Organometallic catalysis for aromatic molecules formation in carbon rich envelopes

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Abstract. Aromatic molecules (PAHs or others) are considered to be an abundant component of the Interstellar Matter. However, their formation process remains a problem since a high production rate is required in order to balance the destruction mainly caused by shocks in the Interstellar Medium. We propose that catalytic reactions, based on organometallic chemistry could contribute efficiently to the formation of such molecules. A simple model has been developed in the envelope of the well observed carbon star IRC+10216. High abundances of small PAHs could be produced in the intermediate envelope from the precursor acetylene molecule. Moreover, the process could be efficient enough to account for the observed depletion of acetylene between the internal and external parts of the envelope (more than one order of magnitude).

Key words: interstellar medium: abundances – interstellar medium: molecules – molecular processes – stars: circumstellar matter – stars: individual: IRC + 10216

1. Introduction

More and more observations of the interstellar medium infrared emission support the existence of aromatic carbonaceous molecules like PAHs, originally proposed by Léger & Puget (1984) and by Allamandola et al.(1985). The observations of the Galactic plane performed with the AROME balloon-borne experiment, allowed the first detection of the emission features at $3.3\,\mu m$ (Giard et al. 1988, 1989 and 1994), and at $6.2\,\mu m$ (Ristorcelli et al.1994), at large scale in the diffuse interstellar medium. Giard et al.(1994) deduce from their measurements and from the dust model of Désert et al. (1990), that PAHs should include about 8% of the cosmic carbon and be homogeneously mixed into the general Interstellar Medium (ISM). They

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infer an average production rate of about $1.5\,10^{-2}\,M_\odot yr^{-1}$ for the Galaxy and address the question of the formation of PAHs. The processes involved as well as the sites of production have given rise to many discussions (Allamandola et al.1985, Omont 1986). In particular, Allamandola et al.(1985) and Jura et al.(1987) proposed that C-rich red giants could be a significant source of PAHs, since they eject an important mass of gas into the interstellar medium. Direct observations of the emission bands attributed to PAHs are difficult in giant star envelopes because of the lack of UV photons required for the excitation mechanism. However, these stars are the precursors of planetary nebulae whose spectra present the IR bands, when they are carbon rich. It is also the case for Post-AGB objects (Buss et al. 1990, Lequeux et al. 1990). Then, one can ask at which stellar evolution stage should the PAH formation start and according to which process.

Chemical models have been developed to study PAH formation in stellar envelopes involving classical nucleation from the precursor acetylene molecule C_2H_2 (Frenklach & Feigelson 1989, Cherchneff et al.1992). However, the chemical growth is restricted to a narrow temperature range ($1000K \pm 200K$), and the resulting production rate is very low. In this scheme, the blocking step is the production of the first aromatic ring. In this paper, we consider the possibility of a different formation process, based on the catalytic cyclotrimerization of acetylene with iron, originally proposed by Chaudret et al. (1991) and Serra et al. (1992) in their study of organometallic chemistry in the ISM. Such a mechanism could take place in circumstellar media but also inside molecular clouds allowing in-situ formation of aromatic molecules. The aim of this paper is to investigate the efficiency of this chemical process in the typical AGB stellar envelope of the well-observed star IRC+10216.

2. Catalytic reactions of organometallic chemistry.

The linkage of one or several metal atoms to one or several organic molecules leads to the formation of organometallic com-
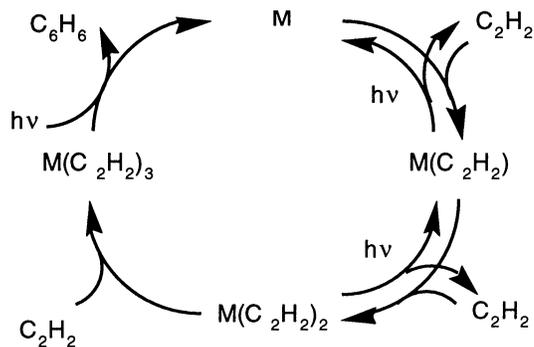
Fig. 1. Scheme for the cyclotrimerization of acetylene to benzene catalysed by the metal M.

plexes. From gas phase mass spectroscopy experiments, Shröder et al. (1991) produced benzene through cyclotrimerization of acetylene via a neutral complex $Fe(C_2H_2)_3$. First, they ionized the $Fe(CO)_5$ molecule which led to substitution of CO by C_2H_2. Secondly, the $[Fe(C_2H_2)_x]^+$ (x=2 to 4) complex was neutralized and then reionized. Spontaneous production of benzene occurred only after the neutralization step. Kline et al. (1985) studied the formation of $Fe(C_2H_2)$ and $Fe_2(C_2H_2)$ complexes in 15K argon matrices. Formation of these complexes at very low temperature indicate that the activation energy should be very low but no value was published up to now.

Cyclotrimerization of unsaturated hydrocarbons to benzene is also known with various cationic metals: $[Fe_n]^+$ for $n = 4$ or 5 (Schnabel et al. 1991), Nb^+ (Buckner et al. 1989) and W^+ (Berg et al. 1994). In these cases, the reaction of ethene (C_2H_4) with these metals leads firstly to the formation of the $[Metal(C_2H_2)_3]^+$ complex which indicates a spontaneous dehydrogenation of ethene into acetylene upon coordination. Then, an external energy of a few eV is required to activate the triacetylenic complex toward benzene formation. We have considered a generic scheme for the cyclotrimerization of acetylene to benzene, described by the set of chemical reactions given in Fig. 1. In this scheme, M can be a metallic atom or a small metallic aggregate.

Berg et al. (1994) have measured the rate constants of the cyclotrimerization of ethene to benzene. They have found rate constant values in the order of magnitude of the Langevin rates computed for a model described by the collision of an induced dipole with an ion. No constant rate for the reaction with neutral metal and acetylene was measured up to now. Nevertheless, Clary et al. (1994) demonstrated that the Langevin rate for a reaction of neutral reagents can be computed with a model described by interactions between two induced dipoles. This theory leads to the following formula:

$$k(cm^3 s^{-1}) = 4.25 \ 10^{-10} (\frac{\alpha_1' . \alpha_2' . IP_1 . IP_2}{IP_1 + IP_2})^{\frac{1}{3}} T^{\frac{1}{6}} (\frac{1}{m_1} + \frac{1}{m_2})^{\frac{1}{2}} (1)$$

where α_i' is the polarizability volume (in Å³), IP_i is the ionization potential (in eV) and m_i is the molecular mass (in g/mol) of the reagent i. Clary et al. (1994) showed that the Langevin rate between neutrals is well verified in various cases: e.g. ground

state carbon atoms react with 1-alkenes or with 1-alkynes with this rate. Chemical reactions of our modelling are not very different from that of the previous example where carbon atom has been replaced by a metal atom and 1-alkyne is chosen to be acetylene. In absence of published rate measurements between neutral metals and acetylene in the gas phase, we computed the rates of our set of reactions using formula (1).

One can notice that a small aggregate of n atoms has an abundance of n^{-1} compared to the atomic state but its cross section is increased by a factor $n^{2/3}$ (in the spherical approximation). Finally, the integrated cross section of clusters containing n metal atoms should be corrected by a factor $n^{-1/3}$ compared to the integrated cross section of isolated metal atoms. Then, it is important to notice that the value of the integrated cross section of 100 metal atom clusters is only 1/4 that of the integrated cross section of 1-metal atom. The constant rates being proportional to the cross sections, the colliding efficiency of a given metal should not vary dramatically if M is considered as free atoms or as small aggregates. Our calculations were performed considering M as a 1-metal atom and we discussed the case of small metal aggregates by modifying in consequence the δ parameter value of the initial depletion defined in the next section. The values of the parameters δ_i value and IP_i, defined in formula (1), do not change significantly from one transition metal to another. Even if the exact nature of the M species can vary, their kinetic parameters can be approximated by those of a given transition metal. In this study, the parameters for M have been deduced from atomic iron because it is the most abundant transition metal according to cosmic abundances. For the intermediate complexes $M(C_2H_2)_x$ (x=1, 2 and 3), the polarizability was chosen to be equal to the sum of the polarizabilities of individual components and the ionization potential was chosen identical to that of the naked metal.

We considered that the collision between M and C_2H_2 leads to a $M(C_2H_2)$ complex with a Langevin rate but this complex is in an excited state because it must evacuate, at least, the metal-acetylene bonding energy. This energy excess U can be evacuated according to three main channels: i) the molecule radiates U through its vibrational modes, ii) the molecule dissipates U by loosing a fragment, iii) the molecule radiates U by a fluorescence emission. In the case of the reaction of metal PAHs, this problem was treated by Marty et al.(1996a) using the unimolecular rate theory (Forst et al. 1972, 1973). From this theory, Marty (1996b) found that only aggregates containing more than ten metal atoms can coordinate acetylene efficiently (the i process being faster than the ii one). In other cases, $M(C_2H_2)$ could be efficiently formed if fluorescence channels exist (the iii process faster than the ii one) but, up to now, no experimental results were reported about the fluorescence of such complexes. Another problem is to estimate the stability of the intermediate complexes $M(C2H2)_x$ ($x = 1$, 2 and 3) under a given radiation field. No experiments have been performed yet on the photodestruction of the organometallic bond of neutral metal-acetylene complexes in the gas phase. In a first approximation, we postulate that every photon of energy higher than the metal-acetylene bonding energy (El) can destroy the organometallic bond (i.e.

dissociation efficiency=1 if $h\nu \geq El$). This is probably too harsh but it leads to the worst case for the formation of benzene via organometallic cyclotrimerization. In the case where M are large clusters of metals (> 50 atoms), the unimolecular theory predicts that the dissociation energy of complexes must be much larger than the bonding energy El, leading to a better efficiency of benzene formation than that predicted by our modelling. Kobitchev et al. (1987) computed a bonding energy of 0.8 eV between Fe and C2H2 from ab-initio calculations at the Hartree Fock level. However, they did not take into account the electronic correlation which must lead to a higher value of energy. The bonding energies of metal-acetylene cations were computed by Sodupe & Bauschlisher (1991) for the first row of transition metals. They found values varying between 0.7 and 1.7 eV, depending on the metal. Hettich et al. (1996) have obtained experimentally $El(Fe^+ - C_6H_6) = 2.38eV$ and $El(Fe^+ - C_2H_2) > 1.5eV$. However, bonding energies of neutral complexes are expected to be lower. In order to deduce approximately $El(Fe - C_2H_2)$, we can make an analogy using the ratio $El(Fe - C_6H_6)/El(Fe^+ - C_6H_6)$. Since Shröder et al.(1991) have found $1.3 \leq El(Fe - C_6H_6) \leq 2.39eV$, we have inferred that $El(Fe - C_2H_2)$ was between 0.8 and 1.5eV. In the absence of an experimental photodissociation spectrum of $M(C_2H_2)$ complexes, the dissociative cross section has been approximated by the geometric section, σ_{geom}, when $h\nu \geq El$. Compared to $M(benzene)^+$ complexes (Hettich et al. 1986), this approximation should be an overestimation of the real cross section of photoabsorption which leads to an underestimation of the rate of benzene formation in our model. In addition, Schnabel et al. (1991) have shown that metals, which are able to perform the cyclotrimerization of acetylene to benzene, have also a good activity for the dehydrogenation of hydrocarbons. They noticed that the reaction of benzene with $[Fe_4]^+$ was leading to the formation of benzyne (C_6H_4), which is known to be very reactive. It can coordinate to metals, and Bauschlicher et al. (1993) computed that Fe^+ could be bonded to the triple bond one like a standard acetylenic derivative. According to this, we propose to take into account another catalytic set of reactions, leading to the formation of the triphenylene PAH ($C_{18}H_{12}$), as described in Fig. 2.

Kinetic parameters were computed in the same way as those of the first catalytic process. Other reaction pathways involving cyclotrimerization could be envisaged. However, in order to simplify the discussion of the results of this study, we used only a restricted set of reactions (see Fig. 1 and 2). In fact, the triphenylene production is a first step toward PAH formation. The complete set of parameters for each compound involved in our modelling is defined in Table 1.

3. Modelling of the chemical scheme in IRC+10216 envelope

In order to take into account the stellar envelope expansion, the chemical scheme described previously must be solved by means of the coupled continuity equations:

$$\frac{\partial n_i}{\partial t} + div(n_i\vec{v}) = P_i - L_i \tag{2}$$
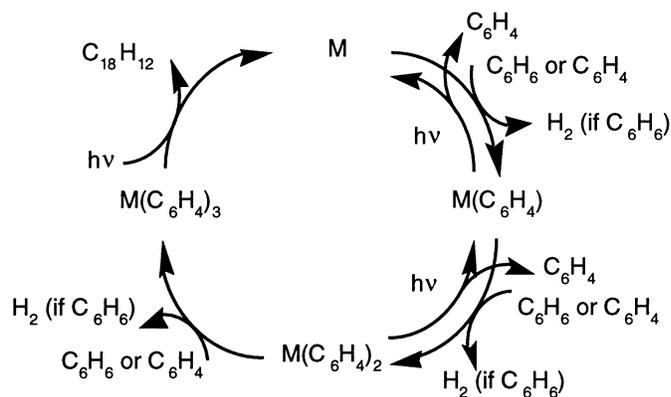
Fig. 2. Scheme for the cyclotrimerization of benzyne (C_6H_4) and benzene to triphenylene ($C_{18}H_{12}$) catalysed by the metal M.

Table 1. Set of physical parameters of the reagents involved in the catalytic reactions of the modelling. The parameters associated to M are those of the iron atom.

species	m(g/mol)	α' (Å²)	σ_{geom}(Å²)	IP(eV)
C_2H_2	26	3.5	6.4	11.40
M	56	8.4	9.3	7.90
$M(C_2H_2)$	82	11.9	10.7	7.90
$M(C_2H_2)_2$	108	15.4	17.1	7.90
$M(C_2H_2)_3$	134	18.9	23.5	7.90
C_6H_6	78	10.3	20	9.25
C_6H_4	76	15	15	9.75
$M(C_6H_4)$	132	23.4	19.3	7.90
$M(C_6H_4)_2$	208	38		7.90
$M(C_6H_4)_3$	284	53.5	49.3	7.90
$C_{18}H_{12}$	228	53	35	7.82

where n_i are the species concentrations, v is the mean flow velocity and P_i, L_i are respectively the product and loss rates of the i compound in the chemical reactions. Considering a steady spherically symetric flow, the equation set can be expressed as:

$$\frac{\partial n_i}{\partial r} = \frac{-2n_i}{r} + \frac{1}{v}(\Sigma k_p n_i n_j - \Sigma k_l n_i n_h) \tag{3}$$

where k_i are the reaction rates. This system has been solved using Runge-Kutta method (4th order). The abundance of acetylene in the internal part of the envelope has been deduced from the measurement of its absorption band at 3.04 μm (Keady et al. 1993). It corresponds to $8.10^{-5}n_H$ (within a factor 2 of accuracy). We have used this value as the initial abundance in the internal envelope. In fact, the acetylene molecule is involved in a large number of ion-molecule or radical-molecule reactions. However, the modelling of Cherchneff et al. (1993) shows that a very small fraction of its initial abundance is effectively converted to subproducts in the internal and intermediate envelope (about 1%). It is only in the external part ($r \geq 3.10^{16}cm$) that C_2H_2 gets completely photodissociated into C_2H. The metal (M) initial abundance has been taken equal to that of free iron, supposed to be the most abundant transition metal in the enve-

lope, as in the Interstellar Medium. We have adopted its cosmic abundance with a depletion factor (δ) to take into account the fraction already included into the grains formed in the internal envelope. This depletion factor will be kept as a free parameter in the model. As it was noticed in Sect. 2, when considering M as a metallic cluster of n atoms, one must multiply the δ value by $n^{1/3}$ in order to compensate for the change both of the cross section and of the abundance (varying respectively as $n^{2/3}$ and n^{-1}). In addition, we have considered that the competitive accretion process $M + M \rightarrow M_2$ was continuing all along the envelope expansion (M_2 is considered as inactive for the cyclotrimerization).

The physical parameters of the envelope (temperature, gas density and dust properties) and the central star characteristics have been deduced from the modellings of Cherchneff et al. (1993) and Rouleau & Martin (1991). In particular, we have considered small grains of amorphous carbon with an average size of $0.05\,\mu m$. The photon density has been determined as the resulting flux coming from the central star ($T \simeq 2000K$, stellar photosphere radius: $R_\star \simeq 10^{14}cm$), and the interstellar radiation field, taking into account the dust extinction inside the envelope. In a first approximation, we have considered a radial scattering direction through the envelope. The dust density distribution is assumed to be a power law with a sharp cut-off at $r \simeq 4.5R_\star$, according to the IR continuum on modelling of Martin & Rodgers (1987) using the dust characteristics supported by Cherchneff et al.(1993). A first estimation of the efficiency of the organometallic process in the envelope can be assessed by comparing the average colliding times between a free M atom and an acetylene molecule or a destructive photon (i.e. with $h\nu \geq El$). The characteristic times are displayed on Fig. 3, as a function of the radial distance in the envelope. The results depend strongly on the bonding energy value. If $El \leq 1eV$, the photodestruction frequency is much higher than the coordination one, everywhere in envelope. On the contrary, if $El \simeq 1.2eV$, the catalytic process can develop within the radius range: $2.10^{15} \leq r \leq 9.10^{15}$. For a higher value, this favourable range increases. We have plotted on Fig. 4 the abundances given by the modelling if the mean value $El = 1.2eV$ is adopted. The formation of aromatic molecules turns out to be very efficient and the steady-state values for C_2H_2 and $C_{18}H_{12}$ abundances are rapidly reached (within $40R_\star$). With a mean expansion velocity of 14km/s (Cherchneff et al. 1993), this corresponds to a very short time scale of about 30 yrs. The various abundances are given in Table 2 as a function of the bounding energy.

4. Discussion and conclusion

Our modelling leads to high abundances of $C_{18}H_{12}$ in the intermediate envelope of IRC+10216, but only if the dissociation energy of the organometallic intermediates ($M(C_2H_2)_n$ and $M(C_6H_4)_n$) is higher than 1.2 eV. This is the main constraint on the organometallic catalysis for the cyclotrimerization of acetylene in this circumstellar medium. We have seen that $Fe - C_2H_2$ bonding energy was expected to be found be-
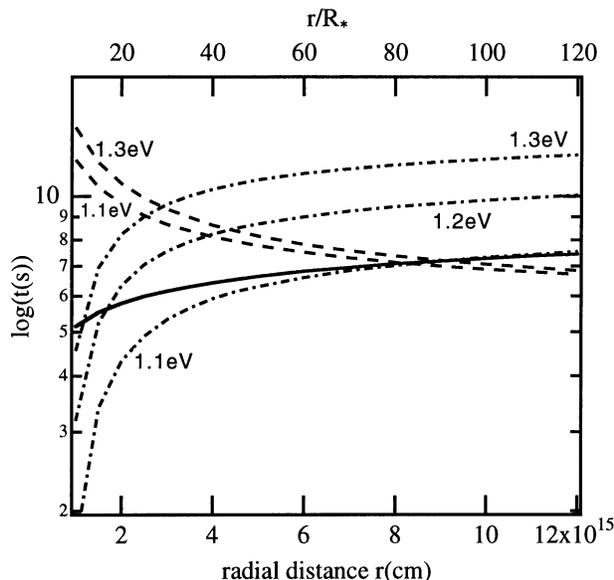

Fig. 3. Comparison of the mean colliding times between an iron atom and i) C_2H_2 (solid curve), ii) a destructive photon ($h\nu \geq El$), with $El = 1.1; 1.2; 1.3\,eV$, originating from the central star (dash-dot curve) or the ISRF (dashed curve).

Table 2. Steady-state abundances of C_2H_2 and $C_{18}H_{12}$ for different values of the metal depletion factor (δ_M) and the bonding energy (El).

$El(eV)$ | δ_M		1	0.1	0.01
1.1	C_2H_2	$5.6\ 10^{-5}$	$5.8\ 10^{-5}$	$6.6\ 10^{-5}$
	$C_{18}H_{12}$	$2.8\ 10^{-9}$	$1.5\ 10^{-9}$	$2.3\ 10^{-10}$
1.2		$1.\ 10^{-6}$	$1.3\ 10^{-6}$	$2.3\ 10^{-5}$
		$8.2\ 10^{-6}$	$8.1\ 10^{-6}$	$1.4\ 10^{-6}$
1.3		$1.3\ 10^{-7}$	$2.5\ 10^{-6}$	$3.5\ 10^{-5}$
		$8.1\ 10^{-6}$	$7.3\ 10^{-6}$	$2.8\ 10^{-7}$
1.5		$3.8\ 10^{-8}$	$3.2\ 10^{-6}$	$3.8\ 10^{-5}$
		$7.9\ 10^{-6}$	$6.9\ 10^{-6}$	$1.8\ 10^{-7}$

tween 0.8 and 1.5 eV. The dissociation energy of organometallic intermediates can be assessed to be equal to their bonding energy if they are small complexes (i.e. less than about 10 atoms). However, if the metallic cores M were aggregates, we have seen in Sect. 2 that, according to unimolecular theory, the intermediate complexes could have a sufficient number of vibrational modes to radiate their internal energy instead of breaking the organometallic bond. As a consequence, large organometallic complexes could have a dissociation energy higher than 1.2 eV even if their bonding energy is smaller.
For a given initial metal abundance, whatever the value of the dissociation energy higher than 1.2 eV, the final steady-state abundance of $C_{18}H_{12}$ does not vary significantly. In the case $El \geq 1.2eV$, the first coordination leading to $Fe - C_2H_2$ becomes much more efficient then the photodestruction, depleting rapidly the gas phase of free C_2H_2 molecules, and then slowing
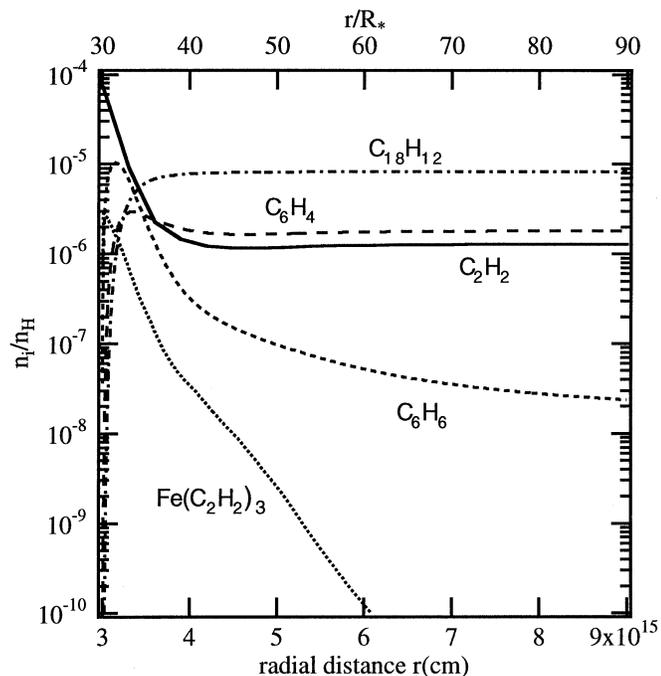
Fig. 4. Relative abundances given by the modelling if $El = 1.2eV$, and $\delta = 0.1$.

down the following step of the cyclotrimerization. We have also studied the effect of the initial depletion of M. The final abundance of $C_{18}H_{12}$ is about the same, $8.10^{-6}n_H$, for $\delta = 1$ to 0.1, with El=1.2eV. This is due to the catalytic property of M. However, if $\delta \ll 0.1$, the production of $C_{18}H_{12}$ falls by more than one order of magnitude. The most favourable cases for the production of $C_{18}H_{12}$ have been obtained for a dissociation energy of the intermediate complexes around 1.2 eV and for a metallic depletion δ included between 1 and 0.1. In the case $\delta \simeq 0.1$, the abundance of free acetylene decreases up to a factor 60 from its initial value in the internal envelope ($r \sim 10R_\star$). The acetylene abundance in the envelope has been measured by means of two independent methods: i) directly deduced from the measurement of its absorption band at $3.04\,\mu m$ (Ridgway et al. 1976, Keady et al. 1993): it corresponds to $8.10^{-5}n_H$ (with a factor 2 of accuracy), ii) indirectly deduced from the emission at 87GHz of its photodissociation product in the external envelope, C_2H (Huggins et al. 1984, Truong-Bach et al. 1987): it gives an abundance at least one order of magnitude lower ($\sim 2.4\,10^{-6}n_H$). Truong-Bach et al. (1987) have shown that an accretion process of acetylene onto the grains could not be sufficient to explain this depletion and they suggest the existence of an unknown very efficient chemical process in the expanding envelope. The catalytic process that we propose in the intermediate envelope, could contribute significantly to this depletion.

More laboratory and theoretical data on the bonding energy and on the cross sections of the involved organometallic species, are needed to improve the modelling and to give more accurate results. In addition, many other reactions involving oligomerization of unsaturated hydrocarbons, should be taken into ac-

count to produce larger PAHs. Similar organometallic processes could also be efficient to form very small grains of metal-aromatic aggregates as already discussed by Marty et al. (1994). Our simplified modelling shows that organometallic catalysis could contribute efficiently to the formation of aromatic molecules in C-rich circumstellar media and should be included in general chemical modellings. Moreover, such processes could take place inside molecular clouds. As discussed by Giard et al.(1994), in-situ formation of PAHs is necessary to account for the large amount of these molecules observed and to provide an homogeneous mixing in the ISM. Interstellar acetylene has bected for the first time by Lacy et al. (1989) in the spectra of three infrared sources embedded in molecular clouds. The inferred abundances ($3\,10^{-4}$ to 10^{-3} of CO) could lead to a significant production of aromatic molecules through the catalytic process proposed in this paper. Moreover, this chemical process is thought to be more efficient in dense interstellar clouds than in circumstellar envelopes because produced molecules are protected from UV radiation by a large dust extinction.

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