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On the growth of carbonaceous grains in circumstellar envelopes

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Abstract. We present a phenomenological description of relevant aspects of the grain surface chemistry on pre-existing carbonaceous seed particles. The production of radical surface sites is calculated by means of modified analogous gas-phase thermodynamic and reaction kinetic data. Our results suggest that surface growth processes mainly take place at sp^3 bonded carbon atoms rather than at the edges of graphitic plates or polycyclic aromatic hydrocarbons and that the resulting grain material will be amorphous diamond-like carbon. Furthermore, we argue that the sticking efficiency of the key growth species C_2H_2 at radical sites is high even for considerable grain drift velocities. The dust growth rate will generally be proportional to the radical surface coverage.

Key words: dust growth – circumstellar matter – stars: carbon – stars: AGB – stars: mass loss

1. Introduction

The carbon-rich circumstellar envelopes (CSE) of cool late-type stars on the asymptotic giant branch (AGB) are known to inject the largest amount of carbonaceous stardust into the interstellar medium (ISM) (Gehrz 1989). However, there is an ongoing debate regarding the possible composition and structure of this solid carbon. Suggestions include (see e.g. Duley (1993), Cadwell et al. (1994) and references therein): (hydrogenated) amorphous carbon, graphite, polycyclic aromatic hydrocarbons (PAH), soot, diamond-like carbon, fulleranes, coal and other kerogen-like materials. Several of the proposed materials differ only in terms of the relative proportion of the various possible bond types of carbon atoms. Although these parameters generally do not determine the complex, probably non-crystalline structure of a carbonaceous grain, the dominant hybridisation state of its constituting atoms can nevertheless serve as a decisive characteristic. Here, we consider three important configurations: sp^2 and sp^3 hybridised carbon and also carbon atoms which are part of an aromatic ring structure[1]. Spectral features due to sp^1 bonded carbon are not evident in astronomical spectra (Whittet 1992).

In CSE of carbon-rich AGB stars the dangling bonds of carbon atoms on a grain surface are expected to be saturated by hydrogen atoms. Efficient grain growth, i.e. addition of carbon to the surface, however, will involve neutral–radical reactions of hydrocarbon species with the surface atoms. Thus, growth reactions preferably occur at temporary radical sites, where an H-atom has been abstracted (dehydrogenation). The kinetic gas temperature and the internal dust temperature in CSE are generally not equal (see e.g. Winters et al. 1994, Krüger et al. 1994). Our kinetic treatment of the chemical surface reactions takes account of these different temperatures and also allows to investigate effects due to grain drift velocities. In this context, we give special attention to the energy transfer to the lattice, where any surplus energy can be efficiently dissipated as opposed to gas phase reactions.

In summary, it is the aim of this paper to describe relevant aspects of the grain surface chemistry on pre-existing carbonaceous seed particles and, thereby, to investigate the nature of the resulting carbonaceous material ejected into the ISM.

2. Surface density of radical sites

In order to determine the reactive fraction of the grain surface, we determine the probability p of a particular carbon surface site $\mathcal{C}$ to have a dangling bond ($\mathcal{C}\cdot$) rather than being saturated ($\mathcal{C}$–H) by a hydrogen-atom

$$p = \frac{[\mathcal{C}\cdot]}{[\mathcal{C}\cdot] + [\mathcal{C}\text{–H}]} \qquad (1)$$

where [. . .] denotes the surface density of the respective site. Note that $\mathcal{C}$ does not denote a carbon surface atom

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[1] Note that sometimes the aromatic bonding configuration is refered to as sp^2 by other authors.

but a reactive site of such an atom. The total number of sites may be greater than the number of surface atoms, since some carbon atoms may have more than one H-atom bonded to them.

Since hydrogen is by far the most abundant element in CSE, we will treat the production of radical sites by the following reaction scheme:

$$\mathrm{r1}: \quad \mathcal{C}{-}\mathrm{H} + \mathrm{H} \leftrightarrows \mathcal{C}\cdot + \mathrm{H}_2 \tag{2}$$

$$\mathrm{r2}: \quad \mathcal{C}\cdot + \mathrm{H} \leftrightarrows \mathcal{C}{-}\mathrm{H} \tag{3}$$

The rates of these gas–surface reactions have not been measured. Furthermore, the reactivity of a surface site will in general depend on the local physical structure of the surface (e.g. pores, edges, defects). The detailed treatment of the local surface structure, however, is clearly beyond the scope of the present paper. In order to provide an average description of the surface reactivity we estimate the reaction coefficients by making the assumption that the surface chemistry is mainly controlled by the local electronic environment. In this case, the reaction cross-section can be assumed equal to the reaction cross-section per equivalent site in an analogous prototype gas-phase reaction. These assumptions are consistent with what is known from alkane chemistry and supported by quantum calculations and experimental investigations (see Belton & Harris (1992) for a detailed discussion).

The procedure outlined above has already been succesfully applied to the modelling of diamond film growth under the conditions of chemical vapour deposition (e.g. Harris & Goodwin (1993) and references therein). Laboratory diamond synthesis itself is in fact remarkably similar to the growth of carbonaceous grains in CSE. However, the different density regime of CSE and hence the different time scales of the chemical processes should be kept in mind.

In order to estimate the surface reaction rates k_s the analogous prototype gas-phase reaction rates k_g are corrected for the effect of collision frequency and for symmetry:

$$k_\mathrm{s} = k_\mathrm{g} i_\mathrm{g}^{-1} \left(\frac{\mu}{m_\mathrm{g}}\right)^{1/2} \tag{4}$$

where μ is the reduced mass of the collision partners in the gas-phase reaction and m_g the mass of the gas-phase species striking the surface. The number of identical reactive sites of the analogous gas-phase hydrocarbon is denoted by i_g. For radical recombination the resulting k_s is halved, since the surface radical site is partially obstructed (cf. Belton & Harris 1992).

In the following we will distinguish three different types of surface sites, depending on whether the corresponding C-atom is in a sp^2, sp^3 or an aromatic bonding configuration. The analogous prototype gas-phase reactions for the different bonding configurations are given in Table 1 along with their forward reaction coefficients k_g^f which are parameterized by the empirical Arrhenius law

$$k_\mathrm{g}^\mathrm{f}(T_\mathrm{r}^\mathrm{f}) = A \exp(-E_\mathrm{a}/RT_\mathrm{r}^\mathrm{f}) \tag{5}$$

where the pre-exponential factor A and the activation energy E_a are derived from experiments and $T_\mathrm{r}^{\mathrm{f/r}}$ denotes a reaction temperature. The reverse reaction coefficient of reaction (2) follows from the thermodynamical relation

$$k^\mathrm{r}(T_\mathrm{r}^\mathrm{r}) = k^\mathrm{f}(T_\mathrm{r}^\mathrm{r}) \exp(\Delta G/RT_\mathrm{r}^\mathrm{r}) \tag{6}$$

with $\Delta G = \Delta H - T_\mathrm{r}^\mathrm{r} \Delta S$ being the change in Gibbs free enthalpy of the reaction. The reverse reaction of (3) is unimolecular. By means of RRK theory (e.g. Forst 1973) its reaction coefficient can be estimated to be

$$k_\mathrm{r2}^\mathrm{r} = \omega \exp(-2E_\mathrm{a}/kT_\mathrm{r2}^\mathrm{r}) \tag{7}$$

where ω is a characteristic frequency of the C–H bond stretch (e.g. $\omega \approx 9.3\,10^{13}\ \mathrm{s}^{-1}$ (Benson 1976)). The activation energy E_a of this reaction approximately equals the change in enthalphy. For dust temperatures typical of CSE the resulting rate can be neglected.

To estimate entropy and enthalpy changes ΔS and ΔH, respectively, we use the group additivity rules devised by Benson (1976) corrected for more recent thermochemical data (Stein & Fahr 1985, Goeres et al. 1996). The resulting values of ΔH and ΔS for $T_\mathrm{r} = 1000$ K are summarized in Table 2. For surface reactions the pure bonding enthalpy change has to be combined with the change in strain energy E_strain which is the result of bonds bending, stretching and twisting in response to interatomic forces. Unfortunately, the strain energy depends on the specific surface structure which is unknown for circumstellar grains (cf. Sect. 1). By means of molecular mechanics E_strain was calculated for different diamond surfaces, some of them also involving sp^2 carbon surface atoms (Harris & Belton 1991, Harris et al. 1991, Belton & Harris 1992). The resulting values for the change in strain energy ΔE_strain range from about -12 kJ/mol to 12 kJ/mol. Aiming at an average description of the surface reactivity we will adopt a mean value of $\Delta E_\mathrm{strain} \equiv 0$, i.e. neglect the effects of change in strain energy. This approximation only affects the calculation of the reverse rate k_r1^r of reaction (2). Fortunately, it turns out that varying ΔE_strain by ± 12 kJ/mol leads to changes in the resulting dehydrogenation probability p always less than 10 %. Given the other assumptions involved in our approach, this particular approximation should have no further consequence for the following discussion.

The ratio of carbon surface atoms which have a dangling bond to those which are saturated by a hydrogen-atom can be determined by applying a steady state analysis for $[\mathcal{C}\cdot]$ in reactions (2) and (3). This ratio is given by

$$\frac{[\mathcal{C}\cdot]}{[\mathcal{C}{-}\mathrm{H}]} = \frac{k_\mathrm{r1}^\mathrm{f} n_\mathrm{H} + k_\mathrm{r2}^\mathrm{r}}{k_\mathrm{r1}^\mathrm{r} n_{\mathrm{H}_2} + k_\mathrm{r2}^\mathrm{f} n_\mathrm{H}}. \tag{8}$$

where n denotes the respective particle densities in the gas-phase.

Since the surface reaction coefficients k show a strong temperature dependence, the reaction temperature T_r is an important quantity regarding the determination of the production of radical sites on the grain surface. In contrast to gas-phase chemistry, where T_r is simply given by the kinetic gas temperature T_g, it is unclear how to define an appropriate temperature T_r at which surface reactions take place: First, gas and dust temperature T_g and T_d, respectively, may be different. Furthermore, the grains may exhibit a drift velocity $v_{\rm drift}$ relative to the bulk of the gas (e.g. Krüger et al. 1994), so that the collisional energy will be increased and the impinging gas particles of mass m_g appear hyperthermal. We introduce a collision temperature $T_{\rm coll}$ corresponding to the total available kinetic energy $E_{\rm kin}$

$$T_{\rm coll} \equiv \frac{2E_{\rm kin}}{3k} \tag{9}$$

$$= \frac{2}{3k}\frac{m_g}{2}\left(\overline{v_{\rm th}^2} + v_{\rm drift}^2\right) \tag{10}$$

$$= T_g\left(1 + v_{\rm drift}^2 / \overline{v_{\rm th}^2}\right) \tag{11}$$

where $\overline{v_{\rm th}^2} = 3kT_g/m_g$ is the mean square of the thermal velocity of the considered gas particle. Please note that, although the impinging gas particles appear to be hyperthermal corresponding to a temperature $T_{\rm coll}$, their rotational degrees of freedom are thermalized according to the kinetic gas temperature.

Unfortunately, little information is available on the kinetics of reactions in which the reaction partners have different temperatures. In their treatment of PAH chemistry, Cherchneff et al. (1992), for instance, assumed that reactions involving aromatic compounds occur at the vibrational temperature of the aromatic species, not at the kinetic gas temperature.

In a first approximation, we assume the reaction temperature T_r to be given by a weighted mean of $T_{\rm coll}$, T_d and T_g, the latter characterizing also any rotational degrees of freedom of the gas particle. The weights assigned to these temperatures are proportional to the corresponding number of degrees of freedom involved (3 for translation, 2 for rotation, 6 for lattice vibrations). Depending on the reactants we arrive at the following expressions for the reaction temperatures of the reaction scheme (2), (3)

$$T_{\rm r1}^{\rm f} = (T_{\rm coll} + 4T_d)/5 \tag{12}$$

$$T_{\rm r1}^{\rm r} = (3T_{\rm coll} + 2T_g + 6T_d)/11 \tag{13}$$

$$T_{\rm r2}^{\rm f} = (T_{\rm coll} + 2T_d)/3 \tag{14}$$

$$T_{\rm r2}^{\rm r} = T_d \tag{15}$$

where we tacitly assumed that energy transfer from the light gas particles to the carbon lattice is inefficient as a result of the low mass ratio of H and C, so that only one surface carbon atom takes part in the dissipation of the collision energy (see, however, Sect. 3). From inspection of Eqs. (12) and (15) we conclude that the calculation of the reaction temperature of hydrogen–abstraction reactions is dominated by T_d as long as $T_{\rm coll}$ is of similar magnitude as T_d, i.e. for drift velocities $v_{\rm drift} \lesssim v_{\rm th}$. Thus, in the limit case of negligible drift velocities our approach yields results analogous to the assumptions made by Cherchneff et al. (1992).

Figure 1 depicts the calculated probability p of dehydrogenation (Eq. (1)) depending on the gas temperature and the H/H_2 ratio. There is no dependence of p on the total hydrogen density. Our results show that for high temperatures and H/H_2 ratios hydrogen is abstracted more easily. For $T \lesssim 1600$ K radical sites are predominantly formed at sp^3 bonded carbon surface atoms. However, a significant drift velocity may increase the reaction temperature T_r and helps to overcome the activation energy barrier even at lower gas temperatures. Raising the dust temperature also leads to a corresponding increase of the reaction temperature and thus of p, independent of the bond type. If the abundances of atomic hydrogen and H_2 are comparable, p is only dependent on the temperature, while for low H/H_2 ratios this ratio itself is the crucial parameter for the determination of the dehydrogenation probability.

It should be noted here, that our *ad hoc* treatment of the reaction temperature will probably only reflect the principal trends of the variation of the dehydrogenation probability p due to the additional energy input resulting from raising the dust temperature or from considering grain drift velocities. In this respect, the corresponding results of Fig. 1 should be taken with caution.

The temperature dependence of the surface reaction rates r_s per site is shown in Fig. 2 for conditions typical of CSE. Radical sites are formed with the (forward) rate $r_{\rm r1}^{\rm f}$ of reaction r1 (Eq. (2)), while the saturation of a surface radical with gas-phase hydrogen mainly proceeds via the second reaction (Eq. (3)) with $r_{\rm r2}^{\rm f}$. Thus, atomic hydrogen is the crucial reactant in determining the radical surface coverage, since, as stated above, spontaneous evaporation of hydrogen atoms from the surface ($r_{\rm r2}^{\rm r}$) is unimportant for these conditions. The difference between the various bonding configurations results from the effectiveness of the hydrogen–abstraction reaction r1 in case of sp^3 bonded carbon. The resulting probability p of dehydrogenation is also depicted in Fig. 2 on a linear scale by dashed lines (note the different scaling of the p–axes for the specific bonding configurations).

3. Growth reactions

After radical sites have been formed, gaseous hydrocarbon species colliding with the grain may bond to these active surface sites (chemisorption). The binding energy of hydrocarbons to the surface depends on the surface morphology which, unfortunately, is unknown for the car-

Table 1. Analogous prototype gas-phase reactions

Surface reaction	Bonding configuration	Prototype gas-phase reaction	A [$cm^3\ s^{-1}$]	E_a [kJ/mol]	i_g	Reference
r1	aromatic	$C_6H_6 + H \rightarrow C_6H_5 + H_2$	$1.1\ 10^{-11}$	39.8	6	Baulch et al. 1992
	sp^2	$C_3H_4 + H \rightarrow C_3H_3 + H_2$	$1.7\ 10^{-12}$	6.3	4	Dagaut et al. 1992
	sp^3	$i\text{-}C_4H_{10} + H \rightarrow t\text{-}C_4H_9 + H_2$	$2.1\ 10^{-10}$	30.5	1	Belton & Harris 1992
r2	aromatic	$C_6H_5 + H \rightarrow C_6H_6$	$1.3\ 10^{-10}$	—	1	Braun-Unkhoff et al. 1988
	sp^2	$C_3H_3 + H \rightarrow C_3H_4$	$5.0\ 10^{-11}$	—	1	Peeters et al. 1994
	sp^3	$i\text{-}C_3H_7 + H \rightarrow C_3H_8$	$3.3\ 10^{-11}$	—	1	Warnatz 1984

Table 2. Thermochemistry of the analogous prototype gas-phase reactions at $T_r = 1000$ K

Surface reaction	Bonding configuration	ΔH [kJ/mol]	ΔS [J/(mol · K)]
r1	aromatic	24.9	24.9
	sp^2	10.2	27.4
	sp^3	-49.2	26.2
r2	aromatic	-469.4	-138.4
	sp^2	-454.7	-141.0
	sp^3	-395.9	-141.2

bonaceous grains in CSE. Nevertheless, there are numerous quantum mechanical and molecular dynamics (MD) calculations devoted to the binding energy of small hydrocarbon species on different types of diamond, i.e. regular sp^3 carbon, surfaces. Resulting values for the onefold chemisorption of C_2H_2, which is by far the most abundant hydrocarbon in the gas-phase of CSE and will be regarded as the main growth species, range from 0.27 eV (Larsson et al. 1993) and 0.52 eV (Alfonso et al. 1994) up to 1.3 eV (Huang et al. 1988) and 1.73 eV (Pederson et al. 1991). Despite the scatter of these values, C_2H_2 binding energies are obviously larger than thermal energies.

The C_2H_2 association reaction may or may not involve an activation energy barrier. This clearly depends on the specific surface structure at hand. The investigation of Huang & Frenklach (1992) indicates that less rigid parts of the growing surface, i.e. surface steps, kinks or edges, probably correspond to lower or no potential energy barrier.

For chemisorption to occur it is crucial to lose the translational energy of the colliding molecule which otherwise would just bounce off the surface. As opposed to gas-phase reactions this is very easily accomplished in surface reactions, since the surplus energy can be efficiently distributed among the many degrees of freedom of the lattice if the gas particles and the lattice particles are of similar mass. Classical mechanics calculations for a one-dimensional, linear chain have shown that translational energy of up to 25 times the binding energy can be dissipated (McCarroll & Ehrlich 1963). This is confirmed by MD simulations of van-der-Waals particles (Head-Gordon & Tully 1992) which yielded sticking probabilities of ~ 0.5 at translational energies of 5 times the adsorption energy. Perhaps most convincingly, this efficient energy dissipation has been demonstrated by the MD simulations of Alfonso & Ulloa (1993). They found that there is a general increase of the sticking coefficient of CH_3 on diamond surfaces as the incident molecule becomes more energetic.

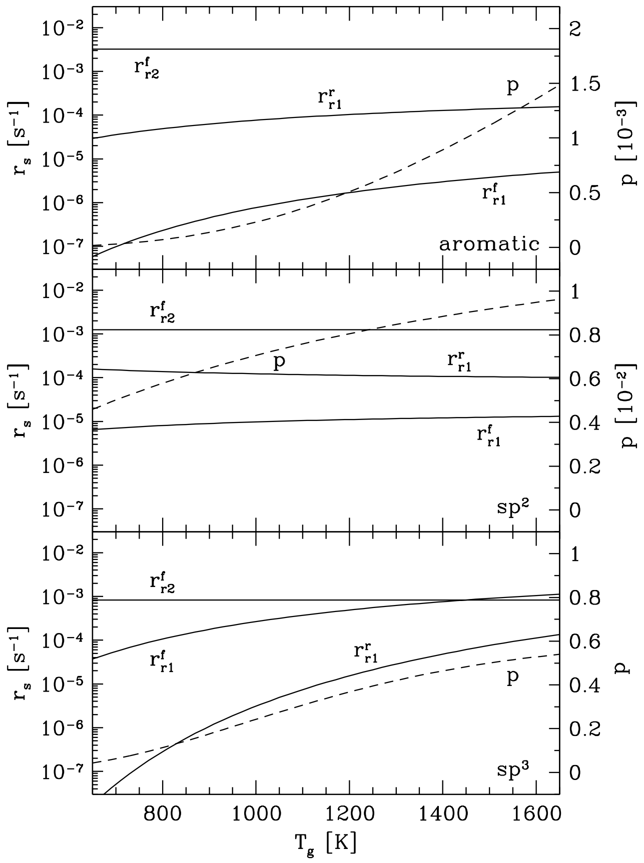

Fig. 2. Temperature dependence of the surface reaction rates r_s per site and the dehydrogenation probability p for different bonding configurations ($n_{\langle H \rangle} = 10^{10}\ cm^{-3}$, $H/H_2 = 10^{-2}$, $v_{drift} = 0$ km/s, $T_d = T_g$). Note the different scaling of the p–axes.

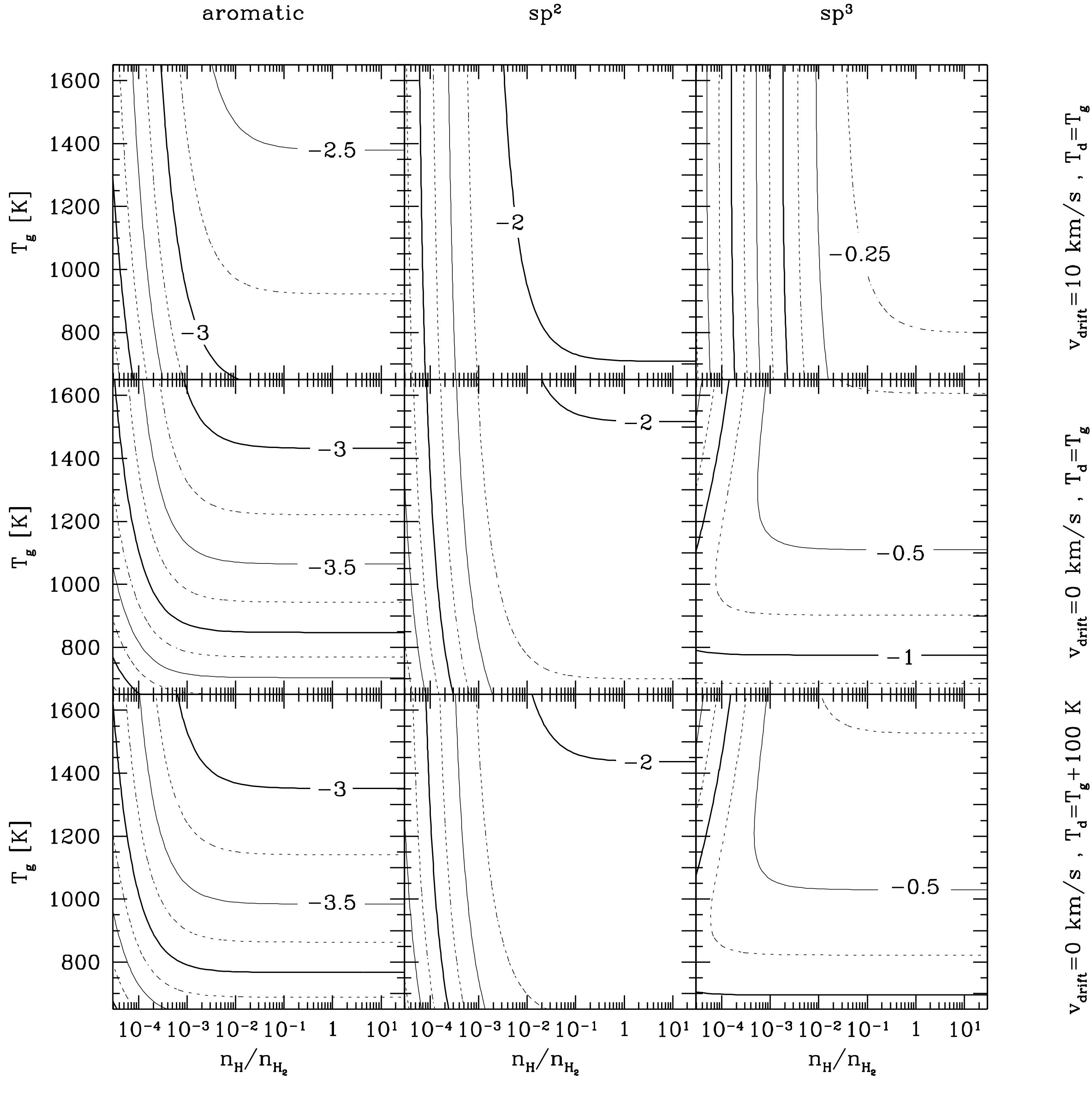

Fig. 1. Contour plots of the dehydrogenation probability $\log p$ of a carbon surface atom for different bonding configurations, grain drift velocities and dust temperatures. Thick lines correspond to $\log p = -1, -2, \ldots$; thin lines to -0.5,-1.5, ...; dashed lines to -0.25,-0.75, ...; in the upper right corner $\log p \rightarrow 0$.

In fact, a collisional energy of 10 eV is dissipated within just two phonon periods which is comparable with the collision time. It is this highly efficient dissipation of collisional energy that inhibits the application of analogous gas-phase association reaction rates to surface *growth* reactions, which involve reacting gas and lattice particles of similar mass.

From the discussion above we draw the conclusion that the nominal reaction probability of C_2H_2 with a carbon surface radical should be near to 1 as long as the grain drift velocity does not exceed 5–10 km/s. An estimate for the inverse timescale $\tau_{\rm acc}$ of carbon accretion onto a grain is then given by the product of the number density of the growth species acetylene, the geometric cross-section $\sigma_{\rm d}$ of the grain and the relative collision velocity $v_{\rm rel}$ times the fraction of reactive surface sites p (cf. Sect. 2) averaged over the grain surface

$$\tau_{\rm acc}^{-1} = 2n_{\rm C_2H_2}\sigma_{\rm d}\langle v_{\rm rel}p\rangle. \qquad (16)$$

Here, we tacitly assumed that the impinging acetylene molecule, whose size is comparable to the mean separation of neighbouring carbon surface atoms, always "hits" one carbon surface atom or the other and that the outcome of the collision only depends on the probability of this surface atom having a dangling bond.

Growth reactions involving non-radical surface sites and C_2H, which is the most abundant hydrocarbon radical in the gas-phase, are also conceivable. By means of a molecular dynamics investigation of an H-covered diamond surface Frauenheim & Blaudeck (1992) found that this reaction proceeds via the abstraction of a surface H-atom directly followed by the chemisorption of the newly formed acetylene molecule.

Apart from the direct reaction mechanisms discussed so far, carbon growth may also proceed via the formation of a trapped precursor state. The adsorption energy $E_{\rm ad}$ of a physisorbed C_2H_2 molecule on metal surfaces is given by 0.35 eV (Zhao et al. 1993). Since the adsorption energy of C_2H_2 on graphite has been determined to 0.28 eV (Peters et al. 1986) a similar value should also apply to the adsorption on carbonaceous grains. Consequently, a hyperthermal C_2H_2 molecule can be physisorbed. Migrating over the surface, it has many chances to find a low-potential-energy-barrier reaction path leading to chemisorption at a radical site before it desorbs. By means of a MD simulation of C_2H_2 physisorbed on a diamond surface Zhao et al. (1993) estimated the average residence time of physisorbed acetylene at 1200 K to be about 5 ps, i.e. much longer than the characteristic time of a single collision.

Introducing characteristic timescales of re-evaporation and thermal hopping or diffusion, $\tau_{\rm ev}$ and $\tau_{\rm h}$, respectively (e.g. Herbst 1993), the number n of surface sites "visited" by a physisorbed C_2H_2 molecule before leaving the surface is given by

$$\begin{aligned} n &= \tau_{\rm ev}/\tau_{\rm h} && (17)\\ &= \exp(0.7E_{\rm ad}/kT_{\rm d}) && (18)\end{aligned}$$

where we estimated the energy barrier to thermal hopping to be 0.3 times the adsorption energy $E_{\rm ad}$ as indicated by geometrical arguments (cf. Herbst 1993). If efficient physisorption of C_2H_2 is possible, e.g. for thermal collisions, the chance to react with a radical site and thus the growth rate is increased up to a factor of $n \sim 10$ for conditions typical of CSE. Consequently, chemisorption of a physisorbed acetylene molecule diffusing across the grain surface may well be an important growth mechanism. This further supports our hypothesis of the acetylene addition reaction being highly efficient.

In the process of onefold chemisorption of C_2H_2 the triple bond between the two carbon atoms is broken creating a dangling bond at the C-atom not bonded to the surface (e.g. Huang et al. 1988, Pederson et al. 1991). The resulting structure is then incorporated into the lattice by reconstruction or rearrangement (isomerization) processes and forms a new part of the grain surface. In the case of carbonaceous surfaces this take place on very short timescales from ps to μs (Belton & Harris 1992, Harris & Goodwin 1993, Colket & Hall 1994).

These rearrangement processes may involve, for instance, bondbreaking (scission reactions) (e.g. Harris & Goodwin 1993) or a combined C–C bond formation and hydrogen-atom transfer or ejection (Huang et al. 1988). The latter reactions lead to the breaking of C–C double bonds and have low or no activation barriers. We therefore expect the sp^2 fraction of the newly formed grain material to be small.

4. Conclusions

We have described relevant aspects of the grain surface chemistry on carbonaceous grains considering three important bonding configurations: aromatic structures, sp^2 and sp^3 bonds. The presented method for the calculation of the radical surface coverage takes account of different gas and dust temperatures and of effects due to grain drift velocities. The dust growth rate will generally be proportional to this radical surface coverage. Furthermore, we argued that the sticking efficiency of the key growth species C_2H_2 at radical sites is high for grain drift velocities up to 5–10 km/s.

Efficient dust formation in CSE takes place at temperatures below $\sim$ 1200 K. Consequently, our findings in Sects. 2 and 3 indicate that surface growth processes mainly take place at sp^3 bonded carbon atoms rather than at the edges of graphitic plates or polycyclic aromatic hydrocarbons.

The observed far-infrared spectra of circumstellar dust shells can be fitted best by radiative transfer models adopting a dust opacity which follows a power law $\lambda^{-\beta}$ for spectral index $\beta = 1 \ldots 1.3$ (e.g. Rowan-Robinson & Harris 1983, Le Bertre 1988). This spectral behaviour corresponds to laboratory results obtained for some sort of amorphous carbon (e.g. Bussoletti et al. 1987, Koike et al. 1995). Furthermore, Muci et al. (1994) found that the ultraviolet extinction observed toward carbon-rich sources also can be best explained by using measured extinction data of amorphous carbon grains produced in the laboratory.

In view of our result that surface growth processes mainly take place at sp^3 bonded carbon atoms, we therefore conclude that the grain material formed in CSE will be amorphous diamond-like carbon. In the general interstellar medium or in the outer parts of the circumstellar dust shell, where the dust becomes optically thin for the interstellar radiation field, the grains could then be processed by UV photons to produce, for instance, some graphitization (e.g. Ogmen & Duley 1988). The structural nature of dust grains in their formation region may thus be rather different from that observed in the ISM.

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