution of the degradation of polyoxymethylene: Application to the origin of the formaldehyde (H$_2$CO) extended source in Comet C/1995 O1 (Hale–Bopp)

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Abstract

The H$_2$CO production rates measured in Comet C/1995 O1 (Hale–Bopp) from radio wavelength observations [Biver, N., and 22 colleagues, 2002a. Earth Moon Planets 90, 5–14] showed a steep increase with decreasing heliocentric distance. We studied the heliocentric evolution of the degradation of polyoxymethylene (formaldehyde polymers: (–CH$_2$–O–)$_n$, also called POM) into gaseous H$_2$CO. POM decomposition can indeed explain the H$_2$CO density profile measured in situ by Giotto spacecraft in the coma of Comet 1P/Halley, which is not compatible with direct release from the nucleus [Cottin, H., Bénilan, Y., Gazeau, M.-C., Raulin, F., 2004. Icarus 167, 397–416]. We show that the H$_2$CO production curve measured in Comet C/1995 O1 (Hale–Bopp) can be accurately reproduced by this mechanism with a few percents by mass of solid POM in grains. The steep heliocentric evolution is explained by the thermal degradation of POM at distances less than 3.5 AU. This study demonstrates that refractory organics present in cometary dust can significantly contribute to the composition of the gaseous coma. POM, or POM-like polymers, might be present in cometary grains. Other molecules, like CO and HNC, might also be produced by a similar process.

Keywords: Comets, composition; Organic chemistry

1. Introduction

To date, about two dozen molecules (excluding ions and radicals) have been detected in cometary environments (Bockelée-Morvan et al., 2005). Most of them are directly produced by sublimation from the nucleus or from ice-coated grains within the first few kilometers after their ejection from the nucleus. However, for certain comets, the radial distribution of some molecules such as CO (Eberhardt et al., 1987; DiSanti et al., 2001) and H$_2$CO (Meier et al., 1993; Wink et al., 1999; Biver et al., 1999) cannot be entirely explained by such simple processes. These molecules present a so-called “extended source,” i.e., involving production throughout the coma and not only at or near the surface of the nucleus. Such behavior could result from other mechanisms such as chemical reactions in the inner coma (Rodgers and Charnley, 1998) or degradation of high molecular weight organic compounds present in cometary grains (Cottin et al., 2004). As these molecules are not produced only by sublimation of the nucleus, their abundance in the gas phase cannot be directly related to their abundance in the nucleus. Nevertheless, the understanding of their production mechanism is of great interest to constrain the composition of the nucleus. In this paper, we focus on the steep heliocentric evolution of H$_2$CO production rates observed at radio wavelengths for Comet C/1995 O1 (Hale–Bopp) by Biver et al. (2002a).
Formaldehyde is an important cometary molecule which has been observed through its radio rotational lines in more than 15 comets. With a production rate relative to water of about 1% (Bockelée-Morvan et al., 2005), it is the most abundant CHO cometary molecule after methanol. An even higher abundance (3.8%) was derived from the mass spectroscopic observations of Comet 1P/Halley by Giotto (Meier et al., 1993). This relative abundance is observed to vary from comet to comet (from 0.13 to 1.3% according to radio observations, Biver et al., 2002b).

Among comets for which the spatial distribution of H$_2$CO has been studied, all observations, except for those concerning Comet C/2002 C1 (Ikeya–Zhang) (DiSanti et al., 2002), suggest that formaldehyde does not come from sublimation of the pristine ices in the nucleus, but rather from an extended source within the coma. This was suggested by the analysis of the H$_2$CO density profiles of 1P/Halley measured by the Giotto Neutral Mass Spectrometer (NMS) (Meier et al., 1993). Maps of the spatial distribution of H$_2$CO at radio wavelengths in Comets C/1989 X1 (Austin) and C/1990 K1 (Levy) (Colom et al., 1992) and in C/1996 B2 (Hyakutake) (Biver et al., 1999) also show that H$_2$CO is produced by an extended source. Finally, radio-interferometric observations have shown an H$_2$CO extended source in Comet C/1995 O1 (Hale–Bopp) (Wink et al., 1999). All these observations show that H$_2$CO is produced with a scale length of about 6800R$_H^{1.4}$ km (Biver, 1997), where $R_H$ is the heliocentric distance in AU. Given that the spatial distribution of H$_2$CO cannot be explained by the photo-dissociation of another gaseous parent, it has been proposed that H$_2$CO could be produced by the decomposition of solid polymers such as polyoxymethylene (H$_2$CO polymers: (–CH$_2$–O–)$_n$, also called POM) (Cottin et al., 2004).

POM has been detected in laboratory analogs of interstellar or cometary ices. It is synthesized by thermal processing of ices containing H$_2$O, H$_2$CO and NH$_3$ (Schutte et al., 1993a, 1993b). POM or POM-like polymers are also produced when ices containing some CH$_3$OH and NH$_3$ but no H$_2$CO in the initial mixture, are irradiated by UVs (Bernstein et al., 1995; Muñoz-Caro and Schutte, 2003). Moreover, this polymer was detected in Comet 1P/Halley by the PICCA mass spectrometer on board the Giotto spacecraft (Huebner, 1987), however this is controversial since it has been shown that the feature attributed to POM in the mass spectrum could be merely the signature of a mixture of organic material made of C, H, O and N atoms (Mitchell et al., 1992). POM is thus likely to be present in cometary grains among other refractory organic components and may produce gaseous H$_2$CO by photo-degradation (UV photolysis) and/or thermal-degradation (heating of the grains after their release from the nucleus).

To test this hypothesis, we have performed an experimental study of POM degradation. Subject to UV irradiation at 122 and 147 nm, POM produces several oxygenated compounds such as H$_2$CO, CO, HCOO$^-$, and CO$_2$ (Cottin et al., 2000). The H$_2$CO production quantum yield is about 1 at both wavelengths. Once heated, POM produces only gaseous H$_2$CO and the polymer is in equilibrium with gaseous H$_2$CO (POM $\leftrightarrow$ nH$_2$CO) (Dainton et al., 1959). The production kinetics have been measured at several temperatures in the 250–330 K range (Cottin et al., 2001; Fray et al., 2004a). The H$_2$CO kinetics have been shown to follow the Arrhenius law according to:

$$\frac{dH_2CO}{dt} = k(T)m_{POM},$$

where $k(T)$ is the number of gaseous formaldehyde molecules produced per gram of POM per second, $A$ the frequency factor (molecules g$^{-1}$ s$^{-1}$) and $E_a$ the activation barrier (J molecule$^{-1}$). These quantitative data have been included in a model of the cometary environment taking into account the production of gaseous compounds from photo- and thermal-degradation of solid organic compounds present in cometary grains. In this way, Giotto measurements of the H$_2$CO density were properly fitted assuming that cometary grains contain about 4% of POM by mass. This work has also allowed us to point out that, at 0.9 AU from the Sun, the thermal-degradation process is dominant with regard to the photolytic one (Cottin et al., 2004; Fray et al., 2004a). Nevertheless, this result is valid only for a heliocentric distance of 0.9 AU and for Comet 1P/Halley.

We have developed a new version of the model to study the effect of the heliocentric distance on H$_2$CO production from POM degradation. This time, we compare the H$_2$CO production rates observed at radio wavelengths using the JCMT, CSO, SEST and IRAM radio telescopes during the long term monitoring of Comet C/1995 O1 (Hale–Bopp), as described in Biver et al. (2002a), with our theoretical expectations. Observations, which have been performed from 4 AU pre-perihelion to 3.5 AU post-perihelion, have shown a steeper heliocentric evolution for H$_2$CO productions rates than for those of other species of similar volatility, such as HCN (Biver et al., 2002a). During the pre-perihelion phase, the H$_2$CO production rate varies with $R_H^{-3.6}$ while that of HCN varies with $R_H^{-2.6}$ . During the post-perihelion phase, the H$_2$CO production rate varies with $R_H^{-4.2}$ while that of HCN varies with $R_H^{-2.8}$.

In Section 2 we describe a general model applicable to any species and new equations that allow us to study the influence of the considered mechanisms (photo- and thermal-degradation of POM) on the total H$_2$CO production. Then in Section 3 we discuss the parameters (such as gas and dust production rates), and their heliocentric dependence, which are required to calculate H$_2$CO production from POM degradation. Results are presented in Section 4 and we discuss their implications in the last section of this paper.

2. Description of the model

The model presented in this section is an extension of the Haser model (Haser, 1957). We assume that (1) the production rates of gas and dust are in steady state and that (2) the motion from the nucleus is radial and at constant velocity with respect to the nucleocentric distance. We consider that a gaseous species can be produced by three different mechanisms: (1) photo-degradation, (2) thermal-degradation of the solid organic component of grains and (3) direct sublimation from the nucleus. This model has already been partially presented in Cottin et al. (2004). Here, we will first describe the
model in detail and present new equations that are applicable to the production of any gaseous species from the degradation of the solid component of grains. They will allow us to evaluate the production of a gaseous species from photo- and thermal-degradation independently. Then we will apply the model to the case of H$_2$CO production from POM degradation with the aim of reproducing the steep heliocentric evolution of H$_2$CO production observed in Comet C/1995 O1 (Hale–Bopp) by Biver et al. (2002a).

2.1. Evolution of solid organic mass on grains

Let us now consider a spherical grain including a mass fraction $\alpha$ of solid polymer, with radius $R$, mass $m$ and density $\rho$. If $m_\alpha$ is the mass of the polymer and $\rho'$ its density, we can define the radius $R_\alpha$ of an equivalent grain made of pure solid polymer:

$$m_\alpha = \alpha m = \alpha \left( \frac{4}{3} \pi R^3 \rho \right) = \frac{4}{3} \pi R^3 \rho' .$$

(1)

Assuming that photo-degradation takes place only at the surface of the grains and that thermal-degradation occurs throughout the highly porous material of the grains, the mass loss of this “pure polymer grain” can then be written:

$$\frac{dm_\alpha(r)}{dt} = - (\sigma_\alpha(r) C_{\text{grain}} + m_\alpha(r) k_{\text{grain}}) .$$

(2)

In this equation:

- $C_{\text{grain}}$ (kg m$^{-2}$ s$^{-1}$) represents the mass lost by photodegradation of the polymer. It is calculated taking into account the production of all gaseous species produced by UV irradiation of the solid polymer. We can therefore write

$$C_{\text{grain}} = \sum_i m_i \int \Phi_\lambda \ dx, \text{ where } m_i \text{ is the mass of the molecule } i \text{ produced with a quantum yield } \Phi_\lambda \text{ and } \Phi_\lambda \text{ is the solar irradiance (photons m}^{-2} \text{s}^{-1} \text{nm}^{-1}).$$

- $k_{\text{grain}}$ (molecules s$^{-1}$) represents the mass lost per second by thermal-degradation of the polymer. $k_{\text{grain}}$ is calculated taking into account the production of all gaseous species produced by thermal-degradation of the solid polymer. Generally, the production of gaseous species by this mechanism follows the Arrhenius law (Cottin et al., 2001; Fray et al., 2004a). Therefore we can write

$$k_{\text{grain}} = \sum_i m_i \left( A_i e^{-E_{ai}/kT} \right), \text{ where } m_i, A_i \text{ and } E_{ai} \text{ are respectively the mass, frequency factor (molecules kg}^{-1} \text{s}^{-1}) \text{ and activation energy (J molecule}^{-1}) \text{ of the molecule } i \text{ and } k \text{ is the Boltzmann constant.}$$

We consider that the dust expansion velocity and dust temperature do not vary with the distance from the nucleus. Note that, as we are modeling the degradation of refractory organics contained in grains, the grains will shrink leading to an increase in their temperature. Nevertheless, as we will see in the conclusions, this effect can be neglected given that the mass of disappearing organics represents only a few percent of the initial grain mass. Therefore, under these assumptions, we can integrate Eq. (2). The evolution of $R_\alpha$ with the nucleocentric distance is:

$$R_\alpha(r) = R_\alpha^0 \beta \left[ 1 - Z e^{-r/L_T} \right] .$$

(3)

In this equation:

- $R_\alpha^0$ is the radius of the equivalent “pure polymer grain” when ejected from the nucleus.
- $\beta = \frac{L_T}{LT}$ and $Z = 1 + \frac{r}{L_T}$.
- $L_T = 3 \nu_{\text{grain}}/k_{\text{grain}}$ is the “thermal-degradation scale length,” i.e., at a distance $L_T$ from the nucleus, $R_\alpha$ is decreased by a factor $1/e$ if only thermal-degradation occurs (Cottin et al., 2004).
- $L_P = 4 \nu_{\text{grain}}/k_{\text{grain}}$ is the “photo-degradation scale length.” At a distance $L_P$ from the nucleus, $R_\alpha = 0$ (i.e., the polymer initially present in the grains is totally degraded into gaseous species) if only photo-degradation occurs (Cottin et al., 2004).

Since these scale lengths have no direct physical meaning if photo- and thermal-degradation are both responsible of the production of gas, we define $r_C = L_T \times \ln (\frac{L_T + L_P}{L_T})$, called hereafter the ‘critical distance,’ which is the distance from the nucleus at which all the polymer initially present in the grains is totally degraded into gaseous species.

2.2. Production of gaseous species from grains

We will call $M$ the gaseous species produced by degradation of the solid organic component of grains that we want to study. To calculate $n_M(r)$, the density of $M$, we use the mass budget equation:

$$\frac{\partial n_M(r)}{\partial t} + \nabla \cdot [n_M(r) v_{\text{gas}}] = \left( \frac{dM}{dt} \right)_D - \left( \frac{dM}{dt} \right)_P ,$$

(4)

where:

- $v_{\text{gas}}$ is the gas expansion velocity (m s$^{-1}$).
- $\left( \frac{dM}{dt} \right)_D$ represents the destruction of the gaseous species $M$ by photolysis. Therefore $\left( \frac{dM}{dt} \right)_D = \beta_M n_M(r)$.
- $\left( \frac{dM}{dt} \right)_P$ represents the production of the gaseous species $M$ from solid polymer degradation. We can write:

$$\left( \frac{dM}{dt} \right)_P = n_{\text{grain}}(r) \left[ \sigma_\alpha(r) C_M + m_\alpha(r) k_M(T_{\text{grain}}) \right] .$$

(5)

In this equation:

- $n_{\text{grain}}(r)$ is the grain density in the coma (grains m$^{-3}$) as a function of the distance from the nucleus. We consider $n_{\text{grain}}(r) = \frac{Q_{\text{grain}}}{4 \pi r^2 v_{\text{grain}}}$ where $Q_{\text{grain}}$ is the grain production rate (grains s$^{-1}$) and $v_{\text{grain}}$ the grain velocity (m s$^{-1}$). As $Q_{\text{grain}}$ and $v_{\text{grain}}$ depend on grain size, a grain size distribution is used to calculate the total production of $M$ (sum of the contributions of each size of grains).
\( C_M \) is the production rate of \( M \) (molecules m\(^{-2}\) s\(^{-1}\)) from photo-degradation of solid polymer. Therefore, \( C_M = \int f_\lambda \Phi^M_c \, d\lambda \), where \( f_\lambda \) is the solar irradiance (photons m\(^{-2}\) s\(^{-1}\) nm\(^{-1}\)) and \( \Phi^M_c \) the production quantum yield of \( M \) from solid polymer.

\( k_M(T_{\text{grain}}) \) is the production rate of \( M \) (molecules kg\(^{-1}\) s\(^{-1}\)) from thermal-degradation of solid polymer at a temperature \( T_{\text{grain}} \) and is taken to be equal to \( k_M(T) = A_M e^{-E_{aM}/kT} \).

Considering a radial gas expansion velocity independent of the distance from the nucleus and an ejection velocity of \( M \) from grains equal to the gas expansion velocity, Eq. (4) can be integrated analytically:

\[
n_M(r) = \frac{Y}{r^2} \left[ l_M (1 - X) (1 - e^{-r/l_M}) \right] + \frac{(3X - 2)Z}{(1/l_M - 1/l_T)} \left( e^{-r/l_T} - e^{-r/l_M} \right) + \frac{(1 - 3X)Z^2}{(1/l_M - 2/l_T)} \left( e^{-2r/l_T} - e^{-r/l_M} \right) + \frac{XZ^3}{(1/l_M - 3/l_T)} \left( e^{-3r/l_T} - e^{-r/l_M} \right),
\]

(6)

where:

\( Y = \frac{Q_{\text{grain}}C_M k_{\text{gas}}}{4V_{\text{gas}} V_{\text{grain}}}; \)

\( X = \frac{C_{\text{grain}} k_M}{C_M k_{\text{grain}}}; \)

and \( l_M = v_{\text{gas}}/\beta_M \) is the photo-dissociation scale length of the gaseous species \( M \).

If \( M \) is produced only by solid polymer thermal-degradation, Eq. (4) can be modified and \( n_M^T(r) \), the density of \( M \) (molecules m\(^{-3}\)) produced only by the thermal-degradation of solid polymer, can be written:

\[
n_M^T(r) = \frac{Y}{r^2} \left[ -X l_M (1 - e^{-r/l_M}) \right] + \frac{3XZ}{(1/l_M - 1/l_T)} \left( e^{-r/l_T} - e^{-r/l_M} \right) + \frac{-3XZ^2}{(1/l_M - 2/l_T)} \left( e^{-2r/l_T} - e^{-r/l_M} \right) + \frac{XZ^3}{(1/l_M - 3/l_T)} \left( e^{-3r/l_T} - e^{-r/l_M} \right).
\]

(7)

Similarly, if \( M \) is only produced by photo-degradation of solid polymer, \( n_M^P(r) \), the density of \( M \) (molecules m\(^{-3}\)) produced only by the photo-degradation of solid polymer, can be written:

\[
n_M^P(r) = \frac{Y}{r^2} \left[ -l_M (1 - e^{-r/l_M}) \right] + \frac{-2Z}{(1/l_M - 1/l_T)} \left( e^{-r/l_T} - e^{-r/l_M} \right).
\]

(8)

As would be expected, \( n_M(r) \) is calculated from Eq. (7) and Eq. (8): \( n_M(r) = n_M^T(r) + n_M^P(r) \). Therefore Eq. (7) and Eq. (8) can be used to calculate the production of any gaseous species from photo- and thermal-degradation of the solid component of grains.

To calculate \( n_M(r) \), we need to know the dust mass production rate (\( Q_{\text{grain}} \) in kg s\(^{-1}\)), grain size distribution, grain temperatures (\( T_{\text{grain}} \)) and grain velocities (\( V_{\text{grain}} \)). The calculations of these parameters as a function of heliocentric distance are presented in Section 3.

2.3. Production of gaseous species from sublimation of the nucleus

Equation (6) only takes into account the production of gaseous species from solid polymer degradation on grains, whereas a fraction of \( M \) could also be produced by direct sublimation of nucleus ices. The density of the native \( M \) produced at (or near) the surface of the nucleus is modeled using the equation established for a “parent molecule” by Haser (1957):

\[
n_M^{\text{nucleus}}(r) = \frac{Q_M^{\text{nucleus}}}{4\pi v_{\text{gas}} r^2} e^{-r/l_M},
\]

(9)

where \( Q_M^{\text{nucleus}} \) is the production rate of the native \( M \).

2.4. Application of the model to H\(_2\)CO production from POM

To calculate the H\(_2\)CO density (molecules m\(^{-3}\)) produced from POM degradation, we have to determine the coefficients \( C_{\text{grain}}, C_{\text{H2CO}}, k_{\text{grain}} \) and \( k_{\text{H2CO}} \). This can be done using the experimental data of Cottin et al. (2000) and Fray et al. (2004a) who have studied respectively the photo- and thermal-degradation of POM. Cottin et al. (2000) have shown that the dominant products of POM photo-degradation at 122 and 147 nm are H\(_2\)CO, CO, HCOOH and CO\(_2\). Using the measured production quantum yields of each product and the solar flux published by Mount and Rottman (1981), we estimate that \( C_{\text{grain}} = 6.76 \times 10^{-9} \) kg m\(^{-2}\) s\(^{-1}\) and \( C_{\text{H2CO}} = 5.07 \times 10^{16} \) molecules m\(^{-2}\) s\(^{-1}\) at 1 AU. Note that H\(_2\)CO production from POM photo-degradation accounts for only 37% of the total mass loss of the grains by this process. The remaining 63% contribute to production of CO, HCOOH and CO\(_2\). (Cottin et al., 2000). Concerning thermal-degradation, two types of POM have been investigated between 250 and 330 K (Fray et al., 2004a); hereafter we will call “POM1” the POM supplied by the “Aldrich” company and “POM2” the POM supplied by the “Prolabo” company. The two polymers may slightly differ in chain lengths. It has been shown that, for both types of POM, H\(_2\)CO is the only gaseous species produced by thermal-degradation of POM and that the production kinetics follow the Arrhenius law (Fray et al., 2004a). We have determined \( E_{\text{A1}} = 99 \times 10^3 \) J mol\(^{-1}\) and \( A_1 = 7.2 \times 10^{32} \) molecules g\(^{-1}\) s\(^{-1}\) for “POM1” and \( E_{\text{A2}} = 81 \times 10^3 \) J mol\(^{-1}\) and \( A_2 = 1.2 \times 10^{30} \) molecules g\(^{-1}\) s\(^{-1}\) for
“POM2.” Note that the pre-exponential factors differ by a factor of 600. Despite this difference, H2CO production kinetics of “POM1” and “POM2” are equal for \( T = 339 \) K and differ by a factor of between 0.012 and 16.2 for temperatures ranging from 200 to 600 K (see Table 1). As the temperature of grains depends on their size, these factors are attenuated when we consider the entire size distribution. Therefore, as we will see in Section 4.2.1, H2CO production rates are not very sensitive to the type of POM we consider. Moreover, we have used a POM density of \( 1.46 \times 10^3 \) kg m\(^{-3}\) (Prolabo).

Table 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( k(T) ) for POM1 (molecules g(^{-1}) s(^{-1}))</th>
<th>( k(T) ) for POM2 (molecules g(^{-1}) s(^{-1}))</th>
<th>Ratio of ( k(T) ) for POM1 to ( k(T) ) for POM2</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>( 9.7 \times 10^6 )</td>
<td>( 8.2 \times 10^6 )</td>
<td>0.012</td>
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<tr>
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<td>( 1.5 \times 10^{12} )</td>
<td>( 1.4 \times 10^{13} )</td>
<td>0.10</td>
</tr>
<tr>
<td>300</td>
<td>( 4.1 \times 10^{15} )</td>
<td>( 9.3 \times 10^{15} )</td>
<td>0.44</td>
</tr>
<tr>
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<td>( 1.2 \times 10^{18} )</td>
<td>( 9.6 \times 10^{17} )</td>
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</tr>
<tr>
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<td>( 3.1 \times 10^{19} )</td>
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</tr>
<tr>
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<td>( 4.7 \times 10^{20} )</td>
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<tr>
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</tr>
<tr>
<td>600</td>
<td>( 1.7 \times 10^{24} )</td>
<td>( 1.1 \times 10^{23} )</td>
<td>16.22</td>
</tr>
</tbody>
</table>

To calculate the H2CO density (molecules m\(^{-3}\)) produced by nucleus sublimation, we assume that the production rate of native H2CO is proportional to that of HCN (see Fig. 1). Indeed the sublimation temperatures of H2CO and HCN are quite close (\( T_{HCN} = 64 \) K and \( T_{H2CO} = 95 \) K, Crovisier, 1997). Moreover, Magee-Sauer et al. (1999, 2002) have shown, from spectral observations of the \( v_3 \) band of HCN and analysis of the spatial distribution of HCN for Comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale–Bopp), that HCN is predominantly released at the surface of the nucleus, while a small contribution from an extended source cannot be ruled out. A similar conclusion has been derived from single-field interferometric observations at radio wavelength for Comet C/1995 O1 (Hale–Bopp) (Snyder et al., 2001). The use of HCN as an indicator of native H2CO rather than H2O, the most abundant component of cometary ices, is also justified by the fact that HCN and H2CO production rates were measured simultaneously with the same radio techniques, whereas H2O production is obtained from sparse infrared observations or from indirect indicators. Moreover we use a H2CO photo-dissociation rate of \( 2 \times 10^{-14} \) s\(^{-1}\) (Crovisier, 1994).

Our objective is to compare the results of this model to the H2CO production rates observed at radio wavelengths during the long-term monitoring of Comet C/1995 O1 Hale–Bopp (Biver et al., 2002a). Therefore the total H2CO density (molecules m\(^{-3}\)) is integrated on the line of sight to calculate the H2CO column density (molecules m\(^{-2}\)), which is afterwards integrated over the field of view of the radio telescope to derive the total number of H2CO molecules observed during an observation. We assume an antenna beam size of 12″ (the real size varied from 10.6″ to 13.6″ depending on the observation) introducing a 10% uncertainty. Finally, the calculated total number of H2CO molecules in the antenna beam is converted into H2CO production rates (molecules s\(^{-1}\)) using the Haser model and assuming that H2CO behaves as a “daughter species,” i.e., a “parent scale length” of \( 6800R \) km (Biver, 1997) and a “daughter scale length” of \( 1.2 \times 10^{22} \) m. This procedure is as close as possible to the one used by Biver et al. (2002a) to convert the observed flux of the H2CO lines into production rates and can therefore be used to compare the equivalent H2CO production rate of our model to those of Biver et al. (2002a).

3. The dust model for Comet C/1995 O1 (Hale–Bopp)

As shown in Section 2, the calculation of the production rates (molecules s\(^{-1}\)) of gaseous species including solid organic compound degradation requires values for \( Q_{grain} \), i.e., the dust mass production rate (kg s\(^{-1}\)) and its grain size distribution, the grain temperature \( T_{grain} \), as well as \( V_{grain} \) and \( V_{gas} \), the grain and gas expansion velocities. Finally, the total gas production rate is needed in order to estimate the dust-to-gas ratio and the grain velocities (as well as the HCN production rate to derive the native H2CO density). The determination of these parameters as a function of heliocentric distance is presented in this section.

3.1. Gas production rates and velocity

The aim of the present study is to test if POM degradation is responsible for the steep heliocentric evolution of the H2CO production rates observed at radio wavelengths in Comet C/
from the analysis of radio line shapes (Biver et al., 2002a), i.e., the gas production rate is taken as the sum of the CO and H2O production rates. The latter are derived from the radio observations of Colom et al. (1999), whereas CO and HCN production rates are from Biver et al. (2002a). The OH, CO, H2CO and HCN production rates are displayed in Fig. 1.

The assumed gas expansion velocity values are those derived from the analysis of radio line shapes (Biver et al., 2002a), i.e., $v_{\text{gas}} = 1.125R_H^{-0.42}$ km s$^{-1}$ (see Fig. 5).

3.2. Dust distribution

3.2.1. Shape of the distribution

The grain size distribution in the coma of Comet C/1995 O1 (Hale–Bopp) has been derived by Crifo and Rodionov (1997) (Eq. (11) of Appendix B). This distribution is plotted in Fig. 2. Data for masses between $10^{-18}$ and $10^{-6}$ kg (i.e., for grain sizes between $6 \times 10^{-3}$ and $6 \times 10^{-4}$ m) are derived from situ measurements, whereas data for grains lighter than $10^{-18}$ kg and heavier than $10^{-6}$ kg are estimated from a linear extrapolation of the measurements (Crifo and Rodionov, 1997). Most of the mass lies in the largest grains and two changes of slope can be observed at approximately $10^{-9}$ and $10^{-7}$ kg (i.e., $3 \times 10^{-4}$ and $6 \times 10^{-5}$ m). A similar distribution was recently measured in Comet 1P/Halley by the Giotto spacecraft (Tuzzolino et al., 2004; Green et al., 2004). Therefore, such a distribution could apply more generally to all comets.

This distribution is then adapted to make it relevant to our study of the heliocentric evolution of production rates of gaseous species. First, we take into account the change of size of the largest grains lifted from the nucleus with the heliocentric distance, since the total gas production rate varies. Secondly, the total dust production rate (kg s$^{-1}$) is adjusted using the measurements performed on Comet C/1995 O1 (Hale–Bopp).

3.2.2. Size of the largest grains lifted from the nucleus of Comet C/1995 O1 (Hale–Bopp)

The balance between the gravitational force of the nucleus and the drag force due to the expansion of the gas influences the size of the largest grains. The grains lifted from the nucleus, $a_{\text{Max}}$, can be written:

$$a_{\text{Max}} = \frac{3m_{\text{gas}}(1-A)c_{\theta}}{\pi G\rho_{\text{grain}}\rho_n R_n L_s} \sqrt{\frac{kT_{\text{gas}} f \cos(z)}{2\pi m_{\text{gas}} R_H^2}}.$$  

We use the same equation where:

- $m_{\text{gas}}$ is the mean molecular mass taken to be equal to: $m_{\text{gas}} = (m_{\text{CO}}Q_{\text{CO}} + m_{\text{H}_2\text{O}}Q_{\text{H}_2\text{O}})/(Q_{\text{CO}} + Q_{\text{H}_2\text{O}})$ where $Q_i$ are the production rates.
- $A$ is the albedo of the grain taken to be equal to that measured for the 1P/Halley nucleus: 0.04 (Keller et al., 1987).
- $\rho_{\text{grain}}$ is the grain density taken to be equal to 1000 kg m$^{-3}$ (Crifo and Rodionov, 1997)
- $\rho_n$ is the nucleus density taken arbitrary to be equal to 500 kg m$^{-3}$
- $R_n$ is the radius of the nucleus considered to be 30 km.
- $L_s$ is the latent heat of sublimation of water ice ($L_s = 2660$ kJ kg$^{-1} = 7.95 \times 10^{-20}$ J molecule$^{-1}$, Kührt, 1999).
- $kT_{\text{gas}}$ is the gas temperature at the surface of the nucleus calculated using the analytical formula given by Crifo and Rodionov (1997) (Eq. (11) of Appendix B).
- $f$ is the icy area fraction taken to be equal to 0.2.
- $z$ is the zenith angle, as this equation is valid for a specific area on the surface of the nucleus. To determine the maximum possible radius, we have considered $\cos z = 1$.
- $c_{\theta}$ is the solar constant ($c_{\theta} = 1367.6$ W m$^{-2}$)

The size of the largest grain that can be lifted from the nucleus is found to be 0.07 cm at 4 AU and 1.24 cm at 1 AU (see Fig. 4) with a heliocentric variation close to $R_H^{-2}$. These results are close to those of Weiler et al. (2003) and agree well with radar observations of centimetric grains in several comets near 1 AU (Harmon et al., 1999).

3.2.3. Dust production rates in Comet C/1995 O1 (Hale–Bopp)

A compilation of the dust production rates measured in Comet C/1995 O1 (Hale–Bopp) is used to assess the grain size distribution. As a very broad dust distribution is concerned, we use measurements performed over different wavelength ranges, each being more sensitive to a given grain size. Submillimeter
(Jewitt and Matthews, 1999) as well as ultraviolet observations (Weaver et al., 1999) are therefore taken into account. Finally, we consider the dust production rates published by Jewitt and Matthews (1999), Weaver et al. (1999), Lisse et al. (1999), Grün et al. (2001) and Weiler et al. (2003). The related dust-to-gas ratios are derived using the total gas production rate, considered to be equal to the sum of the CO and H$_2$O production rates (see Fig. 1), varying with $R_H^{-2.8}$ and $R_H^{-3.4}$ during the pre- and post-perihelion phase, respectively. These values are plotted in Fig. 3. Depending on the authors, different dust-to-gas ratio trends with respect to the heliocentric distance have been proposed, which could be due to different assumptions on the size distribution and on the heliocentric evolution of the grain velocities (Weiler et al., 2003).

To calculate the grain size distribution, we have assumed (1) that the number of grains of a given size varies with the heliocentric distance in the same manner as the total gas production rate and (2) that the dust-to-gas ratio at 1 AU is equal to 8.8. This value corresponds to the measurements performed by Jewitt and Matthews (1999) at submillimeter wavelengths, which are more relevant to our study as they are sensitive to the larger grains. The grain distribution can then be calculated taking into account the variation of the size of the largest grains ($a_{\text{max}}$) with the heliocentric distance. The resulting distributions for different heliocentric distances are presented in Fig. 4. As the comet approaches the Sun, the size of the largest grains increases, thereby increasing the dust-to-gas ratio. Therefore, the dust-to-gas ratio of our distribution varies with $R_H^{-1.3}$.

3.3. Dust velocities

In the cometary environment, grains are accelerated in the inner coma, due to the drag force of the gas. At a given distance from the nucleus, collisions between gas and grains become negligible and no longer influence grain velocities, which then reach a constant value. The latter can be calculated using an analytical formula given by Crifo (1995). It is a function of the grain radius $a$ and the heliocentric distance via the gas production rate $Q_{\text{gas}}$:

$$v_{\text{grain}}(a, Q_{\text{gas}}, \ldots) = \frac{W}{(0.9 + 0.45X^{0.615/2} + 0.275X^{0.615})},$$

where:

$$W = \sqrt{\frac{\gamma + 1}{\gamma - 1}} \left( \frac{\gamma k T_{0\text{gas}}}{m_{\text{gas}}} \right)$$

and

$$X = \frac{2\pi a \rho_{\text{grain}} W R_n}{m_{\text{gas}} Q_{\text{gas}}}.$$

In these equations:

- $\gamma$ is the ratio between the specific heat at constant pressure and volume and is taken to be equal to 4/3 as for a polyatomic gas.
- $T_{0\text{gas}}$ is the gas temperature at the surface of the nucleus and is calculated using the analytical formula given by Crifo and Rodionov (1997).
- $m_{\text{gas}}$ is the mean molecular mass and is assumed to be equal to $m_{\text{CO}} = (m_{\text{CO}} Q_{\text{CO}} + m_{\text{H}_2\text{O}} Q_{\text{H}_2\text{O}})/(Q_{\text{CO}} + Q_{\text{H}_2\text{O}})$ where $Q_i$ are the production rates.
- $Q_{\text{gas}}$ is the total gas production rate (in molecules s$^{-1}$) and is taken to be equal to $Q_{\text{gas}} = Q_{\text{H}_2\text{O}} + Q_{\text{CO}}$.
- $\rho_{\text{grain}}$ is the grain density and is taken to be equal to 1000 kg m$^{-3}$ (Crifo and Rodionov, 1997).
- $k$ is the Boltzmann constant.

Fig. 5 shows the resulting velocities as a function of heliocentric distance and for different grain sizes ($a = 10^{-4}$, $10^{-6}$ and $10^{-8}$ m). Results of our calculation can be compared to the projected velocities determined from the apparent motion of structures (jets, arcs,...) observed at infrared and visible wavelengths in the coma of Comet C/1995 O1 (Hale–Bopp) by Braunstein et al. (1997), Warell et al. (1999), Kidger et al.
Fig. 5. Computed terminal grain velocities as a function of heliocentric distance for different grain radii \((a = 10^{-6}, 10^{-5} \text{ and } 10^{-4} \text{ m})\). For comparison, the dotted line shows the gas expansion velocity measured by Biver et al. (2002a) and the plotted points show the projected grain velocities derived from the apparent motion of dust structures (jets, arc, etc.). The data used to plot these points have been taken from Braunstein et al. (1997) (black squares), Warell et al. (1999) (empty triangle), Kidger et al. (1996) (black triangle) and Tozzi et al. (1997) (empty circles).

(1996) and Tozzi et al. (1997). These values can be considered as lower limits for the terminal velocity of micrometric grains. Our calculated velocities are consistent with these observations. At perihelion, the velocity of the smaller grains is 80% that of the gas.

3.4. Dust temperatures

To calculate the production of gaseous species from solid polymer thermal-degradation, the key factor is the grain temperature \(T_{\text{grain}}\), which is derived from the balance between the energy received from the Sun and the infrared energy re-radiated by the grain.

The balance equation is given by:

\[
\int_{0}^{\infty} Q_{a}(\lambda, a) S(\lambda) \, d\lambda = 4 \pi \int_{0}^{\infty} Q_{a}(\lambda, a) B(T_{\text{grain}}, \lambda) \, d\lambda.
\]  

(14)

Here \(a\) is the grain radius, \(S(\lambda)\) the solar flux at the considered heliocentric distance and \(B(T_{\text{grain}}, \lambda)\) the Planck function. \(Q_{a}(\lambda, a)\) is the absorption efficiency of the grain which depends on the wavelength and the size and physical and chemical properties of the grain. To calculate \(Q_{a}(\lambda)\), Mie theory has been used for compact and pure spherical grains with a refractive index \(m\) of the grain component and the size parameter \(X = 2\pi a^2/\lambda\).

The temperature for porous grains composed of a mixture of silicates and organics has been calculated by successively applying the models of Greenberg and Hage (1990) and Hage and Greenberg (1990), as already done by Gunnarsson (2003) in his study of the CO extended source in 29P/Schwassmann–Wachmann 1.

The model of Greenberg and Hage (1990) makes it possible to calculate an equivalent refractive index, \(m_{\text{core–mantle}}\), for a

\[
(m_{\text{core–mantle}})^2 = m_{\text{mantle}}^2 \left\{ 1 + 3 q^2 \left( \frac{m_{\text{core}}^2 - m_{\text{mantle}}^2}{m_{\text{core}}^2 + 2 m_{\text{mantle}}^2} \right) \right\} \left( 1 - q^3 \left( \frac{m_{\text{core}}^2 - m_{\text{mantle}}^2}{m_{\text{core}}^2 + 2 m_{\text{mantle}}^2} \right) \right)^{-1},
\]  

(15)

where \(q\) is the fractional radius of the silicate core, and \(m_{\text{core}}\) and \(m_{\text{mantle}}\) are the refractive indices of the component of the core and of the mantle respectively. We use the refractive indices of pyroxene (\(\text{Mg}_{0.6}\text{Fe}_{0.4}\text{SiO}_3\); Dorschner et al., 1995) and graphite (Jäger et al., 1998). Graphite is representative of black organic matter, and provides an upper limit for a strongly absorbing organic component of the grains, whereas pyroxene represents the silicate component of grains with very low absorption in the visible range. We assume that organics represent 60% of the mass of grains (Greenberg, 1998). In this case, the fractional radius, \(q\), of the core, is about 0.74.

The model of Hage and Greenberg (1990) is used to calculate the equivalent refractive index \(m_{\text{porous}}\) of aggregates assumed to be made of the “core–mantle” grains, for which the refractive index \(m_{\text{core–mantle}}\) has already been determined.

\[
m_{\text{porous}}^2 = 1 + \frac{3(1 - P)(m_{\text{core–mantle}}^2 - 1)/(m_{\text{core–mantle}}^2 + 2)}{1 - (1 - P)(m_{\text{core–mantle}}^2 - 1)/(m_{\text{core–mantle}}^2 + 2)},
\]  

(16)

where \(P\) is the porosity of the aggregates, taken to be equal to 0.95 (Greenberg and Li, 1998).

The resulting temperature, for grains composed of 60% organics in terms of mass and a porosity equal to 0.95, is displayed in Fig. 6 as a function of the grain radius for different heliocentric distances.

The temperature of the grains larger than \(10^{-3} \text{ m}\) is always very close to the temperature of a black body for every considered heliocentric distance, whereas micrometric grains could
reach higher temperatures (see Fig. 6). Moreover for a given grain size, the temperature varies approximately with \( R_H^{0.5} \).

4. Results

With the parameters presented in the previous section, we are now able to calculate the \( \text{H}_2\text{CO} \) production rates taking into account POM degradation. They have to be compared with the production rates actually observed at radio wavelengths during the long-term monitoring of Comet C/1995 O1 (Hale–Bopp), as described by Biver et al. (2002a). \( \text{H}_2\text{CO} \) was monitored from June 1996 (at \( R_H = 4.1 \) AU pre-perihelion) to October 1997 (at \( R_H = 3.2 \) AU post-perihelion). We attempted to obtain the best fit of our model to the observations by adjusting the free parameters:

1) \( \alpha (%) \) the mass fraction of POM present in each grain.
2) \( Q_{\text{H}_2\text{CO}}^{\text{nucleus}} / Q_{\text{HCN}}^{\text{nucleus}} % \) the native \( \text{H}_2\text{CO} \) production rate relative to HCN.

These parameters control the \( \text{H}_2\text{CO} \) fraction produced respectively by the degradation of POM and the sublimation of nucleus ices.

The best fit is determined by minimizing the chi-square root

\[
\sigma = \left( \sum_i \left[ \frac{Q_{\text{H}_2\text{CO, obs}}(i) - Q_{\text{H}_2\text{CO, mod}}(i)}{Q_{\text{H}_2\text{CO, obs}}(i)} \right]^2 \right]^{1/2} \left( \sum_i \left( \frac{1}{\epsilon(i)} \right)^2 \right)^{1/2} n, \tag{17}
\]

which takes into account the relative uncertainty \( \epsilon \) of each measurement of \( Q_{\text{H}_2\text{CO}} \) (\( n \) is the total number of measurements, \( n = 22 \)).

4.1. Best fit

With the experimental data for ‘POM1’ and the grain distribution presented in Fig. 4, the best fit is found for \( \alpha = 3.1\% \) and \( Q_{\text{H}_2\text{CO}}^{\text{nucleus}} / Q_{\text{HCN}}^{\text{nucleus}} = 3\% \). The derived \( \text{H}_2\text{CO} \) production rates are consistent with observations (see Fig. 7) for all heliocentric distances. For instance, during the pre-perihelion phase, both the calculated and observed \( \text{H}_2\text{CO} \) production rates vary with \( R_H^{-3.6} \). During the post-perihelion phase, \( \text{H}_2\text{CO} \) calculated production rates vary with \( R_H^{-4.1} \) while the observed rates vary with \( R_H^{-4.2} \). However, although the results of the model well match the heliocentric evolution for \( \text{H}_2\text{CO} \) production rates, some points fall outside the errors bars determined from observations. This difference is partly due to day-to-day variations of the production rates, which are superimposed on the global evolution and which are not taken into account in this model.

To reproduce the \( \text{H}_2\text{CO} \) production rates in Comet C/1995 O1 (Hale–Bopp), we must consider that grains contain about a 3% mass fraction of POM. This value is close to the POM mass fraction upper limit of 3% from in situ measurements performed in the coma of 81P/Wild 2 by mass spectrometry (Kissel et al., 2004). Our value is therefore realistic. Moreover, it is also very close to the nominal value (4%) found to reproduce the spatial distribution of \( \text{H}_2\text{CO} \) in Comet 1P/Halley (Cottin et al., 2004). On the other hand, although no native \( \text{H}_2\text{CO} \) is required to reproduce observations between perihelion and 3.5 AU, a small fraction of \( \text{H}_2\text{CO} \) produced directly at the surface of the nucleus must be assumed to fit the data obtained for larger heliocentric distances. This production rate of native \( \text{H}_2\text{CO} \) could be as low as 3% of the HCN production rate (\( Q_{\text{HCN}}^{1\%} / Q_{\text{HCN}} = 3\% \)).

We calculated independently \( \text{H}_2\text{CO} \) production rates related to the three \( \text{H}_2\text{CO} \) production mechanisms (photo- and thermal-degradation of POM and nucleus sublimation) using Eqs. (7), (8) and (9) (see Fig. 8).

At 1 AU, POM thermal-degradation represents more than 90% of total \( \text{H}_2\text{CO} \) production and this mechanism dominates until 3.5 AU (see Fig. 8). These results are consistent with those of Cottin et al. (2004), who have already shown that POM thermal-degradation is predominant at 0.9 AU. The steep heliocentric evolution of \( \text{H}_2\text{CO} \) production rates is due to the predominance of thermal-degradation. For heliocentric distances greater than 3.5 AU, due to the cooling of the grains, POM thermal-degradation becomes less efficient than POM photodegradation. Furthermore, at these large heliocentric distances, the data derived from observations are reproduced by the model only under the assumption that a fraction of \( \text{H}_2\text{CO} \) is produced directly at the surface of the nucleus. At 1 AU from the Sun, this production of native \( \text{H}_2\text{CO} \) could represent less than a few percent of the total production of \( \text{H}_2\text{CO} \). Nevertheless, the production rates of native \( \text{H}_2\text{CO} \) are not well constrained by our model as they depend on assumptions made on the grain distribution and on the few observations obtained at very large heliocentric distances. Therefore it cannot be ruled out that all \( \text{H}_2\text{CO} \) is produced from degradation of POM.
Fig. 8. H$_2$CO production rates as a function of heliocentric distance computed using the experimental data of “POM1.” The different symbols represent different H$_2$CO production mechanisms: POM thermal-degradation (empty triangles), POM photo-degradation (crossed diamonds) and nucleus sublimation (empty circles). The black circles represent the total H$_2$CO production rates.

Fig. 9. Critical distance as a function of the heliocentric distance for different grain sizes. The “critical distance” is the distance from the nucleus at which POM initially present in the grains is completely degraded into gaseous species. It depends on the relative efficiency of photo- and thermal-degradation at a given heliocentric distance. This figure can be divided into two areas separated by the diagonal line. In the area situated on the right of the diagonal line, photo-degradation dominates, whereas in the other area it is negligible with respect to thermal-degradation. The dotted line shows the field of view radius assuming a beam width at half power of 12″ for the radio observations of Comet C/1995 O1 (Hale–Bopp) before perihelion.

The relative influence of thermal and photo-degradation of POM for different heliocentric distances can be understood by studying the kinetics of H$_2$CO production. Fig. 9 represents the critical distance (i.e., the distance from the nucleus at which POM initially present in grains is completely degraded into gaseous species) as a function of the heliocentric distance for different grains sizes.

As thermal-degradation depends heavily on grain temperature, photo-degradation dominates thermal-degradation for heliocentric distances greater than 4 AU, whatever the grains. On the other hand, for heliocentric distances less than 1 AU, thermal-degradation dominates for all grain sizes. Between 1 and 4 AU, thermal-degradation is the dominating process for the hot smaller grains, whereas photo-degradation dominates for the cold larger grains.

The heliocentric evolution of H$_2$CO production rates observed in Comet C/1995 O1 (Hale–Bopp) can be understood by comparing the critical distance to the size of the field of view of the H$_2$CO observations. At heliocentric distances larger than 4 AU, photo-degradation takes place up to distances larger than the field of view (see Fig. 9). Therefore, although POM is degraded, gaseous H$_2$CO cannot be observed by measurements such as those of Biver et al. (2002a). Between 4 and 3 AU, thermal-degradation becomes the predominant process as the critical distance for smaller grains decreases due to their heating. For these heliocentric distances, the critical distance for the smaller grains becomes less than the size of the field of view (see Fig. 9). Thus, POM present in the smaller grains is completely degraded into gaseous H$_2$CO inside the field of view. This explains the very steep increase of H$_2$CO production rates calculated between 4 and 3 AU (see Fig. 8). Finally, as the comet approaches the Sun, POM is completely degraded by thermal processes inside the field of view for larger and larger grains. This explains the steep heliocentric evolution of the H$_2$CO production rates measured by Biver et al. (2002a).

So, comparing the critical distance to the size of the field of view, it can be seen that at large heliocentric distances, extended H$_2$CO production is dominated by photo-degradation of the smallest grains, whereas inside 1.5 AU it is dominated by thermal-degradation of the largest grains.

4.2. Sensitivity of the results

In this sub-section, we study the sensitivity of H$_2$CO production rates to the different parameters used in the computation: chemical type of POM and grain velocity, temperature and distribution.

4.2.1. Sensitivity to the type of POM used for experimental studies

We have studied experimentally the thermal-degradation of two chemical types of POM. As this mechanism is predominant over a large range of heliocentric distances, the parameters $A$ and $E_a$ could influence H$_2$CO production rates. We calculate H$_2$CO production rates considering the experimental data of “POM2” (i.e., $A = 1.2 \times 10^{30}$ molecules g$^{-1}$ s$^{-1}$ and $E_a = 8.1 \times 10^4$ J mol$^{-1}$). We have kept all the parameters presented in Section 3 and $\alpha = 3.1\%$ and $Q_{\text{nucleus}}^{\text{H}_2\text{CO}} / Q_{\text{nucleus}}^{\text{HCN}} = 3\%$ as already used in order to compare the results obtained for “POM1” and “POM 2.” The corresponding H$_2$CO production rates are displayed in Fig. 10.

Close to 1 AU, the H$_2$CO production rates are greater for “POM2” than for “POM1” experimental data. At this heliocentric distance, most of the gaseous H$_2$CO is produced by
Fig. 10. H$_2$CO production rates as a function of the heliocentric distance. The measurements of Biver et al. (2002a) are represented as open squares, the values computed using the experimental data of “POM1” as black circles and the values computed using the experimental data of “POM2” as gray triangles. The latter have been obtained assuming a POM mass fraction in the grains of 3.1% and H$_2$CO production at the surface of the nucleus equal to 3% of HCN production.

thermal-degradation of POM present in the largest grains with temperatures at about 300 K, and at this temperature H$_2$CO production kinetics are faster for “POM2” than for “POM1” (see Fig. 4 in Fray et al., 2004a). For heliocentric distances greater than 1.5 AU, H$_2$CO production rates are only slightly affected by changes in parameters $A$ and $E_a$. In summary, H$_2$CO production rates are only sensitive to the chemical type of POM when thermal-degradation of larger grains takes place inside the field of view.

4.2.2. Sensitivity to grain velocity

As already stated, the velocity of the smaller grains at 1 AU is 80% the gas velocity. The influence of an increase in grain velocity was first studied by multiplying grain velocities by a factor of 1.25 (the velocity of the smallest grains is then equal to the gas velocity). In this case, all parameters being identical to those used in Section 4.1, a decrease in H$_2$CO production rates ranging from 1 to 8% is noted depending on the heliocentric distance. Multiplying the grain velocity by a factor of 0.8, the H$_2$CO production rates increase by 1 to 12%. These variations are not surprising. Indeed, as their velocity decreases, more grains are present inside the field of view and H$_2$CO is produced closer to the nucleus, therefore enhancing the H$_2$CO production rates. However the most important points are that (1) the heliocentric evolution of H$_2$CO production rates is not significantly modified and (2) the H$_2$CO production rates are only slightly affected by grain velocity variations.

4.2.3. Sensitivity to grain temperature

POM thermal-degradation depends heavily on grain temperature as it follows the Arrhenius law. Grain temperature is controlled by two parameters: (1) porosity and (2) organic versus mineral content of the grains. As organics are more absorbent in visible wavelengths than silicates; grain temperature increases with organic content. Moreover, grain temperature also increases with porosity (Greenberg and Li, 1998). Using
the parameters presented in Section 3.4, we investigated the sensitivity of H$_2$CO production rates from POM degradation to the organic content and porosity of grains. Figs. 11a and 11b present the heliocentric evolution of H$_2$CO production rates for different values of these two parameters.

As expected, H$_2$CO production rates depend on grain temperature (see Figs. 11a and 11b), with higher grain temperatures leading to higher production rates. Moreover, higher porosity and organic content of the grains, i.e., higher grain temperatures, lead to a flatter evolution of the H$_2$CO production rates with the heliocentric distance. Therefore, considering a given heliocentric evolution of the dust-to-gas ratio, reproduction of the measurements of Biver et al. (2002a) could be achieved only for certain pairs of values of porosity and organics content of grains (see Figs. 11a and 11b).

4.2.4. Sensitivity to the dust-to-gas ratio

The dust-to-gas ratios measured in Comet C/1995 O1 (Hale–Bopp) are highly scattered and different trends with respect to the heliocentric distance can be observed (see Section 3.2). For the fit computed in the previous sections, we use a grain distribution presenting an increasing dust-to-gas ratio as the comet approaches the Sun (see Fig. 3).

First, in order to study the influence of the value of the dust-to-gas ratio (without a change its heliocentric evolution), we consider three grains distributions: (1) the distribution presented in Section 3.2 (case ‘b’), (2) a distribution with a dust-to-gas ratio 2 times lower (case ‘a’) and (3) a distribution with a dust-to-gas ratio 2 times higher (case ‘c’). The results, for the best fits to the H$_2$CO production rates measured by Biver et al. (2002a) are displayed in Table 2 for each distribution. In each case, observed values are still well fitted with reasonable POM content and negligible H$_2$CO production from nucleus sublimation with respect to POM degradation. The fraction of POM present in grains required to fit the observed values is approximately inversely proportional to the considered dust-to-gas ratio. This means that the POM production rate (kg s$^{-1}$) is constant whatever the value of the dust-to-gas ratio (see Table 2).

In conclusion, the POM production rate (kg s$^{-1}$) is constant and more constrained than the POM mass fraction in grains. Consequently, it would be more meaningful to consider POM production rate (kg s$^{-1}$) than POM mass fraction in grains. This POM production rate is about $6.6 \times 10^4$ kg s$^{-1}$ at 1 AU (see Table 2).

Secondly, the influence of the heliocentric dependence on the dust-to-gas ratio has also been studied. We have constructed a new grain size distribution (case ‘d’) which presents a constant dust-to-gas ratio equal to 5. This distribution presents the same cut-off for larger grains as was used above (see Fig. 4). The parameters leading to the best fit using this distribution, all others parameters being equal to those presented in Section 3, are reported in Table 2. Note in Table 2 that the standard deviation ($\sigma$) increases by a factor 2 compared to the previous cases. Indeed the computed heliocentric evolution of H$_2$CO production rates is flatter than for the case with an increasing dust-to-gas ratio as the comet approaches the Sun. Nevertheless, the observed values can be well reproduced if the grains are colder than previously, i.e., if the organic content is decreased from 60 to 40% (see Fig. 12 and Table 2). Indeed, even though the dust-to-gas is now constant with respect to the heliocentric distance, a decrease in the organic content of the grains (i.e., a decrease in their temperature) leads to a steeper heliocentric evolution of H$_2$CO production rates.

Thus, the effect of the heliocentric evolution of the dust-to-gas ratio is compensated by a decrease in the grain temperature. Therefore, considering a constant dust-to-gas ratio equal to 5, an organic mass content of the grains of 40%, $\alpha = 7\%$ and $Q_{\text{H}_2\text{CO}} / Q_{\text{HCN}} = 0\%$, the calculated H$_2$CO production rates vary with $R_H^{4.0}$ during the pre-perihelion phase and with $R_H^{-4.7}$ during the post-perihelion phase (see Fig. 12). Thus, the steep heliocentric evolution of H$_2$CO production rates could be reproduced irrespective of the heliocentric evolution of the dust-to-gas ratio.

4.2.5. Summary

The grain velocities and chemical type of POM only slightly affect the heliocentric evolution of the H$_2$CO production rate. In fact, it depends mainly on the grain temperature and the heliocentric distance.
Abundant evidence based on observations indicates that the gaseous H$_2$CO observed in the cometary environment is not produced only by sublimation from the surface of the nucleus, but also directly in the coma (Meier et al., 1993; Wink et al., 1999). It has been proposed that gaseous H$_2$CO could be released by the degradation of polyoxymethylene (H$_2$CO polymers, also called POM) which could be present in grains (Huebner, 1987). To check this hypothesis, we experimentally studied the photo- and thermal-degradation of POM (Cottin et al., 2000, 2001; Fray et al., 2004a) and developed a model of the cometary environment taking into account gas production by the degradation of the refractory organic component present in grains (Cottin et al., 2004). We have shown that the H$_2$CO spatial distribution measured by the Giotto spacecraft in the coma of Comet 1P/Halley can be explained if we consider that the grains contain a few mass percent of POM. In the present article, we have shown that the very steep heliocentric evolution of H$_2$CO production measured at radio wavelengths by Biver et al. (2002a) in Comet C/1995 O1 (Hale–Bopp) between 4 AU pre-perihelion and 3 AU post-perihelion is also reproducible by considering that POM is present in grains and that it is degraded into gaseous H$_2$CO by solar UV photons and/or heating (see Fig. 7). Our studies have been focused on the H$_2$CO extended source and we have demonstrated that solid POM is a possible parent for gaseous H$_2$CO.

According to our different assumption, the grains of Comet C/1995 O1 (Hale–Bopp) could contain a few mass percent of POM, with a nominal value of 3.1%. The mass fraction of POM depends on the assumed dust-to-gas ratio as shown in Section 4.2, whereas the production rate of POM (in kg s$^{-1}$) does not depend on this ratio. Concerning H$_2$CO production at the surface of the nucleus, it could represent less than 2% of total H$_2$CO production at 1 AU (see Table 2) and could remain negligible up to 3 AU. Moreover our calculations cannot be used to rule out the possibility that all H$_2$CO is produced from degradation of POM.

Moreover, we have shown that POM thermal-degradation could be the predominant H$_2$CO production mechanism at heliocentric distances up to 3.5 AU. It could account for about 95% of the total H$_2$CO production rate at 1 AU (see Table 2). Moreover the predominance of this H$_2$CO production mechanism as well as the heliocentric evolution of the dust-to-gas ratio could be responsible for the steep heliocentric evolution of the H$_2$CO production rates.

This work, combining experimental and model studies, has two important implications:

1) The contribution of the refractory organic component of cometary grains to the composition of the gaseous coma can no longer be considered negligible. Such a mechanism could then explain the production of other species possibly produced by an extended source such as HNC, CN and CO.

2) The presence of POM or POM-like polymers in cometary grains and nuclei is highly probable. Then, direct detection of POM in cometary environment is a major goal for future in situ studies.

Given that gaseous H$_2$CO may be produced by degradation of solid POM present in grains, this mechanism could explain the production of other species. As for H$_2$CO, the heliocentric evolution of HNC production rates measured by Biver et al. (2002a) is very steep. Irvine et al. (1998) and Rodgers and Charnley (1998) have suggested the formation of HNC through gas phase reactions in the coma. Nevertheless, this mechanism is not efficient enough to reproduce the observed levels of HNC in Comet C/1999 H1 (Lee) and Comet C/2002 C1 (Ikeya–Zhang) (Rodgers and Charnley, 2001; Rodgers et al., 2003). Consequently, Rodgers et al. (2003) propose that HNC could be injected into the coma through the destruction of an unknown precursor. The latter could be HCN polymers or hexamethylenetetramine (C$_6$H$_{12}$N$_4$, also called HMT), compounds which have already been proposed as parent molecules of CN radicals (Retigg et al., 1992; Bernstein et al., 1995). We have therefore undertaken an experimental analysis of the photo- and thermal-degradation of both compounds. Some preliminary results have already been published (Fray et al., 2004b), but more laboratory work is required to include their degradation para-
meters in our model and conclude as to whether or not they are good candidates to explain the origin of HNC and/or CN.

The in situ measurements of the *Giotto* spacecraft inside the coma of 1P/Halley have shown that CO is not entirely produced by nucleus sublimation (Eberhardt et al., 1987). Moreover DiSanti et al. (2001) have measured, from observations at infrared wavelengths, the spatial distribution of CO in Comet C/1995 O1 (Hale–Bopp). Between 2 and 1.5 AU, they observed a change in the CO spatial distribution, which becomes more extended, as well as a relatively abrupt increase of CO production rates. These facts suggest a thermal threshold like the one observed for H$_2$CO at 3–4 AU. Therefore, as already proposed by Greenberg and Li (1998), some CO could originate from the grains. As for HNC and CN, probing this hypothesis requires a complete experimental study of CO production from the degradation of complex organics starting from an appropriate refractory parent candidate. Note that our experimental study shows that CO is not produced by thermal-degradation of POM and therefore this mechanism cannot be used to explain the CO extended source (Cottin et al., 2004; Fray et al., 2004a).

The combination of experimental work and modeling is an effective tool that can be used to infer the presence and amount of organic compounds in the nucleus of comets. So far, from independent measurements in Comet 1P/Halley (Cottin et al., 2004; Fray et al., 2004a) and Comet C/1995 O1 (Hale–Bopp), we have shown that the presence of POM with a mass percent of about 3% in the cometary nucleus and grains is highly probable. Note that no attempt has yet been made to directly detect POM or POM-like polymers in cometary environments. Direct detection of POM in cometary grains or at the surface of the nucleus should therefore be made a major goal of future studies. The COSAC instrument, on board the surface landing probe of the *Rosetta* spacecraft, mainly composed of a GC-MS (gas chromatograph coupled with mass spectrometer), is devoted to the identification of complex organic molecules. However laboratory experiments, carried out with a setup that reproduces the flight configuration and simulates the in situ operating conditions, have shown that POM will be difficult to detect due to its degradation into H$_2$CO inside the heated columns of the chromatograph (Szopa et al., 2004). Therefore, COSAC will likely not make it possible to distinguish between H$_2$CO ices and POM, whereas some others organic compounds, like HCN polymers, will easily be detected if present. The COSIMA instrument, which is a secondary ion mass spectrometer, could provide insight on the presence of POM although it cannot separate all the different compounds present on cometary grains. POM has three intense vibration bands near 10 µm (8.1, 9.5 and 10.7 µm, see Schutte et al., 1993a; Fray et al., 2004a). Unfortunately these bands overlap with the 10 µm silicate band. POM has also two less intense bands at 3.35 and 3.43 µm (Fray et al., 2004a). However, interpretation of the emission features observed in comets between 3.2 and 3.6 µm is very complex due to the contribution of CH-stretching bands of methanol and other species (Bockelée-Morvan et al., 1995). Therefore, the direct detection of POM in cometary grains and/or nuclei will not be easy to achieve and new methods will have to be developed.

Another prospect is the study of the H$_2$CO extended source in a large number of comets to measure the POM production rate (kg s$^{-1}$) and compare it with other species such as CH$_3$OH for example. It appears that there is a correlation between CH$_3$OH and H$_2$CO production rates in different comets (Biver et al., 2002b) and it has already been shown that POM or POM-like polymers are easily synthesized in cometary ice analogs containing CH$_3$OH even if H$_2$CO is missing in the initial mixture (Muñoz-Carо and Schutte, 2003; Bernstein et al., 1995). POM production rates (kg s$^{-1}$) could be derived by studying the spatial distribution of H$_2$CO in the coma, as already done by Cottin et al. (2004). Such distributions have already been measured for C/1989 X1 (Austin) and C/1990 K1 (Levy) (Colom et al., 1992) and for C/1996 B2 (Hyakutake) (Biver et al., 1999) by cross-mapping at radio wavelengths. Such observations will provide new constraints on H$_2$CO production for a larger sample of comets, allowing us to compare the production rates of POM with those of other species.

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Polyoxymethylene as a formaldehyde parent in Comet Hale–Bopp


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