

ON THE n -DEPENDENCE OF THE REACTION RATE FOR $C^+ + C_n \rightarrow C_{n+1}^+$ IN INTERSTELLAR SPACE

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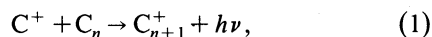
ABSTRACT

The rate of the radiative association reaction $C^+ + C_n \rightarrow C_{n+1}^+ + h\nu$ is considered under the conditions in interstellar space. The lifetimes of the energized C_{n+1}^+ ion are estimated from the Rice-Ramsperger-Kassel-Marcus (RRKM) model of unimolecular decomposition and compared with the lifetime of infrared emission. It is shown that this reaction proceeds efficiently with the Langevin rate for $n \geq 4$. Thus, the carbon chain can grow very quickly once it reaches C_4 . This may explain the observed abundance of long carbon chain molecules in interstellar space.

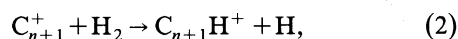
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I. INTRODUCTION

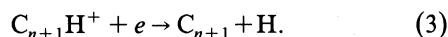
The long chain cyano-polyacetylene compounds HC_nN with $n = 5, 7, 9$, and 11 , recently discovered in interstellar space by radio astronomers (Avery *et al.* 1976; Kroto *et al.* 1978; Broten *et al.* 1978; Bell *et al.* 1982) provide remarkable evidence of extraordinary chemical conditions in molecular clouds. It is particularly noteworthy that their relative abundances vary only slowly from one compound to the next. The value of $n(HC_nN)/n(HC_{n+2}N)$ in TMC-1 has been reported to be ~ 4 for the series of HC_3N to HC_9N by Broten *et al.* (1978) from the direct observation and to be 2.3 for the series of HC_3N to HC_7N by Bujarrabal *et al.* (1981) from a more detailed analysis. The reported $n(HC_7N)/n(HC_{11}N)$ value of 0.7 in IRC+10216 (Bell *et al.* 1982) is amazing. Various chemical schemes have been invoked (Schiff and Bohme 1979; Mitchell, Huntress, and Prasad 1979) to explain the large abundance of these molecules. Recently Suzuki (1981) has proposed a new scheme in which the long carbon chain is built by a succession of the radiative recombination reaction,



the ion-molecule reaction,



and the electron recombination reaction,



This scheme and its analog, in which the C_n molecule is replaced by HC_n , successfully explains the efficient production of long carbon chains in molecular clouds with high densities and low optical depths. A similar scheme for building long chain carbon molecules was earlier proposed by Thaddeus (private communication). Reactions (2) and (3) are known from normal ion-molecule reactions (Herbst and Klemperer 1973; Watson 1976; Dalgarno and Black 1976) to have large cross sections. The purpose of this paper is to estimate the cross section for the reaction (1), in particular its dependence on n , the carbon atom chain length. We use a statistical argument based on the RRKM model to calculate the decomposition rate of the excited C_{n+1}^+ species. The idea that the radiative association is efficient for large molecules has already been used for discussing formation of interstellar molecules by Williams (1972) for neutral reactions to produce hydrocarbons and by Herbst and Klemperer (1973) for the reaction $HCO^+ + H_2 \rightarrow H_3CO^+ + h\nu$. The simplicity of the homonuclear carbon chains allows us to use this idea somewhat more systematically.

II. LIFETIME OF ENERGIZED $(C_{n+1}^+)^*$

Reaction (1) is a radiative association reaction (Bates and Spitzer 1951; Black and Dalgarno 1973) and is rather inefficient for small n because the spontaneous emission time (10^{-3} to 10^{-8} s) is much longer than the duration of the encounter between C^+ and C_n (10^{-10} to 10^{-11} s). The energized $(C_{n+1}^+)^*$ system, therefore, cannot get rid of the excess energy easily, so its most likely

fate is decomposition back to C^+ and C_n . Here we assume that the radiative association is the only exothermic product channel of the $C^+ + C_n$ reaction. Available data of heats of formation (Franklin *et al.* 1969) support this assumption (Suzuki 1982).

For large values of n , however, the rate of reaction (1) grows rapidly because of the large number of vibrational modes of the C_{n+1}^+ ion which can take a portion of the total vibrational energy to prevent a sufficient amount of this energy from accumulating in a dissociative vibration. The origins of this sharing of vibrational energy are readily seen by considering typical collisions of C^+ with C_n . The interaction between C^+ and C_n is highly attractive at long ranges, speeding up the relative motion. The C^+ ion may initially be directed at any part of the C_n chain, so their collision would excite the vibrations of C_n in the vicinity of first impact of C^+ with C_n , thereby temporarily leaving $(C_{n+1}^+)^*$ with insufficient energy in the C_n-C^+ vibration to redissociate. The most stable position for the C^+ ion to insert is at the ends of the C_n chain. However, the ends are not necessarily the sites of initial impact and attachment of C^+ to C_n . Hence, it is expected that the C^+ ion migrates from the point of initial impact to the chain end, and in doing so it undergoes multiple interactions with the C_n chain, thereby further exciting the vibrations of the C_{n+1}^+ ion. It is therefore reasonable to assume a statistical distribution of vibrational modes of the C_{n+1}^+ ion. This statistical distribution then enables us (Freed 1979) to invoke the RRKM theory (Robinson and Holbrook 1972) to calculate the unimolecular decomposition rate of $(C_{n+1}^+)^*$.

The linear C_{n+1}^+ has $s = 3n - 2$ vibrational modes. We use the crude approximation (Einstein model) that these s modes have similar frequency ν and can count various energies in the unit of $h\nu$. This approximation is probably reasonable for the stretching modes. The effect of bending vibrational modes, which are much lower in frequency, is considered later.

The total excess energy of C_{n+1}^+ above the ground vibronic state at the time of encounter $E = jh\nu$ is composed of the dissociation energy $E_d = mh\nu$ and the relative kinetic energy $E_k = ih\nu$ of C_n and C^+ . The total density of states ρ at energy $jh\nu$ is proportional to the number of ways of distributing the j quanta in s vibrational modes, that is,

$$\rho_E \propto g_j = \frac{(j+s-1)!}{j!(s-1)!} = \frac{(m+i+s-1)!}{(m+i)!(s-1)!} \quad (4)$$

The total density of reactive states is proportional to the number of ways α of placing m quanta in the reactive vibrational modes and distributing the remaining i quanta among the s vibrational modes, that is,

$$\rho_E^* \propto \alpha g_i^* = \frac{\alpha(i+s-1)!}{i!(s-1)!} \quad (5)$$

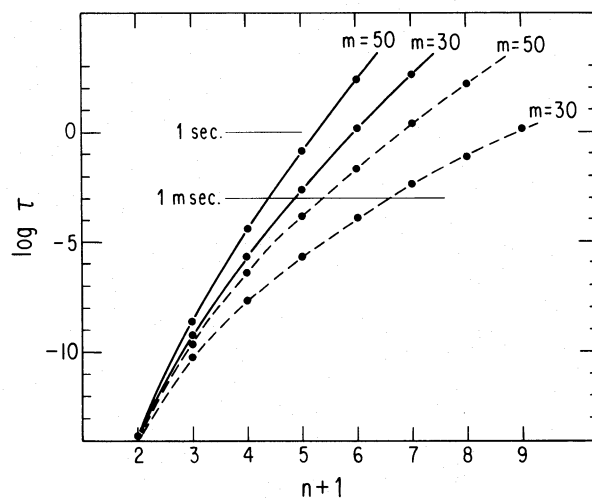


FIG. 1.—Calculated lifetime of activated $(C_{n+1}^+)^*$. Broken curves (for $m = 30$ and 50) represent calculated values using eq. (6), and solid curves represent values including the effect of low-frequency bending vibration.

Since the dissociation may, in principle, occur from either end of the C_{n+1}^+ chain, we use $\alpha = 2$. The effect of rotation is neglected because of the large moment of inertia.

The microcanonical dissociation constant is proportional to the fraction of the reactive state ρ_E^*/ρ_E . Thus, we have the dissociation rate constant

$$k_E = 2\nu \frac{(i+s-1)!j!}{i!(j+s-1)!} \quad (6)$$

For a real system neither i nor j is an integer. Thus, we replace the factorials with gamma functions using the relations $\Gamma(n) = (n-1)!$ and the continuity of $\Gamma(z)$ for $z > 0$ (Whittaker and Watson 1927). For interstellar conditions where the kinetic temperature is very low ($T_k \sim 30$ K), the relative kinetic energy of C_n and C^+ is much lower than $h\nu(\nu/c \sim 1500 \text{ cm}^{-1})$, that is, $1 \gg i > 0$. Thus approximating $\Gamma(i+1) \approx \Gamma(1) = 1$, $\Gamma(i+s)\Gamma(i+m+1)/\Gamma(i+m+s) = \Gamma(s)\Gamma(m+1)/\Gamma(m+s)$, and $j \approx m$, we have

$$k_E = 2m\nu \frac{\Gamma(s)\Gamma(m)}{\Gamma(s+m)} = \frac{2E_d}{h} B(m, s), \quad (7)$$

where $B(m, s)$ is the Eulerian integral of the first kind (Whittaker and Watson 1927). This equation with $s = 3n - 2$ gives the n -dependence of the dissociation rate of C_{n+1}^+ after the reactive collision between C_n and C^+ .

The lifetime of $(C_{n+1}^+)^*$, $\tau = 1/k_E$ is plotted in Figure 1 for a typical set of values $\nu/c = 1500 \text{ cm}^{-1}$, $m = 30$ ($E_d = 5.6 \text{ eV}$) and 50 ($E_d = 9.3 \text{ eV}$) for $n+1 = 2-9$. It is noted that τ increases very rapidly with $n+1$, reaching 1 ms at $n = 5-6$ and 1 s at $n = 6-7$.

For a fixed value of the dissociation energy $E_d = mh\nu$, the m -dependence of k_E is given by $B(m, s)$. Thus for $m \gg s$, the m -dependence of the lifetime of C_{n+1}^+ can be approximated by (Marcus and Rice 1952)

$$\tau = k_E^{-1} \propto \frac{(m+s-1)!}{(m-1)!} \sim \left[m + \frac{s-1}{2} \right]^s. \quad (8)$$

If the value of m is increased by a factor of ξ , the lifetime increases by about $\xi^s = \xi^{3n-2}$.

From this argument, we see that the low-frequency bending vibrations of the carbon chain further magnify the lifetime of activated $(C_{n+1}^+)^*$. The frequencies of the lowest and the highest bending modes of C_{n+1}^+ are estimated to be

$$\nu_l/c \sim \frac{4000}{(n+1)^2} \text{ cm}^{-1}, \quad (9)$$

and

$$\nu_h/c \sim 690 - \frac{2000}{(n+1)^2} \text{ cm}^{-1}, \quad (10)$$

respectively, from a normal coordinate analysis (T. Rolfe, unpublished) based on the bending force constants of diacetylene (Ferigle and Weber 1955) and cyanoacetylene (Turrell, Jones, and Maki 1957). Thus, if we use the crude estimate $\nu_b \sim (\nu_l + \nu_h)/2$ as the average frequency of the bending vibrations, the average m values of the $2(n-1)$ bending vibrations are $m = 99-127$ (for $E_d = 5.6$ eV) and $m = 164-211$ (for $E_d = 9.3$ eV) for $n+1 = 3-10$.

How the energy is distributed among the n stretching vibrations and the $2(n-1)$ bending vibrations is a more involved question, but if we assume equipartition, the effective m value m_e is calculated from

$$m_e = \frac{(3n-2)E_d}{h[n\nu_s + (2n-2)\nu_b]} \sim \frac{3E_d}{h(\nu_s + 2\nu_b)} \quad (11)$$

to be approximately, $2m$, that is, $\xi = 2$. Thus, from equation (8), we estimate that the lifetime is increased by a factor of about 2^{3n-2} over the previous calculated values because of the bending vibrations. These effects of bending vibrations in magnifying the lifetime of the activated $(C_{n+1}^+)^*$ are plotted in Figure 1.

We believe that the increase of lifetime due to low-frequency bending vibrations given above is an underestimate for the following reasons: (1) We used the average of ν_h and ν_l ; but because of the extremely nonlinear form of equation (7) in m , the effect of ν_l must be more than that of ν_h . (2) Since the relative kinetic energy of C^+ and C_n is small, the low-energy bending vibration is initially excited more than the stretching vibration. (3) The neutral C_3 molecule is known to have an anomalously low bending frequency

of 63.1 cm^{-1} (Gausset *et al.* 1965). If such low frequency appears in C_{n+1}^+ also, the effective m values must be much higher. For these reasons we think that the lifetimes of $(C_{n+1}^+)^*$ calculated in this paper represent the minimum values.

III. STABILIZATION OF $(C_{n+1}^+)^*$

The energized $(C_{n+1}^+)^*$ formed from C_n and C^+ stabilizes by spontaneous emission of infrared radiation, the so-called inverse vibrational predissociation (Herzberg 1966). Since the relative kinetic energy of C_n and C^+ is very low in interstellar space and since space is essentially collision-free, spontaneous emission of only a very few infrared photons (often just one photon) is sufficient for this stabilization. If the time of such spontaneous emission is shorter than the decomposition lifetime of the energized $(C_{n+1}^+)^*$ ion as calculated in the previous section, the radiative association reaction given in equation (1) occurs efficiently. For such a case we use the Langevin formula (Landau and Lifshitz 1965)

$$k = \sigma v = 2\pi e(\alpha/M)^{1/2}, \quad (12)$$

for estimating the rate constant k and the cross section σ , for the radiative recombination reaction given in equation (1), where α is the polarizability of C_n and M is the reduced mass of C^+ with respect to C_n . This rate constant may further be enhanced by ion-quadrupole interaction at very low temperature (Takayanagi 1982).

The rate for spontaneous emission can be calculated by (Townes and Schawlow 1955)

$$1/\tau_s = \frac{4\omega^3}{3\hbar c^3} |\mu_{ij}|^2 = 3.14 \times 10^{-7} (\nu/c)^3 |\mu_{ij}|^2, \quad (13)$$

where in the last expression, the frequency ν/c in the units of cm^{-1} and the transition dipole moment μ_{ij} in the units of debyes should be used to obtain the rate in the units of s^{-1} . This formula gives a typical rate of 10 s^{-1} , that is, a lifetime of 100 ms for $\mu_{ij} = 0.1$ debyes and $\nu/c = 1500 \text{ cm}^{-1}$.

For a highly excited vibrational state with many vibrational modes, the emission lifetime is considerably shorter. The transition dipole moment is proportional to $v^{1/2}$ for the vibrational transition $v \rightarrow v-1$, and the presence of s modes (about half of which are infrared active) increases the rate of spontaneous emission by a factor of $s/2$. Using $v = m/s$, we see that the emission lifetime is shortened by about $vs/2 = m/2$. Thus, for $m = 50-100$, the lifetime is on the order of 1 to a few milliseconds. The effect of the vibrational anharmonicity in reducing the vibrational transition moments is probably not serious if s is large because then $v \sim m/s$ is much smaller than m . A more detailed estimate of the infrared emission time has recently been considered by Herbst (1982).

IV. CONCLUSION

Combining the results of §§ II and III, we estimate that the rate coefficient of the radiative association $C^+ + C_n \rightarrow C_{n+1}^+ + h\nu$ reaches the Langevin value given by equation (12) for $n \approx 4$, and thereafter the reaction proceeds with very high rates. For lower n values, the reaction is slower and the relative yield of established C_{n+1}^+ is given by

$$\phi = \frac{\tau_s^{-1}}{\tau_s^{-1} + k_E}. \quad (14)$$

The net overall reaction rate is then given by

$$k_{\text{total}} = k \frac{\tau_s^{-1}}{\tau_s^{-1} + k_E}, \quad (15)$$

where k is the Langevin rate given in equation (12). Our calculation shows that $\phi = 0$, 10^{-7} , and 10^{-3} for $n = 1$, 2, and 3, respectively. Suzuki (1981, 1982) has studied the hydrocarbon reaction scheme and found that C_3^+ is produced without radiative association through the reaction $C_2H + C^+ \rightarrow C_3^+ + H$. Thereafter, the reaction discussed in this paper will build the long chain. The actual value of ϕ may well be a few orders of magnitude higher for the reasons given at the end of the previous section. Thus the formation of C_4^+ may be reasonably efficient, and long chain molecules can be produced in interstellar space. Even for C_3^+ , if the bending vibration is much lower than estimated from equation (12) as for the neutral C_3 , ϕ would be considerably larger.

In conclusion, our calculation shows that the radiative association in equation (1) occurs rapidly for $n \geq 4$ and gives a support for the efficiency of the chemical scheme

in equations (1)–(3) through which long chain carbon molecules build up fast in the area where C^+ is abundant. This may explain the abundance of long chain molecules in space (Avery *et al.* 1976; Kroto *et al.* 1978; Broten *et al.* 1978; Bell *et al.* 1982) and especially the abundance in a cloud of low magnitude of extinction (Bell, Feldman, and Matthews 1981). The case of building such long chain carbon molecules also supports Douglas's conjecture (1977) that diffuse interstellar lines are caused by long chain carbon molecules.

The building of long chains can start from CN rather than from C_2 . The Langevin cross section then is much larger because of the charge-dipole interaction between CN and C^+ (Takayanagi 1980; Sakimoto and Takayanagi 1980; Chesnavich, Su, and Bowers 1980). This may favor building of the cyano compounds. The reaction $C + C_n^+ \rightarrow C_{n+1}^+ + h\nu$ is much less efficient than the reaction considered in this paper because (a) C_n^+ is deficient due to reaction (2), and (b) the charge transfer reaction $C + C_n^+ \rightarrow C^+ + C_n$ is exothermic by ≥ 1 eV and the excess energy will destroy the activated $(C_{n+1})^*$. Reactions of C_n or NC_n with C may be stabilized by the mechanism discussed in this paper, but the overall rate coefficient for such a neutral-neutral reaction is clearly much lower. There are many questions of this sort which complicate the problem, but discussion of them in detail is outside the scope of this paper.

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