Electron-attachment rates for carbon-rich molecules in protoplanetary atmospheres: the role of chemical differences

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ABSTRACT

The formation of anionic species in the interstellar medium from interaction of linear molecules containing carbon, nitrogen and hydrogen as atomic components (polyynes) with free electrons in the environment is modelled via a quantum treatment of the collision dynamics. The ensuing integral cross sections are employed to obtain the corresponding attachment rates over a broad range of temperatures for the electrons. The calculations unequivocally show that a parametrization form often employed for such rates yields a broad range of values that turn out to be specific for each molecular species considered, thus excluding using a unique set for the whole class of polyynes.

Key words: astrochemistry – ISM: evolution, molecules

1 INTRODUCTION

In spite of the fact that the physical conditions in the Interstellar Medium (ISM) and in many of the planetary atmospheres are seemingly unfavourable to chemical evolutions (e.g. low particle densities and fairly low temperatures) a very rich chemistry exists in such regions and has been followed by observations for a long time (Snow & McCall 2006; Herbst & van Dishoeck 2009). Among the recently discovered species, six different anionic molecules have been detected in the denser regions of the ISM, i.e. HC₄⁻ (n= 4, 6, 8) and C₆N⁻ (n= 1, 3, 5) (McCarthy et al. 2006; Brünken et al. 2007; Cernicharo et al. 2007; Agúndez et al. 2010) and furthermore N-containing anions C₇N⁻ (n= 1, 3, 5) were found in Titan’s upper atmosphere (Vuitton et al. 2009). It is therefore well established by now that several molecular anions have been found in the interstellar and planetary environments, so that it is now crucial to understand as much as possible the ion chemistry of the species involved and the likely paths to the formation of such systems: the final rate constants for their formation are in fact important for the astrochemical modelling that tries to establish the most realistic reaction networks in that environment.

Given the low densities of the mutual species present in the ISM, it is also a realistic possibility that such anionic molecules be formed in reaction with electrons, the latter being produced abundantly in the outer regions of the denser clouds and in the planetary atmospheres (Sakai et al. 2007). Estimates of the electron temperatures in that environment suggest values that can go up to 1000 K or above. The reactions of such electrons with molecular species can therefore lead to the eventual formation of a negative ion through a variety of dynamical processes. For example, dissociative electron attachment (DEA) is a well known process

\[ M - H + e^- \rightarrow M^- + H \]  

whereby some of the bound atoms in the initial partner are detached after forming a stable residual anion, a process related to the sign and the value of the electron affinity (EA) of the M⁻H species (Sebastianelli et al. 2011). Another option in the ISM environment is the radiative stabilization (RS) of the threshold resonances associated to the formation of a temporary negative ion (TNI) upon electron attachment close to zero energy

\[ M + e^- \rightarrow [M^-]^* \rightarrow M^- + h\nu \]  

a process which we have recently argued as possible for the formation of \([C_6H_4]-\) (Carelli et al. 2011). The DEA processes are also known to be more likely to occur at low energies and to chiefly involve a dehydrogenation path

\[ e^- + HCCCN \rightarrow CCCN^- + H \]  

which has, in fact, been suggested by our calculations as occurring via resonant intermediates in several polyynes anions (Sebastianelli & Gianturco 2012). An additional feature
that should favor RS in competition with DEA is the occurrence of virtual states and of zero-energy resonances in unsaturated species like C₉₀ (Lucchese et al. 1999). Such special "compound states" are suggested to be very efficient in "soaking up" threshold electrons, thereby leading to anionic formation (Sebastianelli & Gianturco 2012) and have been found by our calculations to also exist in anionic polyynes (Sebastianelli & Gianturco 2012).

2 CALCULATING ATTACHMENT RATES

The question of having such variety of processes thus relates to scattering cross sections over the full range of low-energy regions where either DEA and RS processes are found to occur. They often reveal a broad variety of resonances for which specific states that occur as the collision energy goes down to zero. They often reveal a broad variety of resonances for which special "compound states" are suggested to be very efficient in "soaking up" threshold electrons, thereby leading to anionic formation (Sebastianelli & Gianturco 2012) and have been found by our calculations to also exist in anionic polyynes (Sebastianelli & Gianturco 2012).

In our present models it describes a convolution over electron Attachment (EA), \( k_{\text{EA}} \), can be related to the rates of metastable anion formations, \( k_{\text{TNI}} \), and to the autodeattachment and radiative stabilization rates, \( k_{\text{ad}} \) and \( k_{\text{rs}} \) respectively (Carelli 2012).

\[
k_{\text{EA}} = \frac{k_{\text{rs}}}{k_{\text{ad}} + k_{\text{rs}}} \cdot k_{\text{TNI}}
\]

when anionic formation is assumed to be in a steady state (Herbst 1980). Since it is also assumed that \( k_{\text{ad}} \gg k_{\text{rs}} \) one can further write

\[
k_{\text{EA}} = \frac{k_{\text{rs}}}{k_{\text{ad}}} \cdot k_{\text{TNI}}.
\]

Therefore the rates of electron attachment, \( k_{\text{EA}} \), have a clear upper bound in the calculated \( k_{\text{TNI}} \) rates which use Eqn.(4) unless \( k_{\text{ad}} \approx k_{\text{rs}} \). The present calculations for polyynes are thus providing from first principles electron attachment rate values which are, generally speaking, larger than the true rates of formation of anionic species. They are also shown here to exhibit a very marked dependence on the chemical features of the carbon-rich linear molecules examined in the present work.

3 RESULTS AND DISCUSSION

We have carried out detailed calculations of the integral cross sections, as in Eqn.(4), over a broad range of collision energies using the computational method well established in our group (Lucchese & Gianturco 1996) as already given in detail in various papers on polyyne species - e.g. see: Sebastianelli & Gianturco (2012); Sebastianelli et al. (2012). It is also customary in evolutionary models of chemical networks in the ISM and in planetary atmospheres to represent general two-body reactions via a parametric form of

\[
[M^- (R_e)] \rightarrow \frac{k_{\text{rs}}}{k_{\text{ad}} + k_{\text{rs}}} [M^-] + \text{A}^{-}.
\]

both in competition with the auto-detachment process

\[
M(R_e) + e^- \rightarrow [M^-] + k_{\text{ad}} \quad M(R_f) + e^-.
\]
Table 1. Fit coefficients for the polyynes presented in this paper, where \( \alpha \) is in \( \text{cm}^2 \text{s}^{-1} \), \( \beta \) is dimensionless, and \( \gamma \) in K. Note that \( \alpha(b) = a \times 10^b \). See text and Eqn. (12) for further details.

| Molecule | \( \alpha \)     | \( \beta \) | \( \gamma \) |
|----------|-----------------|----------|-----------|
| HC\(_4\)H | 2.689(-10)      | 0.486   | 4.174    |
| NC\(_2\)N | 1.887(-10)      | 0.373   | -5.440   |
| NC\(_4\)N | 21.798(-10)     | -0.019  | 7.688    |
| HCN \(_5\) | 3.321(-8)       | -0.304  | 19.036   |
| NC\(_5\)N | 7.218(-8)       | -0.482  | 7.625    |

Figure 1. Computed \( k_{\text{FIN}} \) rates from Eqn. (1) for three different carbon-rich linear molecules without permanent dipoles. See text for further details.

For their corresponding rate coefficients - e.g. see Woodall et al. (2007)

\[
k_{2B} = \alpha \left( \frac{T}{300 \text{ K}} \right)^\beta \exp\left( -\gamma / T \right) \text{ cm}^3 \text{s}^{-1}, \tag{12}\]

where, in our case, \( T \) is the electron temperature \( T_e \). The present calculations can therefore be profitably represented by a set of three parameters: \( \alpha, \beta, \gamma \), that can be associated to each polyyne species considered within the chemical network.

The molecules which we consider correspond to primary molecules for which electron attachment rates can be calculated: the symmetric polyynes (HC\(_4\)H, NC\(_2\)N, and NC\(_4\)N) and the polar polyynes (HC\(_3\)N and HC\(_5\)N) as exemplary choices for the class of molecules which have been also experimentally observed (see present introduction).

The data reported by Fig.1 and Fig.2 show the temperature dependence of the \( k_{\text{FIN}} \) from the present calculations over a very broad range of \( T_e \); from nearby zero to 5000 K.

The data in both figures are then fitted using the customary expression of Eqn. (12) and the corresponding parameter values are also reported (see also Tab.1).

The following features could be gleaned from these data:

(i) There is a dramatic change in size when going from polar to non-polar molecular partners: the rates increase for the former by nearly two orders of magnitude over the whole range of \( T_e \);
(ii) The polar targets also show a strong increase at low \( T_e \), values, decreasing at larger temperatures; the opposite occurs for the symmetric polyynes, whose rates increase as \( T_e \) increases;
(iii) The parameters for the polar systems are fairly robust, in the sense that change little with the number of carbon atoms, a molecular index often used in astrochemical networks;
(iv) The symmetric polyynes show instead a more marked dependence on the number of C atoms and also have larger rates with N atoms in the chains.

The data insets of Fig.1 and Fig.2 also report the \( k_{\text{FIN}} \) behaviour in the low-\( T_e \) regimes, i.e. from threshold to 250 K, in order to show more clearly the difference in behaviour among chemical partners.

The marked increase of the rates near threshold and their drops at vanishing energies are again very clear for the polar molecules, as well as the larger sizes of their rates at low \( T_e \). On the contrary, the symmetric polyynes show all a steady increase in size from threshold and overall sizes which are much smaller that those for their asymmetrical counterparts.

In conclusion, the present quantum calculations of formation rates for electron attachment processes within a representative sampling of carbon-rich linear molecules show rather clearly that the parametrization of such two-body processes is markedly dependent on the chemical species being considered. Although the length of the chains (i.e. the number of C atoms) plays some role, as does the presence of other heteroatoms like nitrogen, we found here that the strongest chemical discriminator is provided by the presence of permanent electric dipole moments in the molecules in question. The asymmetric polyynes are seen here to yield much larger rates, especially for \( T_e \) values from threshold to about 100 K, and to exhibit an increase at lower temperatures, the opposite behaviour from that shown by symmetric molecular partners.

Such differences should therefore be taken into consideration when anionic formation rates are explicitly included in evolutionary chemical networks, where they can provide more detailed, chemically-controlled, final stationary abundances for neutral and charged species. The latter
data would obviously be critical for a better comparison with observations - e.g. see [Agúndez et al. (2010)].

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