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Ionic origins of carbenes in space

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Among the many molecules now known to enrich interstellar space are carbenes, molecules which have two electrons available on a carbon atom for chemical bonding. The dicarbenes :C=C: and :C=C=C: occur widely in the Universe, mainly in comets and the atmospheres of carbon stars[1]. Other carbenes, including: :C=S, :C=O, :C=C=C=O and :C=NH, have been identified in cool molecular gas clouds[1]. The origin of these molecules may involve ionizing radiation which, in these environments, can drive reactions between ions and molecules towards the formation of ionic carbene precursors. I now report experiments which suggest that a much higher proportion of the ion chemistry in partially ionized regions in space is directed towards the formation of carbene molecules than has previously been recognized. I identify plausible reaction paths which lead to both known and previously unknown carbenes, such as the cyclopropenylidene ring and long carbon-chain molecules. The cyclopropenylidene ring has recently been reported to be ubiquitous in the Galaxy[2,3], whereas long carbon-chain molecules have been implicated in the origin of diffuse interstellar lines[4].

The reaction paths reported here that lead towards ionic carbene precursors have been identified using the selected-ion flow tube (SIFT) apparatus which allows the measurement of specific reaction rates and product distributions of individual ion/molecule reactions[5,6] Each step in a path towards ionic growth has been studied in isolation. The ion/molecule reactions reported here have all been observed to proceed near the collision rate at room temperature and hence without activation energy. This allows the laboratory results at room-temperature to be applied to the much cooler conditions of interstellar environments.

The atomic carbon ion is fundamental to the proposed carbene ion chemistry. Measurements in our laboratory have shown that C^+ reacts quickly with acetylenes and substituted acetylenes to establish carbene cations. With acetylene for example, the $:C_3H^+$ carbene cation, a resonance hybrid of $HC^+{=}C{=}C:$ and $HC{\equiv}C{-}C:^+$, is established at the collision rate with a reaction rate constant, k, of 2.2×10^{-9} cm^3 molecule^{-1} s^{-1} (ref. 7). Carbene ions of this type are most suited to molecular growth in two important ways. First they may grow heteroatomic chain molecules because of their ability to coordinate to non-bonded electron pairs according to reaction (1), where X is the heteroatom,

$$H(C_2)_n{-}C:^+ + :XR \rightarrow H(C_2)_n^+{=}C{=}X + R \qquad (1)$$

Second, they may grow hydrocarbon-chain molecules because of their tendency for C—H bond insertion according to reaction (2):

$$R(C_2)_n{-}C:^+ + H{-}R' \rightarrow R(C_2)_n{-}CH^+{-}R' \qquad (2)$$

The product ion in reaction (2) may dissociate or lose energy by radiative or collisional stabilization. Reactions of types (1) and (2) will produce unsaturated neutral carbenes in subsequent neutralization reactions. These may involve H atom loss by recombination with an electron or the transfer of a proton to a recipient molecule, M. The neutral carbenes produced in this manner are indicated in reactions (3) and (4)

$$H(C_2)_n^+{=}C{=}X + e(M) \rightarrow :(C{=}C)_n{=}C{=}X + H(MH^+) \qquad (3)$$

$$R(C_2){-}CH^+{-}R' + e(M) \rightarrow R(C{\equiv}C)_n{-}\ddot{C}{-}R' + H(MH^+) \qquad (4)$$

and involve either cumulative double bonds or conjugated triple bonds.

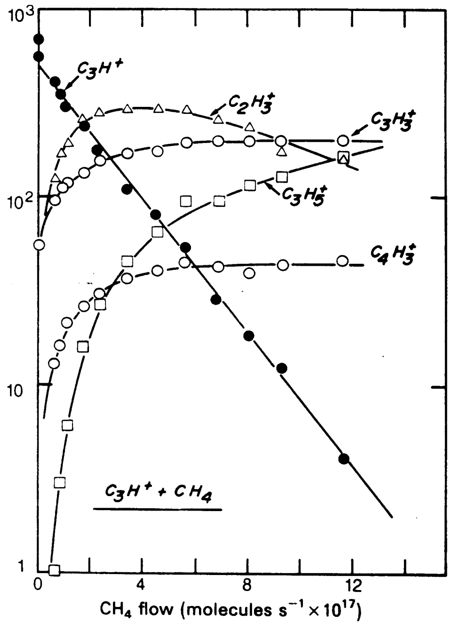

Fig. 1 Variations of ions observed with the addition of methane into the reaction region of a SIFT apparatus in which C_3H^+ has been established initially as the predominant ion[8]. The C_3H^+ is derived from propylene by electron impact at 45 eV. $P = 0.353$ torr, $\bar{v} = 7.4\times10^3$ cm s^{-1}, $L = 46$ cm, $T = 297$ K, where P, $\bar{v}$, L and T are the pressure, average flow velocity, reaction length and temperature.

In reactions of type (1), $:C_3H^+$ has been shown to abstract an oxygen atom from various interstellar molecules to form an ion which may give tricarbon monoxide on neutralization[8]. There is also an analogous sulphur chemistry which leads to the prediction of the formation of tricarbon sulphide, :C=C=C=S, in the presence of H_2S in the interstellar medium. A higher multi-carbon monoxide ion was also observed to be formed in our laboratory by addition of :CO to $:C_3H^+$, which suggests an analogous addition by radiative association and thus formation of :C=C=C=C=O in interstellar regions rich in carbon monoxide. Of course, $:C_3H^+$ itself may neutralize by proton transfer or electron/ion recombination to form the dicarbene :C=C=C:.

Other reactions of C^+ are expected to lead to $:C_3H^+$ and higher members of the homologous $H(C_2)_n{-}C:^+$ series of carbene cations, as well as substituted carbene cations of the type $R(C_2)_n{-}C:^+$. For example, we have observed that C^+ reacts with cyanoacetylene to form $:C_3H^+$ and $:C_4N^+$ in a proportion of 4:1 with $k = 6.1\times10^{-9}$ cm^3 molecule^{-1} s^{-1}, and with diacetylene to produce $:C_5H^+$ and $:C_3H^+$ in a proportion of 10:1 with $k = 1.6\times10^{-9}$ cm^3 molecule^{-1} s^{-1} (refs 9, 10). Similar reactions with higher polyacetylenes and the known interstellar polycyanoacetylenes[1] should produce the corresponding higher carbene cations $:C_5H^+$, $:C_7H^+\cdots:(C_2)_n{=}CH^+$ and $:C_6N^+$, $:C_8N^+\cdots:C^+{-}(C_2)_n{-}CN$. The former groups of ions in turn should spawn the cumulative dicarbenes $:(C{=}C)_n{=}C:$ directly by recombination with electrons or by proton transfer. Reactions with oxygen- or sulphur-bearing molecules will establish higher members of the unsaturated heteroatomic carbenes $:(C_2)_n{=}C{=}O$ and $:(C_2)_n{=}C{=}S$. The reactions of $:C^+{-}(C_2)_n{-}CN$ are uncertain but analogous reactions followed by neutralization by electron transfer could produce non-carbene chain radicals of the type $XC^{\cdot}{-}(C_2)_n{-}CN$, where X may be O or S.

The reaction of $:C_3H^+$ with methane is particularly noteworthy as it allows formation of the cyclopropenylidene ring carbene in only three steps. This reaction has been observed to be rapid, $k = 5.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1}; $C_3H_3^+$ is one of the product ions (Fig. 1). Available thermochemical data dictate that only

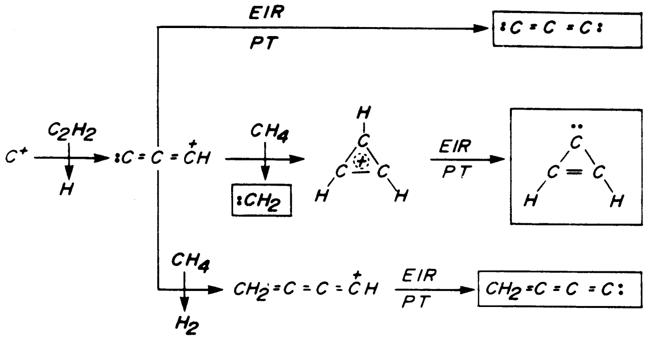

Fig. 2 Ion/molecule reactions which lead to the proposed formation of neutral carbenes from $:C_3H^+$. EIR, electron/ion recombination; PT, proton transfer.

formation of the cyclopropenium ion is exothermic with methylene as the required neutral product[8]. Neutralization of this ion by electron/ion recombination or proton transfer can lead to cyclopropenylidene. We can therefore anticipate the formation of this ring carbene as well as methylene in ionized interstellar regions containing abundant acetylene and methane in the manner shown in Fig. 2. The formation of $C_3H_3^+$ from the reaction of $:C_3H^+$ with H_2, which has been proposed as an alternative intermediate step in the formation of $:C_3H_2$, is less definitive because both the cyclopropenium and the linear propargyl cations are possible products[11]. Figure 1 also demonstrates that another channel for the reaction of $:C_3H^+$ with CH_4 is the production of $C_4H_3^+$ which may neutralize to form the carbene $:C{=}C{=}C{=}CH_2$. The next member of the homologous series of these carbenes also appears to be accessible, in this case through the reaction of CH_3^+ with diacetylene, which has been seen to produce $C_3H_3^+$ in 1 of 10 reactive collisions with $k = 1.3 \times 10^{-9}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ (ref. 10). The $C_5H_3^+$ cation may neutralize to form $:C{=}C{=}C{=}C{=}CH_2$ (or $:CH{-}C{\equiv}C{-}C{\equiv}CH$).

Reactions of type (2) were observed to predominate, with the carbene cations $:C_3H^+$ and $:C_4H^+$ in reactions with HCN, CH_3CN, and HC_2CN. Exclusive addition reactions were observed in our laboratory to proceed with unexpectedly high efficiency at the collision rate[8,9]. The high efficiencies suggest that analogous addition reactions proceed in the interstellar medium by radiative association as in reaction (5)[12].

$$R{-}C{:}^{+} + H{-}R' \rightarrow R{-}CH^{+}{-}R' + h\nu \qquad (5)$$

Neutralization according to reaction (4) will then produce the carbene. Reactions of type (2) were observed which correspond to the possible formation of the substituted carbenes $:C(C_2H)CN$, $:C(C_2H)CH_2CN$, $:C(C_2H)C_2CN$ and $:C(C_2CN)_2$.

In summary, the observed ion chemistry clearly points towards the formation of many carbenes including methylene, completely unsaturated chain-like carbenes (with some incorporating an oxygen, sulphur or nitrogen atom), slightly hydrogenated chain-like carbenes and one aromatic ring carbene. I have shown that formation of these carbenes can be initiated by rapid reactions of C^+ with simple interstellar molecules. Also, radiative association reactions are proposed which may lead to larger substituted carbene molecules. Formation of all these carbenes should provide further opportunities for molecular growth in the interstellar medium. This growth would not be restricted to reactions with ions but could involve reactions of carbenes with neutral molecules or other carbenes. In terrestrial organic chemistry, carbenes are among the most versatile and synthetically useful reactive intermediates, and they should have a similar function in extraterrestrial chemistry. For example, there are intriguing possibilities for the growth of graphite-like molecules from carbenes with either cumulative double bonds or conjugated triple bonds. Side-on interaction between two carbenes of one type or the other can lead to ring formation through cross-bonding, the inverse of the pyrolitic decomposition of graphite[13]. Alternatively, the long-chain carbenes may aggregate to form small interstellar grains, as suggested by Douglas[4].

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