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Radial mixing in protoplanetary accretion disks

III. Carbon dust oxidation and abundance of hydrocarbons in comets

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Abstract. The oxidation of carbon dust and its conversion into CO and some hydrocarbon compounds as intermediate products is studied for protoplanetary accretion discs. The disc model is based on the one-zone α-disc approximation. The radial mixing of the combustion products into the cold outer disc region by turbulent diffusion is considered in the transport-diffusion-reaction equations for the chemistry. It is shown that considerable amounts of CH_4 and C_2H_2 formed as by-products of carbon oxidation are mixed into cold disc regions beyond a distance of 10 AU where they can be included into the ice mixture of cometary nuclei formed in that region. This may explain the high abundance of these gases recently observed in comets Hyakutake (C/1996 B2) and Hale-Bopp (C/1995 O1). This mixing of hydrocarbons from carbon oxidation cannot, however, explain the high abundance of some other molecular species like C_2H_6 or CH_3OH, which have to be formed by different processes.

Key words. accretion, accreation disks – molecular processes – solar system: formation – comets: general

1. Introduction

The material of a protoplanetary accretion discs contains a rich mixture of gases, ices, and dust. In the outer parts of the disc one encounters material which originates from the parent molecular cloud which fell onto the protostellar disc during the star formation process and was incorporated into the disc material after having passed through the low Mach-number accretion shock standing atop the disc surface. The dust component is not likely to have significantly changed its composition by passing through the accretion shock and it is assumed that the dust composition of the outer protostellar disc essentially equals that of the parent molecular cloud. How this mixture of dust components might look like in the outer disk is described, for instance, in Pollack et al. (1994).

One of the major components of this mixture is some kind of carbon dust. Since the mixture of elements in the interstellar medium and in protoplanetary discs is oxygen rich, the carbon dust component is not stable in this environment. It would be converted into CO if chemical reactions between the carbon dust grains and oxygen bearing species from the gas phase were possible. The sole reason why carbon dust grains survived in the interstellar medium between their formation in the carbon rich environment of a circumstellar dust shell around a carbon star and their ultimate incorporation into the protoplanetary accretion disc of our Solar System is, that during their residence time in the interstellar medium the grains have never been heated sufficiently that the activation energy barriers involved in the carbon oxidation process can be surmounted.

As the central star accretes material from its protostellar disc, the hot inner disc zone close to the star is continuously replenished by mass accretion from the outer disc region. Material from the outer disc slowly spirals inwards into the inner disc regions and gradually heats up as it comes closer to the star. In the inner region of the disc ($r \lesssim 1$ AU) the discs midplane temperature exceeds 1000 K for at least the first 5×10^5 years of disc evolution (cf. Ruden & Lin 1986). In this region the carbon dust is rapidly destroyed by oxidation, as is shown in Gail (2001, henceforth called Paper I).

Since the disc is convectively unstable (cf. Ruden & Lin 1986; D'Alessio et al. 1998), the revolution of the disc matter around the central star is superposed by convectively driven turbulent motions. This turbulent motion induces a radial and vertical mixing of disc material from different zones of the protoplanetary disc. The observational finding of crystalline silicate dust material in comet Hale-Bopp indicates that such large-scale mixing actually took place in the Solar Nebula (cf. Hanner et al. 1994; Nuth 1999; Nuth et al. 2000). In Paper I we have shown that by mixing processes crystalline dust material from the zone where the initially amorphous dust of interstellar origin is annealed and develops a crystalline structure (at $T \approx 800$ K) is transported into the cold outer disc regions where the cometesimals are formed.

In this paper we concentrate on the radial mixing of the products of combustion of carbon grains. As was shown in Paper I the carbon dust is oxidised by reactions with

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OH radicals in a zone of the disc where the midplane temperature roughly equals 1100 K. This temperature is considerably lower than the temperature where carbonaceous material burns under terrestrial conditions. This lower temperature results from the slow increase of temperature as the disc matter drifts inwards by accretion, which occurs on timescales of the order of $10^4 \ldots 10^5$ yrs, depending on the distance r from the star. The carbon grains do not burn as in a flame but they are very slowly oxidised once the concentration of OH radicals resulting from water vapour dissociation has reached a level where the oxidation timescale becomes shorter than diffusional mixing timescales. An immediate consequence of this low oxidation temperature is that only part of the solid carbon is immediately converted into CO while a considerable fraction forms CH_4 and some C_2H_2, as has been found in Finocchi et al. (1997a). The methane then is converted in a sequence of reactions into CO which involve reactions with free O atoms. The abundance of free oxygen atoms in the gas phase (by dissociation of H_2O) reaches a level sufficient for converting the methane into CO only at a much higher temperature (≈1350 K) as that required for oxidation of solid carbon by OH. As a consequence of the delayed final oxidation of the carbon compounds in the oxygen rich environment one obtains a considerable concentration of the intermediate products methane and acetylene of carbon oxidation (Finocchi et al. 1997a).

These intermediate products, CH_4, C_2H_2 and some other hydrocarbons, if mixed into the cold outer part of the disc, cannot be oxidised in this region because there exist no gas phase species which can react with hydrocarbons to form CO. The hydrocarbons are metastable in this region. Only in the far outer regions of the disc where the disc becomes transparent for cosmic rays or in a surface layer of the disc subject to irradiation by UV and X-rays from the protosun these molecules may become involved in the ion molecule chemistry triggered by cosmic rays and ionising radiation. Thus, radial mixing in the protoplanetary accretion disc builds up a certain level of concentration of hydrocarbon compounds in the outer disc regions up to about 30 AU, resulting from carbon combustion in the region $r < 1$ AU. Beyond this region the products of carbon oxidation cannot by mixed during the first 10^6 years of disc evolution (Wehrstedt & Gail 2002).

Observations of comets C/1996 B2 (Hyakutake), C/1995 O1 (Hale-Bopp) and C/1999 H1 (Lee) have shown that cometary ices contain a significant amount of hydrocarbons (cf. the review by Crovisier & Bockelée-Morvan 1999). Especially CH_4, C_2H_6 and C_2H_2 are quite abundant. This suggests that at least some fraction of the hydrocarbons observed to exist in cometary nuclei ices are products of the oxidation of the carbon dust which have been mixed into the cold regions of the Solar Nebula.

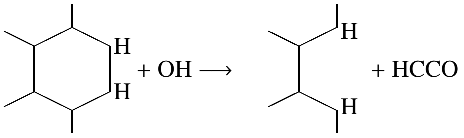
In this paper we study the interplay between carbon dust oxidation, gas phase reactions of the product molecules, and radial mixing in the disc in order to determine the abundance of carbon compounds from carbon combustion in the cold regions of the Solar Nebula where the nuclei of the comets were formed 4.6 Gyrs ago. The model calculations are done for a simple stationary Keplerian α-disc model in the one-zone approximation. The restriction of the disc model to the one-zone approximation only allows to treat radial mixing processes and excludes a treatment of vertical mixing processes in the disc, though these might be important for the gas-phase chemistry because of the strong UV and X-ray irradiation of the disc surface due to the young proto-sun (Aikawa & Herbst 1999, 1999; Willacy & Langer 2000). With this caveat, we shall show that radial mixing of the combustion products of carbon grains may be responsible for some of the hydrocarbons observed to exist in cometary ices.

The plan of this paper is as follows: in Sect. 2 we describe the chemical reactions considered and the method used for their solution, Sect. 3 discusses the system of transport-diffusion-reaction equations, Sect. 4 presents the results of a model calculation and Sect. 5. gives some final remarks.

2. Carbon combustion and formation of CO

2.1. Oxidation of carbon grains

The oxidation of carbon particles is a process which has extensively been studied in the laboratory. In Duschl et al. (1996) and Finocchi et al. (1997a) the results for the basic oxidation mechanism of solid carbon obtained in the chemistry of flames are applied to the problem of destruction of carbon dust grains in protoplanetary accretion discs. Under conditions encountered in the early Solar Nebula the basic reaction scheme for oxidation of solid carbon into CO starts with the reaction



(1)

where a OH radical attacks a six-ring at the periphery of a large PAH and cracks carbon-carbon bonds. The rate for this starter reaction is

$$R_{\rm car} = A_{\rm car}\, n_{\rm OH}\, v_{\rm th,OH}\, \alpha_{\rm car}. \tag{2}$$

$A_{\rm car}$ is the total area of all carbon grains per unit volume (as defined in Paper I), $n_{\rm OH}$ the particle density of OH radicals, $v_{\rm th,OH}$ their rms thermal velocity

$$v_{\rm th,OH} = \sqrt{\frac{kT}{2\pi m_{\rm OH}}}. \tag{3}$$

$\alpha_{\rm car}$ is the efficiency for the reaction of OH with solid carbon, which is known from laboratory measurements on carbon combustion.

The details of the calculation of the rate $R_{\rm car}$ for an ensemble of carbon grains with different radii are described in Paper I.

2.2. The pathway to CO

The next step in the reaction sequence is (El-Gamal 1995)

$$\mathrm{HCCO} + \mathrm{H} \xrightarrow{k_0} \mathrm{CO} + \mathrm{CH_2}\,. \tag{4}$$

This reaction generates the first CO molecule in the gas phase following the chemi-sputtering reaction (1). The backwards reaction would be strongly endothermic and is forbidden. The HCCO also is formed from C_2H_2 by the reaction

$$C_2H_2 + O \xrightarrow{k_1} HCCO + H \tag{5}$$

where C_2H_2 is a follow up product from the CH_2 formed by reaction (4). The rate equation for the formation and destruction of HCCO is

$$\frac{d\,n_{HCCO}}{d\,t} = R_{car} - R_{01} + R_{30} \tag{6}$$

with

$$R_{01} = k_0 n_H n_{HCCO} \tag{7}$$

$$R_{30} = k_1 n_{C_2H_2} n_O. \tag{8}$$

The CH_2 radical formed by reaction (4) then equilibrates with other hydrocarbons of the sequence CH_n ($n = 0 \ldots 4$) by means of the rapid exchange reactions

$$C + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CH + H \tag{9}$$

$$CH + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CH_2 + H \tag{10}$$

$$CH_2 + H_2 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} CH_3 + H \tag{11}$$

$$CH_3 + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} CH_4 + H. \tag{12}$$

In the temperature region where carbon oxidation occurs these reactions are fast and in a quasi-equilibrium state. The corresponding set of rate equations is

$$\frac{d\,n_C}{d\,t} = -k_2 n_{H_2} n_C + k_{-2} n_H n_{CH} \tag{13}$$

$$\begin{aligned}\frac{d\,n_{CH}}{d\,t} &= +k_2 n_{H_2} n_C - k_{-2} n_H n_{CH}\\ &\quad -k_3 n_{H_2} n_{CH} + k_{-3} n_H n_{CH_2}\end{aligned} \tag{14}$$

$$\begin{aligned}\frac{d\,n_{CH_2}}{d\,t} &= +k_3 n_{H_2} n_{CH} - k_{-3} n_H n_{CH_2}\\ &\quad -k_4 n_{H_2} n_{CH_2} + k_{-4} n_H n_{CH_3}\\ &\quad +R_{01} + R_{34}\end{aligned} \tag{15}$$

$$\begin{aligned}\frac{d\,n_{CH_3}}{d\,t} &= +k_4 n_{H_2} n_{CH_2} - k_{-4} n_H n_{CH_3}\\ &\quad -k_5 n_{H_2} n_{CH_3} + k_{-5} n_H n_{CH_4} - R_{12}\end{aligned} \tag{16}$$

$$\frac{d\,n_{CH_4}}{d\,t} = +k_5 n_{H_2} n_{CH_3} - k_{-5} n_H n_{CH_4}\,. \tag{17}$$

In Eq. (15) the rate term R_{01} describes the gain of CH_2 by reaction (4). The rate terms R_{34} and R_{12} will be explained soon.

The carbon dust oxidation reaction (1) leads to production of CO molecules in the reaction step (4) and to the buildup of a population of hydrocarbon molecules CH_n ($n = 1 \ldots 4$), most of which are in the form of CH_4. The main loss process for this group of molecules is the reaction between two CH_3 molecules

$$CH_3 + CH_3 \xrightarrow{k_6} C_2H_4 + H_2, \tag{18}$$

which forms a C = C bond. The rate for this process is

$$R_{12} = k_6 n^2_{CH_3}. \tag{19}$$

This rate occurs as loss term in (16). The reverse reaction is endothermic and can be neglected.

Reactions between two CH_3 molecules also result in the formation of C_2H_5 and C_2H_6, but this is followed by reactions finally leading back to CH_3. This side-chain of reactions is considered separately.

The ethylene formed by reaction (18) is in equilibrium with C_2H_3 by means of the fast exchange reaction

$$C_2H_3 + H_2 \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} C_2H_4 + H. \tag{20}$$

The C_2H_3 is destroyed by the reaction

$$C_2H_3 + H \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} C_2H_2 + H_2. \tag{21}$$

The backwards reaction is endothermic, but not to such an extent that it can be neglected. The rate term for C_2H_3 destruction is

$$R_{23} = k_8 n_H n_{C_2H_3} \tag{22}$$

and that for re-formation

$$R_{32} = k_{-8} n_{H_2} n_{C_2H_2}. \tag{23}$$

The rate equations for the formation and destruction of C_2H_4 and C_2H_3 thus are

$$\frac{d\,n_{C_2H_4}}{d\,t} = R_{12} - k_{-7} n_H n_{C_2H_4} + k_7 n_{H_2} n_{C_2H_3} \tag{24}$$

$$\frac{d\,n_{C_2H_3}}{d\,t} = k_{-7} n_H n_{C_2H_4} - k_7 n_{H_2} n_{C_2H_3} - R_{23} + R_{32}. \tag{25}$$

The acetylene formed in reaction (21) is in equilibrium with C_2H by means of the fast exchange reaction

$$C_2H_2 + H \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} C_2H + H_2. \tag{26}$$

Thus, following reaction (18) a population of C_2H_n ($n = 1 \ldots 4$) molecules is build up.

The main loss process for this group of hydrocarbons are the oxidation reactions

$$C_2H_2 + O \xrightarrow{k_1} HCCO + H \tag{27}$$

$$C_2H_2 + O \xrightarrow{k_{10}} CH_2 + CO \tag{28}$$

$$C_2H + O \xrightarrow{k_{11}} CH + CO. \tag{29}$$

In all three reactions a CO molecule is formed, either directly or in a second step (reaction 4) following reaction (27). Because all three reactions have nearly equal rate coefficients, the first two reactions are more efficient in forming CO than the third one because of a much higher C_2H_2 abundance. These two reactions form the second CO molecule from the two C atoms

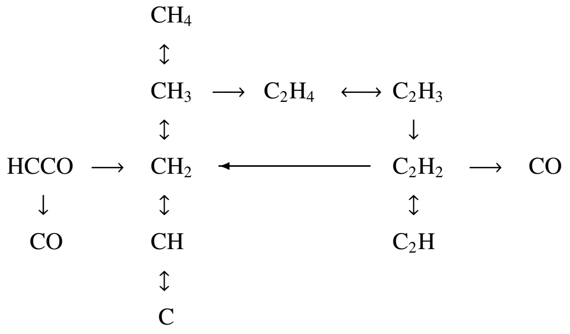


Fig. 1. Reaction cycle for the conversion of the second carbon atom into CO.

injected into the gas phase as HCCO by reaction (1). The rate of CO formation by reaction (28) is

$$R_{34} = k_{10} n_{\rm O} n_{\rm C_2H_2}\,. \tag{30}$$

At the same time one of the two CH_3 molecules consumed in reaction (18) is recycled as CH_2 molecule which is introduced back into the chain of reactions (13), … (17). This occurs in Eq. (15) as the source term R_{34}. The rate of looping back to HCCO by reaction (27) is R_{30} defined by (8). The rate equations for the formation and destruction of C_2H_2 and C_2H now are

$$\frac{{\rm d}\,n_{\rm C_2H_2}}{{\rm d}\,t} = R_{23} - R_{32} - R_{34} - R_{30}$$

$$-k_{-9} n_{\rm H} n_{\rm C_2H_2} + k_9 n_{\rm H_2} n_{\rm C_2H} \tag{31}$$

$$\frac{{\rm d}\,n_{\rm C_2H}}{{\rm d}\,t} = k_{-9} n_{\rm H} n_{\rm C_2H_2} - k_9 n_{\rm H_2} n_{\rm C_2H}. \tag{32}$$

The conversion of the two carbon atoms liberated by the starter reaction (1) into CO occurs in two steps. The first CO molecule is formed at once by reaction (4), the rate term R_{01} in (33) corresponds to this process, while the second CO molecule is formed by the sequence of reactions just described, the rate term R_{34} in (33) corresponds to this second process. The formation of the second CO molecule occurs via a cyclic process, by which one CH_3 molecule acts as a catalyst which undergoes a sequence of reactions, starting by reacting with a second CH_3 molecule, until finally one CH_3 molecule is converted into CO while the other CH_3 molecule is recovered. Figure 1 schematically shows this reaction cycle.

Besides these reactions, a number of less efficient side-reactions of the reaction chain leading to CO and other hydrocarbons are active. Some of them are discussed in Finocchi et al. (1997a). These reaction path's are not included in the present model calculation. We consider only the main route to CO which accounts for the dominating part of the CO formation rate. More detailed calculations based on a big reaction network are given in Finocchi & Gail (1997b), but the results for CO production based on the extended reaction network are not significantly different from what one obtains from the present reduced set of reaction equations.

The equation for CO formation by carbon combustion is

$$\frac{{\rm d}\,n_{\rm CO}}{{\rm d}\,t} = R_{01} + R_{34}. \tag{33}$$

2.3. Grouping of equations

For computational purposes we found it to be advantageous to combine the set of equations into a few groups. We define

$$n_0 = n_{\rm HCCO} \tag{34}$$

$$n_1 = n_{\rm C} + n_{\rm CH} + n_{\rm CH_2} + n_{\rm CH_3} + n_{\rm CH_4} \tag{35}$$

$$n_2 = n_{\rm C_2H_4} + n_{\rm C_2H_3} \tag{36}$$

$$n_3 = n_{\rm C_2H_2} + n_{\rm C_2H}. \tag{37}$$

For n_0 we have the equation

$$\frac{{\rm d}\,n_0}{{\rm d}\,t} = R_{\rm car} + R_{30} - R_{01}. \tag{38}$$

Adding Eqs. (13)…(17) yields the equation

$$\frac{{\rm d}\,n_1}{{\rm d}\,t} = R_{01} + R_{34} - R_{12}. \tag{39}$$

Similar, adding Eqs. (24) and (25) yields

$$\frac{{\rm d}\,n_2}{{\rm d}\,t} = R_{12} - R_{23} \tag{40}$$

and finally adding Eqs. (31) and (32) yields

$$\frac{{\rm d}\,n_3}{{\rm d}\,t} = R_{23} - R_{34} - R_{30}. \tag{41}$$

This set of equations is a closed system for calculating n_0, n_1, n_2, and n_3. The rate of creation of any molecule of the groups described by n_0, n_1, n_2, and n_3 is $R_{\rm car}$ while the loss rate for all groups together is $R_{01} + R_{34}$.

Within each of the groups 1, 2, and 3 the relative abundance of the group members is determined by the fast exchange reactions with H and H_2. The reactions for transition from one group to the next are much slower (cf. Fig. 3 or Tables 3 and 4 in Finocchi et al. 1997a). For determining the relative abundances within the groups we may use the stationary equations with the intergroup transition terms neglected and solve for the individual particle densities in terms of the group densities. We obtain

$$n_{\rm CH_4} = \frac{n_1}{\mathcal{N}_1} \tag{42}$$

with

$$\mathcal{N}_1 = \left[1 + \frac{k_{-5} n_{\rm H}}{k_5 n_{\rm H_2}}\left(1 + \frac{k_{-4} n_{\rm H}}{k_4 n_{\rm H_2}}\left(1 + \frac{k_{-3} n_{\rm H}}{k_3 n_{\rm H_2}}\left(1 + \frac{k_{-2} n_{\rm H}}{k_2 n_{\rm H_2}}\right)\right)\right)\right]. \tag{43}$$

The particle densities of the other members of this group follow from

$$n_{{\rm CH}_{m-1}} = \frac{k_{-m} n_{\rm H}}{k_m n_{\rm H_2}}\, n_{{\rm CH}_m}. \tag{44}$$

For the rate R_{12} one then obtains

$$R_{12} = k_6 \left(\frac{k_{-5} n_{\rm H}}{k_5 n_{\rm H_2}}\right)^2 \frac{n_1^2}{\mathcal{N}_1^2}. \tag{45}$$

For the second group we obtain

$$n_{C_2H_4} = \frac{n_2 k_7 n_{H_2}}{k_7 n_{H_2} + k_{-7} n_H} \tag{46}$$

$$n_{C_2H_3} = \frac{n_2 k_{-7} n_H}{k_7 n_{H_2} + k_{-7} n_H}. \tag{47}$$

For the rate R_{23} we obtain

$$R_{23} = k_8 \frac{k_{-7} n_H}{k_{-7} n_H + k_7 n_{H_2}} n_H \, n_2. \tag{48}$$

For the third group we obtain

$$n_{C_2H_2} = \frac{n_3 k_9 n_{H_2}}{k_9 n_{H_2} + k_{-9} n_H} \tag{49}$$

$$n_{C_2H} = \frac{n_3 k_{-9} n_H}{k_9 n_{H_2} + k_{-9} n_H} \tag{50}$$

and the rate R_{34} follows as

$$R_{34} = k_{10} \frac{k_{-9} n_H}{k_{-9} n_H + k_9 n_{H_2}} n_O \, n_3. \tag{51}$$

These equations define the set of rate equations which we solve in order to determine the abundance of the combustion products of carbon grains in the protostellar accretion disc. The production rate of CO is given by (33).

2.4. Formation of CO_2

CO is the dominating carbon-oxygen compound at high temperatures in the inner disc regions. Also at very low temperatures the carbon not bound in carbon grains is mainly bound in CO, other carbon bearing species having only very low abundances in the outer part of the protoplanetary disc, provided the composition in that region equals that of the parent molecular cloud. At medium temperatures, however, if it is assumed that conversion to CH_4 is kinetically forbidden (e.g. Fegley & Prinn 1989), most of the CO will be converted into CO_2. The most efficient reaction for the interconversion of CO and CO_2 is

$$CO + H_2O \underset{k_{-12}}{\overset{k_{12}}{\rightleftarrows}} CO_2 + H_2. \tag{52}$$

At high temperatures also

$$CO + OH \underset{k_{-13}}{\overset{k_{13}}{\rightleftarrows}} CO_2 + H \tag{53}$$

becomes important. These reactions are responsible first for the formation of CO_2 from CO as the disc material slowly spirals inwards into regions of increasingly higher temperature and reaction (52) proceeds from the left to right. Later, by continued inwards migration of the disc material, temperatures become unfavourably high for the existence of CO_2 and reactions (52) and (53) then proceeds from the right to the left and in this way are responsible for the re-formation of CO from CO_2. Thus, Eq. (33) has to be changed into

$$\begin{aligned} \frac{\mathrm{d}\, n_{CO}}{\mathrm{d}\, t} &= R_{01} + R_{34} - k_{12} n_{CO} n_{H_2O} + k_{-12} n_{CO_2} n_{H_2} \\ &\quad - k_{13} n_{CO} n_{OH} + k_{-13} n_{CO_2} n_H \end{aligned} \tag{54}$$

to account for the reactions (52) and (53) and we have to add to our system the equation for CO_2

$$\begin{aligned} \frac{\mathrm{d}\, n_{CO_2}}{\mathrm{d}\, t} &= +k_{12} n_{CO} n_{H_2} - k_{-12} n_{CO_2} n_{H_2} \\ &\quad + k_{13} n_{CO} n_{OH} - k_{-13} n_{CO_2} n_H. \end{aligned} \tag{55}$$

2.5. Formation of C_2H_5 and C_2H_6

The formation of C_2H_5 and of ethane is possible by a side chain of the main reaction route from carbon dust to CO and CO_2 considered up to now. These molecules may be formed by the following reactions

$$CH_3 + CH_3 \underset{k_{-14}}{\overset{k_{14}}{\rightleftarrows}} C_2H_5 + H \tag{56}$$

and

$$C_2H_5 + H_2 \underset{k_{-15}}{\overset{k_{15}}{\rightleftarrows}} C_2H_6 + H. \tag{57}$$

This fast exchange reaction establishes an equilibrium between C_2H_5 and C_2H_6. A second route to ethane formation is the three-particle reaction

$$CH_3 + CH_3 + M \xrightarrow{k_{16}} C_2H_6 + M \tag{58}$$

which occurs at a small but non-negligible rate since pressures in the inner region of the accretion disc are not as low as they usually use to be in astrophysical problems. A third route to ethane is

$$CH_4 + CH_4 \xrightarrow{k_{17}} C_2H_6 + H_2\,. \tag{59}$$

2.6. Formation of methanol CH_3OH

According to observations of cometary nuclei, methanol is a very abundant component in the ice mixture of comets. For this reason we include in our calculation of the chemistry as a test case the reactions for the formation of CH_3OH by

$$CH_3 + OH \underset{k_{-18}}{\overset{k_{18}}{\rightleftarrows}} CH_3O + H. \tag{60}$$

The CH_3O is in equilibrium with CH_3OH by means of the rapid hydrogen addition/abstraction reaction

$$CH_3O + H_2 \underset{k_{-19}}{\overset{k_{19}}{\rightleftarrows}} CH_3OH + H \tag{61}$$

CH_3O and CH_4OH are treated in the calculation as a single group as before.

2.7. Reaction rates and equilibrium constants

The rate coefficients are approximated in the standard Arrhenius form

$$k = A\, T^{\alpha}\, \mathrm{e}^{-E_a/kT}. \tag{62}$$

Table 1. Rate coefficients for the chemical reactions used in the model calculation.

Rate	A $\mathrm{cm^3 s^{-1}}$	α	E_a/k [K]	Source
k_0	2.50×10^{-10}	0	16 100	1
k_1	3.60×10^{-18}	2.10	790	3
k_2	6.64×10^{-10}	0	11 700	2
k_3	2.40×10^{-10}	0	1760	3
k_4	1.20×10^{-10}	0	0	3
k_5	1.14×10^{-20}	2.74	4740	3
k_6	1.66×10^{-8}	0	16 500	2,1
k_7	2.00×10^{-11}	0	0	1
k_8	2.00×10^{-11}	0	0	3
k_9	1.00×10^{-10}	0	14 000	3
k_{10}	8.40×10^{-18}	2.10	790	3
k_{11}	1.70×10^{-11}	0	0	3
k_{-12}	2.94×10^{-14}	0.50	7550	2
k_{13}	1.05×10^{-17}	1.50	250	3
k_{14}	5.00×10^{-11}	0	6800	3
k_{-14}	6.00×10^{-11}	0	0	3
k_{15}	5.10×10^{-24}	3.60	4250	3
k_{-15}	2.15×10^{-24}	1.50	3370	3
k_{17}	1.70×10^{-15}	1.00	22 640	4
k_{18}	3.75×10^{-10}	0	7800	1

Sources:
(1): El-Gamal (1995), (2): UMIST data-file (Millar et al. 1997),
(3): Baulch et al. (1994), (4) NIST.

The coefficients of this representation used in the model calculation are listed in Table 1 together with the sources, where the data have been taken from. The rate k_{16} is taken from Baulch et al. (1994).

The rate coefficients for the reverse reactions are calculated by means of the principle of detailed balancing from rate coefficients of the forward reactions and the mass action constant for the reaction in chemical equilibrium. The mass action constants are calculated from thermodynamical data given in Barin (1995). The free enthalpy of formation of molecules from the free atoms is fitted by the following expression

$$\Delta G = \frac{a}{T} + b + cT + dT^2 + eT^3. \tag{63}$$

Results for the fit coefficients for the molecules used in the present calculation are given in Table 2. The accuracy of this analytical fit to the tabular values is generally better than 10^{-3} in the temperature region 300 … 2000 K.

3. The transport–diffusion-reaction equations

In a protoplanetary accretion disc the matter within the disc slowly migrates inwards by viscous accretion with a drift velocity v_r. Additionally, during the intermediate phase where (i) mass infall has ceased and the formation of the central star is nearly finished while the remaining disc gradually is accreted onto the star and (ii) massive formation of planetesimals has not yet begun, the protoplanetary disc is convectively unstable over most parts of the disc (cf. Ruden & Lin 1986; D'Alessio et al. 1998). The turbulent convective flows result in an efficient mixing of the disc material both in the radial and the vertical direction. In Paper I we have discussed this mixing processes and its implications for the dust components in the accretion disc. Here we concentrate on the mixing of combustion products of carbon oxidation into the cold outer disc zones where these combustion products later may be incorporated into the ice component of the planetesimals. We assume as in Paper I that the disc is vertically well mixed such that there are no significant concentration gradients of gas phase species in the vertical direction. Radial mixing, operating on a much longer timescale, in conjunction with the radial inwards drift results in radial concentration gradients of gas phase species within the disc. The transport-diffusion-reaction equation describing the temporal and radial variation of the concentration c_i of species i with respect to hydrogen nuclei is (cf. Paper I)

$$\frac{\partial c_i}{\partial t} + v_{\mathrm{r},i}\frac{\partial c_i}{\partial r} = \frac{1}{rn}\frac{\partial}{\partial r} rnD_i \frac{\partial c_i}{\partial r} + \frac{R_i}{n}\cdot \tag{64}$$

$v_{\mathrm{r},i}$ is the radial drift velocity of species i and D_i its diffusion coefficient, induced by turbulent mixing. Since we are considering gas phase species, the drift velocity and the diffusion coefficient are the same for all species. n is the particle density of H nuclei and R_i is the rate of creation or destruction of species i, as described in the preceding section.

The drift velocity v_r for all species is given by the solution of the equations for the structure of the accretion disc. The diffusion coefficient D is related by

$$D = \frac{\nu}{Sc} \tag{65}$$

to the coefficient of turbulent viscosity ν in the disc. This quantity also is obtained from a solution of the equations for the disc structure in the α-approximation of Shakura & Sunyaev (1973). The Schmidt-number Sc is an empirical constant which usually is determined from laboratory measurements of mixing in turbulent flows. We choose in the model calculation a value of $Sc = 1$ which yields a lower limit for D which in turn results in a slight underestimation of the efficiency of the diffusion process. This choice is preferred over the probably more realistic choice of $Sc = 0.7$ in order not to overestimate the role of diffusional mixing. For more details with respect to the choice of Sc see Paper I.

For calculating the mixing of the combustion products of the carbon grains within the protostellar disc, we have to solve six such equations for the groups 0,… 3 defined above and two for the concentrations of CO and CO_2 molecules. These equations are coupled to the equation for the destruction and mixing of carbon dust grains as described in Paper I. They cannot be solved independently from the equations for the concentration and mixing of carbon grains, but there is no back coupling to that equations because in an oxygen rich environment a growth of carbon grains is not possible.

Table 2. Fit coefficients for the approximation (63) for the free enthalpy of formation ΔG of a compound from the free atoms. Units are J/mole, pressures are in bar. Data from Barin (1995).

Molecule	*a*	*b*	*c*	*d*	*e*
H_2	1.06769×10^{6}	-4.41615×10^{5}	1.03979×10^{2}	6.40612×10^{-3}	-7.56253×10^{-7}
CH	7.43838×10^{5}	-3.44391×10^{5}	9.20348×10^{1}	8.53870×10^{-3}	-1.55497×10^{-6}
CH_2	1.74071×10^{6}	-7.75871×10^{5}	2.02387×10^{2}	1.41851×10^{-2}	-2.42352×10^{-6}
CH_3	2.79512×10^{6}	-1.24068×10^{6}	3.23768×10^{2}	2.03837×10^{-2}	-3.57358×10^{-6}
CH_4	4.59997×10^{6}	-1.68987×10^{6}	4.60008×10^{2}	2.72121×10^{-2}	-5.02918×10^{-6}
C_2	-5.18061×10^{3}	-5.94870×10^{5}	1.12562×10^{2}	5.90139×10^{-3}	-9.83454×10^{-7}
C_2H	1.42354×10^{6}	-1.09086×10^{6}	2.29673×10^{2}	9.62207×10^{-3}	-2.02675×10^{-6}
C_2H_2	2.35939×10^{6}	-1.65637×10^{6}	3.60940×10^{2}	1.28570×10^{-2}	-2.49538×10^{-6}
C_2H_3	4.23944×10^{6}	-1.85210×10^{6}	4.57332×10^{2}	2.09662×10^{-2}	-3.89347×10^{-6}
C_2H_4	5.36679×10^{6}	-2.28443×10^{6}	5.94532×10^{2}	2.52283×10^{-2}	-4.83266×10^{-6}
C_2H_5	6.63096×10^{6}	-2.45504×10^{6}	6.85807×10^{2}	3.26708×10^{-2}	-6.19303×10^{-6}
C_2H_6	3.97121×10^{6}	-2.84507×10^{6}	7.68025×10^{2}	9.61891×10^{-2}	-2.78540×10^{-5}
OH	1.15321×10^{6}	-4.34309×10^{5}	9.81838×10^{1}	5.95049×10^{-3}	-6.97288×10^{-7}
H_2O	2.74226×10^{6}	-9.42013×10^{5}	2.18481×10^{2}	1.08875×10^{-2}	-1.34636×10^{-6}
CO	1.26946×10^{6}	-1.08346×10^{6}	1.30093×10^{2}	3.94470×10^{-3}	-4.33689×10^{-7}
CO_2	2.22110×10^{6}	-1.62175×10^{6}	2.85410×10^{2}	2.69311×10^{-3}	-3.80432×10^{-7}
CH_3O	6.18606×10^{6}	-1.64280×10^{6}	4.79459×10^{2}	1.06008×10^{-2}	-1.52592×10^{-6}
CH_3OH	2.84997×10^{6}	-2.05244×10^{6}	5.31756×10^{2}	7.14428×10^{-2}	-2.01010×10^{-5}

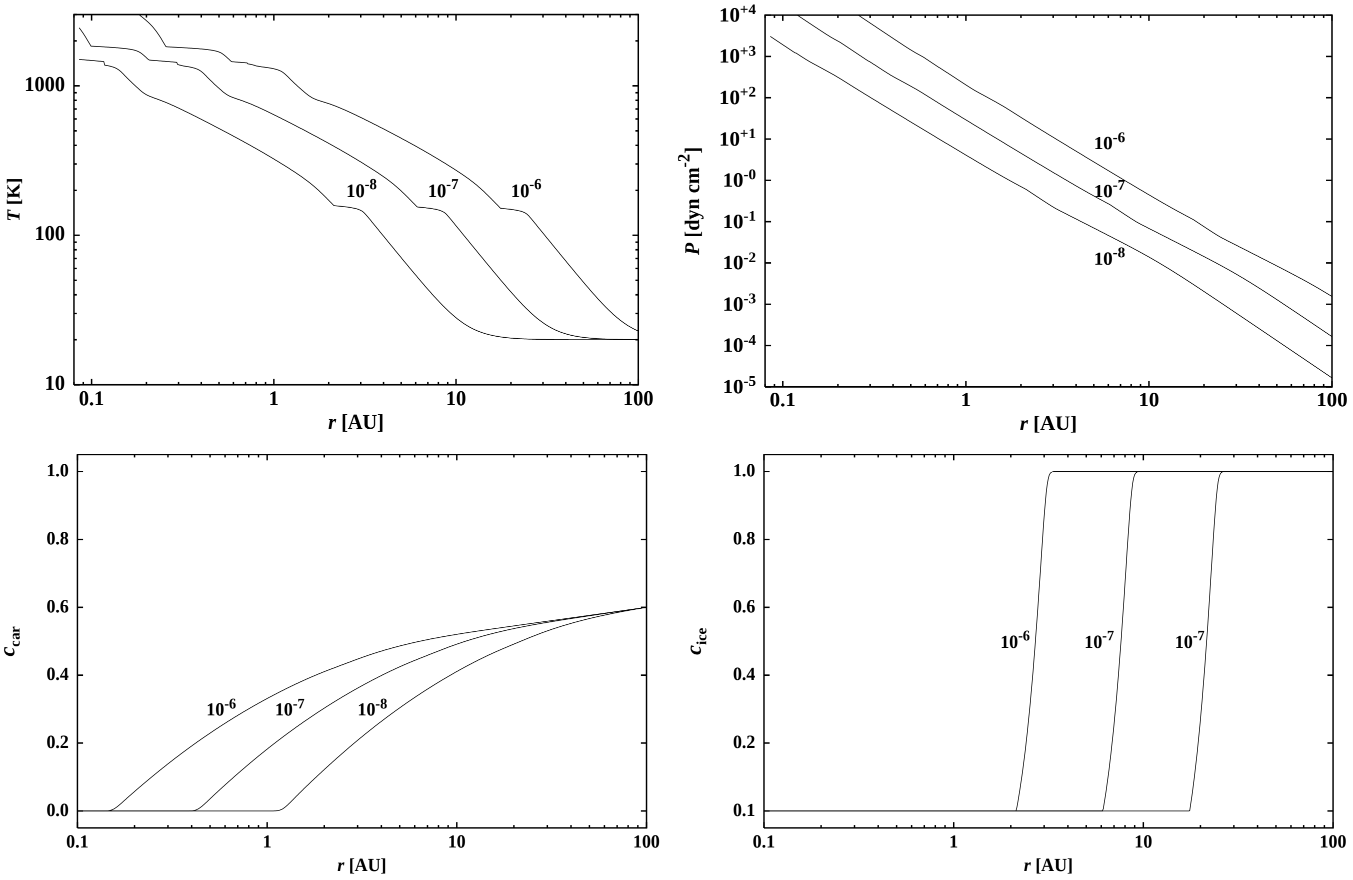


Fig. 2. Radial disc structure in models for a stationary accretion disc including radial mixing processes for the three different accretion rates indicated at the lines (in units $10^{-7}\ M_\odot\ \mathrm{yr}^{-1}$). *Top left:* temperature in the midplane. *Top right:* pressure in the midplane. *Bottom left:* degree of condensation of carbon in carbon grains. *Bottom right:* fraction of the oxygen not bound in solids and CO, which is condensed as water ice.

In this paper we consider stationary accretion discs, which are a reasonable approximation of the inner region up to approximately 30 AU for protoplanetary accretion discs around solar like protostars at an age of about 10^6 years (e.g. Ruden & Lin 1986; Wehrstedt & Gail 2002). In the stationary case the solution of the diffusion Eq. (64) requires the prescription of appropriate boundary conditions. For molecules of the groups 0, 1, 2, and 3 it seems plausible to assume that (i) such molecules are completely converted into CO in the hot innermost regions of the disc and (ii) that such molecules have negligible abundances in the outermost disc regions where material is present which essentially is material from the parent molecular cloud. This material has passed through the accretion shock at the disc surface but in the outer region of a disc temperatures behind the shock never become high enough in order to strongly modify the composition of the infalling material (cf. Mitchell 1984; Neufeld & Hollenbach 1994). Though one observes in molecular clouds a lot of C-H-compounds, their density is usually low (e.g. van Dishoek et al. 1993). Thus we prescribe the following boundary conditions

$$c_i = 0 \quad (i = 0, 1, 2, 3) \quad \text{at} \quad r = r_i\,, \; r = r_\mathrm{a} \tag{66}$$

where r_i and r_a are the inner and outer radii of our disc model, respectively. This does not consider that some of the gases are supplied to the inner disc in non-negligible quantities by means of interstellar ices. With this choice of initial conditions we intend to show, however, that even in the absence of an interstellar contribution there result high abundances of hydrocarbons in the regions where comets are thought to have formed.

For the CO molecule we have the following boundary conditions: at the outer radius r_a the matter essentially has the composition of the molecular cloud. For the dust we assume in this calculation the dust model of Pollack et al. (1994) according to which about 60% of the total carbon is in carbon grains and the remaining 40% are in the gas (+ice) phase, essentially as CO. Thus, we prescribe (counting CO as group 4 in our calculation)

$$c_4 = 0.4\epsilon_\mathrm{C} \quad \text{at} \quad r = r_\mathrm{a}. \tag{67}$$

ϵ_C is the abundance of C relative to H by number. The inner boundary of our disc model is chosen close to the star. Temperatures are high in this region and all carbon compounds are converted into CO. The inner boundary condition then is

$$c_4 = 1.0\epsilon_\mathrm{C} \quad \text{at} \quad r = r_i. \tag{68}$$

For the CO_2 molecule we prescribe the boundary conditions (66).

The chemistry considered in this paper only considers gas phase reactions between neutral molecules, which is appropriate for the warm inner regions of the protoplanetary disc where dust oxidation and the chemical follow up reactions of this process occur. It completely neglects the ion-molecule chemistry triggered by UV radiation, X-rays, cosmic rays, and long-lived radioactive nuclei and the role played by reactions on dust surfaces. The molecular species formed during carbon combustion in the inner part of the disc and mixed into the outer parts may be subject to further chemical reactions in this disc region. Since many of the processes due to the finite penetration depth of the ionising radiation or particles in the region $r \lesssim 30$ AU are limited to a surface layer extending over only some fraction of the total disc height, an appropriate treatment of such processes requires a consideration of vertical mixing in the disc, which is not included in the present disc model. For this reason such processes are neglected in the present calculation.

Table 3. Parameters used for the calculation of the disc model.

accretion rate	$\dot{M}$	10^{-6}, 10^{-7}, 10^{-8}	$M_\odot\,\mathrm{yr}^{-1}$
stellar mass	M_*	1	$M_\odot$
effective temperature	T_eff	4500	K
stellar luminosity	L_*	5	$L_\odot$
viscosity parameter	α	3×10^{-3}	
molecular cloud temp.	T_mol	20	K
inner disc radius	r_in	5	R_*
outer disc radius	r_out	100	AU

4. Model calculation

4.1. Disk model

The calculation of the radial mixing in the disc and of the chemical reactions of the carbon oxidation products in the gas phase requires to calculate a self consistent model for the accretion disc including the chemistry since this determines some important input parameters for the calculation of the chemistry, the temperature for instance, which depend itself on the chemistry in the disc. This calculation follows essentially the lines described in Paper I. There is only one modification compared to that paper that now pyroxene is considered as a separate dust component. This, however, does not result in significant changes of the model structure as described in Paper I.

Models are calculated for a protostellar accretion disc around a single star with the set of parameters shown in Table 3. The model is a stationary one-zone Keplerian α-disc model. The stellar parameters correspond to a star of one solar mass in a stage of evolution where the star is already visible, i.e. the process of mass infall and star formation is nearly finished and the remaining disc gradually disappears by accretion onto the star (cf. Stahler & Walter 1993). This is just that phase of the disc evolution which we want to consider. The viscosity parameter α is set to a value which results in a timescale for disc disappearance in time dependent one-zone model calculations which is of the order of the observed timescale of roughly 10^7 years (Ruden & Pollack 1991). Slightly higher values for α are favoured by others (e.g. Lin & Papaloizou 1996; Stepinski 1998).

The calculation is done for a mass accretion rate of $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$. This rate is suggested by typical disk masses of $0.1\,M_\odot$ around solar mass stars and typical disc lifetimes of 10^6 years (e.g. Beckwith & Sargent 1993). This accretion rate is generally thought to be representative for the early stages of the evolution of a protoplanetary disc prior to the onset of planetary formation. For comparison also models with an accretion rate of 10^{-6} and $10^{-8}\,M_\odot\,\mathrm{yr}^{-1}$ are calculated.

The former corresponds to an early evolutionary stage where the parent molecular cloud is not yet dissipated and the system is hidden behind a thick dust shell. The latter mass accretion rate probably corresponds to a late stage of the disc evolution where planet formation already is underway. Observationally determined mass accretion rates for young stellar objects of age less than 10^6 yr seem to support our assumption of a mass accretion rate of $10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$ for the pre-planet-formation phase though the scattering of observationally determined accretion rates is large (e.g. Hartmann 2000; Calvet et al. 2000).

In order to achieve a good radial resolution of the model and a good accuracy of the solution of the diffusion equations a fine grid of 200 radial grid points per decade is used. A control calculation with a finer resolution of 1000 grid-points per decade yielded nearly identical results.

4.2. Abundance of combustion products

The main purpose of this paper is to determine the radial variation of the concentration of hydrocarbons within the disc which are formed at about 0.5 AU by oxidation of carbon grains. We have solved the coupled system of stationary transport-diffusion-reaction equations for the groups n_0, n_1, n_2, and n_3 defined in Sect. 2.3 and determined from this the abundance of the individual molecules. Because stationarity is assumed the results of the present model calculation can only be applied for the inner disc region up to at most 30 AU since only in this part of the disc after about 10^6 years stationary conditions are reached (e.g. Ruden & Lin 1986; Wehrstedt & Gail 2002). Also the results of the present calculation cannot be applied to processes occuring after about 10^6 years because then most likely gaps are formed in the disc after the onset of formation of the big planets. This most likely makes any further mixing from the innermost disc regions into the outer parts of the disc impossible.

4.2.1. Reaction time scales

In calculating the abundances of molecules of the different groups defined in Sect. 2.3 we assumed that the intra-group reaction timescales are much shorter than the inter-group reaction timescales. This requires a check. Figure 3 shows characteristic timescales for some of the important reactions, defined as

$$\tau_{\mathrm{react}} = n_{\mathrm{mol}} \left| \frac{\mathrm{d}\,n_{\mathrm{mol}}}{\mathrm{d}\,t} \right|^{-1} = \frac{1}{k n_{\mathrm{react}}}. \tag{69}$$

n_{mol} is the number density of the molecule of interest, k the rate constant for the reaction of this molecule with a second molecule, the particle density of which is denoted as n_{react}. The timescales are calculated for the disc model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$. Intra-group reactions are plotted in Fig. 3 with full lines, inter group reactions with dashed lines. For comparison the characteristic timescale

$$\tau_{\mathrm{hyd}} = \frac{r}{v_r} \tag{70}$$

is shown as dotted line, which is the timescale for changes of pressure P and temperature T as experienced by an element of matter as it slowly migrates inwards during mass accretion. The characteristic timescale $\tau_{\mathrm{diff}} = r^2/D$ for radial diffusion is of the same order of magnitude (see Paper I).

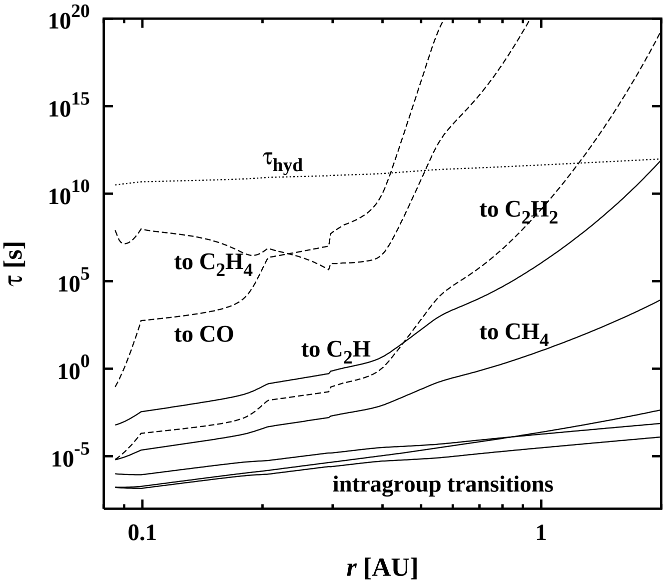


Fig. 3. Characteristic timescales for some chemical reactions involved in the formation of hydrocarbons and CO. Full lines: intra-group reaction timescales. Dashed lines: inter-group reaction timescales. Dotted line: hydrodynamic timescale for the change of P and T for an inwards drifting matter element. Some important reactions are labeled by their products. Model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$.

The condensation reaction (18) to form C_2H_4 from CH_3 and the reaction (28) for the final formation of a CO molecule are clearly much slower than all other reactions. The intra-group reactions timescales are faster than the characteristic loss timescales of each group, such that within each of the groups the group members are in an equilibrium state with respect to the hydrogen abstraction and addition reactions. This justifies our procedure to collect all molecules into groups which are linked by the fast hydrogen abstraction and addition reactions and to consider the reaction kinetics only for groups and not for individual molecules.

Figure 3 also shows that for the model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$ the chemical reactions proceed in the warm inner part of the disc ($r \lesssim 1$ AU) on a much shorter timescale than the hydrodynamic timescale. The chemistry in this region, thus, is in a nearly stationary state, except for the slow formation of CO. From Fig. 3 one also infers that the conversion of hydrocarbons into CO ceases if matter is mixed from the inner disc region $r \lesssim 1$ AU into the region $r \gtrsim 1$ AU.

4.2.2. Abundance of hydrocarbons

Figure 4 shows the radial variation of the concentration of particles from groups 0, … 3 as defined in Sect. 2.3, and the concentration of CO and CO_2 molecules. Only the group n_1 of CH_n ($n = 0 \ldots 4$) molecules and the group n_3 of C_2H_2 and C_2H have significant abundances. The high abundance of the group CH_n results from the slow reaction from CH_3 to C_2H_4, cf. Fig. 3.

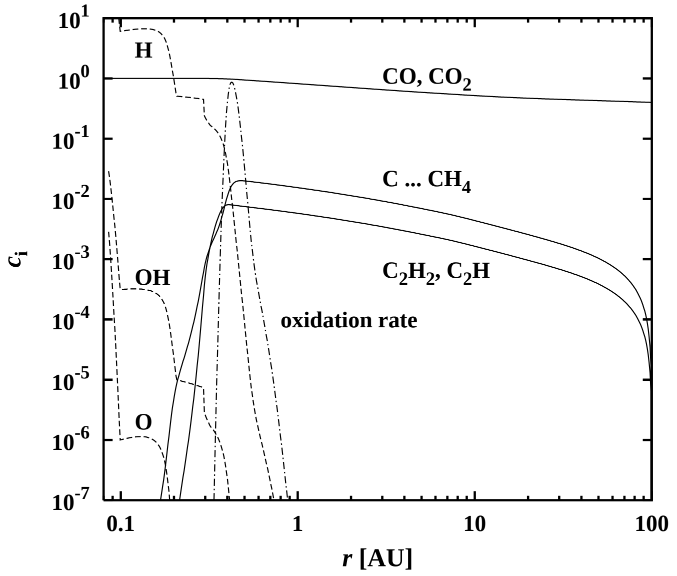


Fig. 4. Full lines: radial variation of the concentration of the four groups of hydrocarbon molecules formed as intermediate products of carbon oxidation. The concentrations are normalised to the concentration of C nuclei. Dashed lines: concentration of H atoms and of the oxidising agents O and OH, also normalised to the concentration of carbon nuclei. Dash-dotted line: oxidation rate for solid carbon, normalised to its peak value. Note that in the outer disk region part of the carbon is fixed in carbon grains. Model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$.

The group of C_2H_4 and C_2H_3 molecules has quite a low abundance, resulting from a slow formation via reaction (18) and a rapid destruction via reaction (21).

The rather high abundance of the group n_3 results from the slow loss via reaction (28) due to the low abundance of free oxygen atoms O. The dashed lines in Fig. 4 show the concentration of free oxygen atoms and of OH, which are responsible for the oxidation processes (2), (27), and (28). Figure 4 also shows the abundance of free H atoms, which is important for the basic reaction (4) and for the hydrogen abstraction/addition equilibrium.

The dash-dotted line in Fig. 4 shows the rate of carbon oxidation (2) normalised by its peak value. The steep increase at ≈1 AU with decreasing radius is due to the steep increase of the concentration of OH with increasing temperature and the rapid decline is due to the rapid combustion of carbon. The production of hydrocarbons by carbon combustion is limited to a narrow cylinder within in the disc centred in our model on ≈0.5 AU. The products then are distributed across the whole disc by turbulent mixing.

The carbon combustion starts at about 950 K, peaks at about 1150 K and comes to completion at about 1300 K. In this temperature regime the methane is formed and part of the solid carbon is converted into CO. At an only slightly higher temperature than that where carbon black oxidation peaks the methane is converted into C_2H_2. Since free oxygen atoms appear in non negligible abundances only at temperatures where corundum is already vaporised, the oxidation of C_2H_2 to CO is only possible in the hot region where all dust is vaporised. As a result, in a broad intermediate region a rather high acetylene abundance piles up in the gas phase, though the element mixture of the disc material is carbon rich and no acetylene could exist in this mixture under chemical equilibrium conditions.

Figure 5 shows the concentration of the individual molecules normalised to the concentration of C nuclei. Methane CH_4 and acetylene C_2H_2 are the dominating combustion products which can be found all over the disc. All other hydrocarbons included in this calculation have low abundances. The abundance of CH_4 and C_2H_2 relative to CO is typically of the order of 0.8% in the region beyond ≈10 AU where the cometesimals are thought to be formed, which filled the Oort cloud and which are now observed as long period comets.

The small hump in the abundance of molecules of group 1 at about 0.2 AU results from the onset of acetylene oxidation, which is accompanied by CH production.

For comparison Fig. 6 shows the concentration of the products of carbon oxidation if radial mixing is neglected, but inwards drift of the disc material is retained in the model calculation. The results are very different from what one obtains with radial mixing. First, one finds no hydrocarbons in the outer disc regions, as is to be expected. Second, the abundances of CH_4 and of C_2H_2 in the oxidation region are higher than in the case where radial mixing is considered. The results obtained without mixing are essentially the same as that obtained in Finocchi et al. (1997a), except that here no ion-molecule reactions are considered. Comparison of Figs. 5 and 6 clearly shows that radial mixing is of fundamental importance for the chemistry in the protoplanetary disc.

The abundances of the molecules in models with higher or lower accretion rate are quite similar to the results for the model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$ at radii corresponding the same midplane temperature and are not shown for this reason.

The present calculation refers to a stationary disc model. In time dependent disc models material from the inner disc region is not mixed in significant quantities into the region beyond about 30 AU during the first 10^6 years of disc evolution (Wehrstedt & Gail 2002; Bockelée-Morvan 2002). The present calculation, thus, only demonstrates that some quantities of the oxidation products of carbon are mixed into the cold disc regions beyond 10 AU where cometary nuclei are thought to be formed, but the results of this model cannot predict quantitatively correct the amounts of hydrocarbons from carbon oxidation in the outer disc. This holds especially for the region beyond about 30 AU into which diffusional transport cannot mix material from the warm inner disc region during the lifetime of the gaseous disc of probably 10^7. This region requires to study diffusional mixing coupled with time dependent disc models. Such calculations are currently under way.

4.2.3. Abundance of CO and CO_2

Figure 5 shows the radial variation of the concentration of CO and CO_2, resulting from the solution of the transport-reaction-diffusion equation. As it is to be expected, there exist a region in the disc where most of the gas-phase carbon is not bound in CO but in CO_2. The abundance of CO_2 peaks in our model for $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$ at $r = 2.2$ AU or at a midplane temperature of

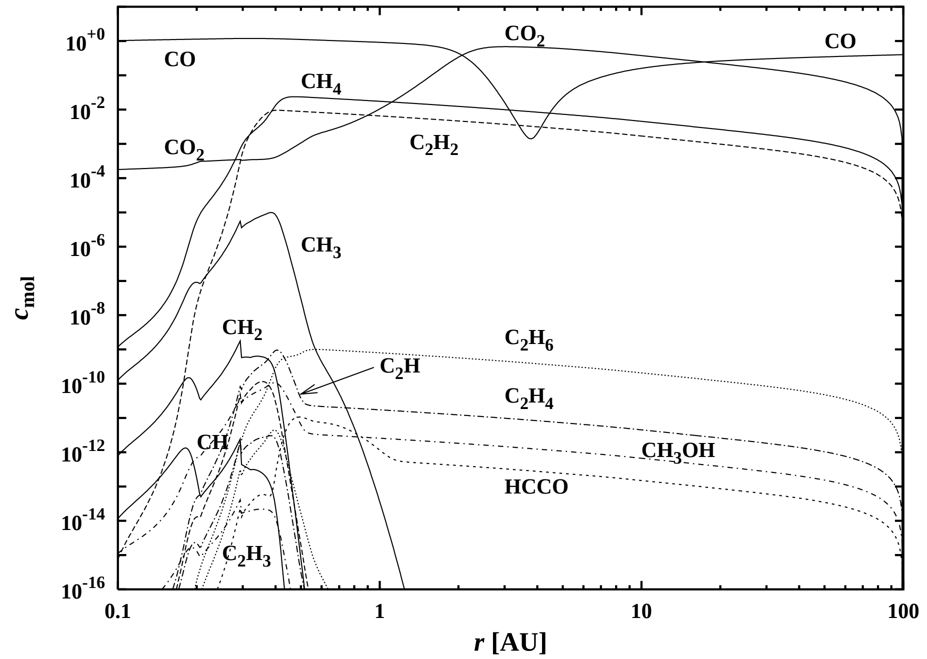


Fig. 5. Radial variation of the concentration of the combustion products of carbon. The concentrations are normalised by the concentration of C nuclei. Model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$.

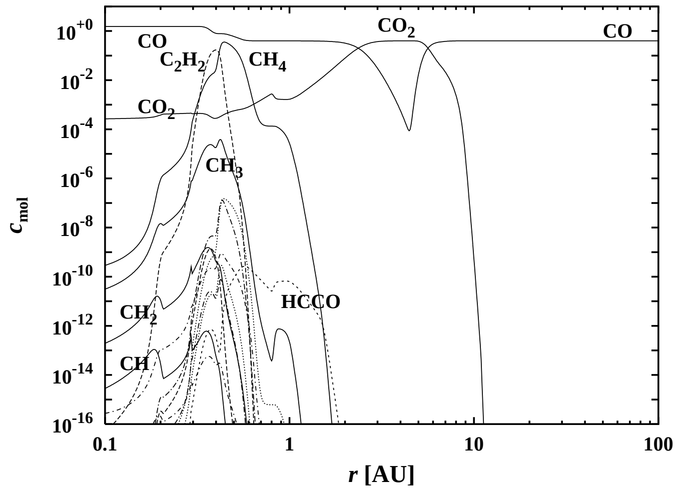


Fig. 6. Radial variation of the concentration of the combustion products of carbon if radial diffusion is neglected, but inwards drift is considered. The concentrations are normalised by the concentration of C nuclei. Model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$.

$T = 300$ K. Equal abundances of CO and CO_2 are encountered at $r = 2.05$ AU or $T = 400$ K and at $r = 17.5$ AU or $T = 50$ K. Between these radii CO_2 is the dominant carbon bearing gas-phase species, not CO.

The CO_2 in the outer parts of the disk is formed via the reaction $CO + H_2O \rightarrow CO_2 + H_2$ at $r \approx 5$ AU (for the model with $\dot{M} = 10^{-7}\,M_\odot\,\mathrm{yr}^{-1}$, cf. Fig. 6) at a temperature of about 100 K. This temperature is less than the sublimation limit at 150 K of H_2O ice but the vapour pressure of H_2O at 100 K is already non-negligible.

4.2.4. Abundances of methanol and ethane

The abundance of ethane resulting from gas phase reactions of the oxidation products of carbon black turns out to be rather low, cf. Fig. 5. The concentration of C_2H_5 is even lower. The low abundances result from the rather large destruction rate coefficient k_{-14} and the small rate coefficient k_{14} for the formation of C_2H_5. The formation reactions (58) and (59) contribute little to the formation of C_2H_6.

Figure 5 also shows the radial variation of the concentration of methanol. The concentration of CH_3OH also is low which, again, results from a low efficiency of formation and a higher efficiency of destruction by gas phase reactions.

4.3. Hydrocarbons in cometary nuclei

Radio and infrared observations of comets Hale-Bopp and Hyakutake (cf. Bockelée-Morvan et al. 2000; Crovisier & Bockelée-Morvan 1999) and recently of comet Lee (cf. Mumma et al. 2001) have revealed the existence of a number of hydrocarbons and of some nitrogen and sulphur compounds in the cometary nuclei ice. The abundances of the most abundant of the carbon compounds relative to H_2O (abundance = 100) is shown in Table 4 together with results of the present model calculation for a distance of 20 AU from the protosun. With respect to H_2O it is assumed that in the outer disc all oxygen not bound in dust, CO, and CO_2 is bound in H_2O. The numbers for the model calculation refer to the abundances in the gas phase prior to precipitation on grain surfaces. The relative abundance in the ices are somewhat different from the relative abundances in the gas phase, depending on the vapour pressure and the properties of the substances and how easy or difficult it is to incorporate them into the ices. The comparison of the total abundances of the hydrocarbons obtained from the model calculation to their abundances in comets at best can reveal general trends. For a more realistic comparison modeling of the trapping of gases in the ice coatings of dust grains and their incorporation into planetesimals would be required, which is out of the scope of this paper.

Table 4. Abundances of some carbon compounds in comets Hyakutake (C/1996 B2), Hale-Bopp (C/1995 O1) and Lee (C/1999 H1) at ≈1 AU with respect to H_2O, compared to the results of the model calculation at $r = 20$ AU. Data from Bockelée-Morvan et al. (2000), Crovisier & Bockelée-Morvan (1999) and Mumma et al. (2001).

Molecules	Hyakutake	Hale-Bopp	Lee	model
H_2O	100	100	100	100
CO	6–30	23	1.8	21
CO_2		6		18
CH_4	0.7	0.6	0.81	0.21
C_2H_2	≈0.5	0.1	0.27	0.081
C_2H_6	0.4	0.3	0.67	9.8×10^{-9}
CH_3OH	2	2.4	2.1	3.2×10^{-11}
H_2CO	0.2–1	1.1		

With these caveats in mind an inspection of Table 4 and Fig. 5 shows that the prediction of the model calculation of high abundances of CH_4, C_2H_2 and of CO_2 in the region of cometary nuclei formation are in accord with the observed high abundance of these species in comets of the Solar System. The methane and acetylene should exist in considerable amounts in cometary ices for the simple reason that they are formed during the combustion of interstellar carbon dust in warm regions of the protoplanetary disc and are mixed outwards by turbulence induced diffusive transport. Also CO_2 is abundant due to its formation from CO in the Jupiter-Saturn region of our Solar System and by diffusive mixing into cooler regions.

The mixing of combustion products from the inner disc region to the cold outer disc region easily explains a high CH_4 abundance in the region of comet formation, which otherwise has always been a problem (cf. the discussions in Fegley & Prinn 1989 and in Mumma et al. 1993).

An inspection of Table 4 and Fig. 5 also shows, however, that carbon combustion and radial mixing alone cannot explain all the abundant carbon compounds in cometary ices. The low abundance of ethane C_2H_6 formed during carbon dust combustion obviously is at odds with its high abundance in comets. The observed ethane either results from a different source or it is formed by chemical processes not included in the present model calculation.

Mumma (1996) and Mumma et al. (1996) proposed an origin of the C_2H_6 detected in comet Hyakutake from H addition reactions on grain surfaces to C_2H_2 ice of interstellar origin. Generally a pure gas phase chemistry cannot explain an abundance ratio of C_2H_6 and CH_4 of the order of about unity, even not by ion molecule reactions in molecular clouds. It can be formed however, by hydrogen addition reactions on ice surfaces (e.g. Hasegawa & Herbst 1993; Hiraoka et al. 1998). The same type of reasoning as applied by Mumma et al. (1996) and recently by Mumma et al. (2001) to C_2H_2 ice of interstellar origin can also be applied to the C_2H_2 ice resulting from mixing carbon combustion products from the inner disc to outer disc regions. Temperatures are low in the comet nuclei formation region, especially at the disc surface, and free H atoms should be present at least at the disc surface due to irradiation with UV photons and X-rays from the young star (cf. Aikawa & Herbst 1999, 1999). The hydrogen addition to C_2H_2 ice in the protoplanetary disc, then, should at least be responsible for some fraction of the ethane observed in comets or even for most of the methane.

The model calculation also yields a very low abundance of CH_3OH, contrary to what is observed in comets. We have not considered H_2CO in the present model calculation, but Table 4 of Finocchi et al. (1997a) shows that destruction processes of H_2CO are more rapid than production mechanisms, resulting in a low abundance of this molecule if formed by gas-phase reactions. Mumma et al. (2001) argue that the abundant molecules CH_3OH and H_2CO are the results of H addition to CO on ice surfaces at very low temperature. The cometary abundances of these species then are not related to carbon combustion and radial mixing but to a different production mechanism. In this sense our finding of a low abundance of methanol in the products of carbon combustion in a protoplanetary disc is not in odds with the present finding that a high CH_4 and C_2H_2 in comets may result from carbon combustion and mixing.

5. Concluding remarks

This paper considers some important chemical reactions of the products of carbon dust oxidation in the warm inner zone ($r \lesssim 1$ AU) of a protoplanetary accretion disc and the mixing of these products into the outer disc regions by turbulent diffusion. It is shown that radial mixing results in a rather high abundance of CH_4 and C_2H_2 in the outer disc regions beyond 10 AU where water ice is stable and where most likely the nuclei of the present day long period comets in our Solar System have been formed 4.6 Gyr ago. These gas phase species then are expected to exist in significant amounts in the ice mixture of cometary nuclei. This is in accord with the observed high abundance of CH_4 and C_2H_2 in cometary ices.

The model calculation presented in this paper shows that at least some fraction of the observed CH_4 and C_2H_2 ices should result from the oxidation of the interstellar carbon dust grains and from mixing the burning products into the formation zone of comets. The model cannot explain, however, the observed high abundance of C_2H_6 and of CH_3OH. These molecules can be formed by gas phase reactions from the combustion products of carbon black only in very small quantities. The present model shares this property with models for the chemistry in molecular clouds, if only gas phase reactions are considered. Calculations of models for the chemistry in molecular clouds considering grain surface reactions with H atoms (Aikawa & Herbst 1999, 1999; Willacy & Langer 2000) and laboratory investigations of H atom reactions with organic ices at very low temperature (Hiraoka et al. 1998) have shown, however, that C_2H_6, CH_3OH, and H_2CO are formed in large quantities by surface reactions of C_2H_2 and of CO with H atoms.

Since the outer regions of the accretion disc and the disc surface in less far extended regions of the disc are very cold, it seems well possible that the C_2H_2 formed in the inner disc and mixed outwards and precipitated as part of the ice mixture on grain surfaces later is partially processed on the surfaces into C_2H_6 by free H atoms. The abundant species CH_3OH and H_2CO cannot be formed by carbon oxidation. They probably are products of a different mechanism not related to carbon dust oxidation. This, at the same time suggests, that also some of the CH_4 and C_2H_2 present in the cold disc zones might result from the same processes that formed CH_3OH and H_2CO because of the similarities in molecular abundances in comet Hale-Bopp and in hot molecular cores (cf. Bockelée-Morvan et al. 2000). The present model calculation neglects all such processes since the primary process, turbulent mixing into the outer disc region, presently is calculated only for stationary disc models, which is not realistic for the transport into the outermost disc regions. Such calculations are postponed until time dependent models for disc evolution and mixing are available.

Despite the strong simplifications of the model calculation, it shows that at least some fraction and perhaps even most part, but not all, of the hydrocarbons observed to exist in cometary nuclei might originate (i) from the destruction of the interstellar carbon dust in protoplanetary accretion discs and (ii) from extended radial mixing processes operating in such discs.

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