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THE SYNTHESIS OF BENZENE IN THE PROTO–PLANETARY NEBULA CRL 618

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ABSTRACT

We show that the physical conditions in CRL 618 are such that efficient formation of benzene, C_6H_6, occurs. A combination of high temperatures, high densities, and high ionization rates drives an efficient ion-molecule chemistry involving condensation reactions of acetylene and its derivatives, rather than reactions involving atomic hydrogen, as was suggested for the interstellar synthesis of benzene. We find a column density of benzene within a factor of 2 of that observed providing that the material is trapped in a long-lived reservoir of gas in the disk around CRL 618. We note that the chemistry can give rise to other carbon chain molecules as well as a large abundance of benzonitrile, C_6H_5CN.

Subject headings: astrochemistry — stars: AGB and post-AGB — stars: individual (CRL 618)

1. INTRODUCTION

Benzene, C_6H_6, is the smallest of the cyclic aromatic molecules. It is abundant on Earth (in petrol, plastics, detergents, etc.) and also more widely in the solar system (in the atmospheres of Jupiter and Saturn, for example) but until recently was unknown in the further reaches of the universe. It is difficult to detect, in that its emission lies in the infrared regime and is not directly observable from the ground. One of the many successes of the *Infrared Space Observatory* (*ISO*) was the detection of benzene in the proto–planetary nebula (PPN) CRL 618 (Cernicharo et al. 2001b). The detection of benzene in this object is significant because it heralds the beginning of an astrochemistry that is not solely based on linear carbon molecules and small species. It also may prove to be the first step to the formation of polycyclic aromatic hydrocarbons, which are thought to be responsible for unidentified infrared bands and diffuse interstellar bands. Furthermore, understanding the formation of benzene and a chemistry in which rings form readily may eventually help us to understand the formation processes behind prebiotic molecules. Here we present a gas-phase chemical model of CRL 618 in which we show that efficient benzene formation is related to a high flux of ionizing radiation. Such a flux may have occurred early in the history of the solar system.

CRL 618 is a carbon-rich PPN (rather than oxygen-rich) with high-velocity outflows, with speeds of up to 200 km s^{-1}, which are constrained by a disk, with an angular size of about 1″, of hot (>200 K), dense (~10^7 cm^{-3}) gas (Martín-Pintado et al. 1995). It exhibits a complex chemistry and is in transition from the asymptotic giant branch (AGB) to the planetary nebula (PN) phase of stellar evolution. This transition is poorly understood but is thought to occur rapidly, probably in less than 1000 yr, and is important in determining the varied morphologies observed in PNs as compared to spherically symmetric stars. In addition, this transition may help determine the nature of the material returned to the interstellar medium as the star approaches the end of its life.

2. CHEMICAL MODEL OF CRL 618

To date, over 50 molecules have been detected in circumstellar envelopes (Olofsson 1996), mostly in the carbon-rich AGB star IRC +10°216 and some 122 in the interstellar medium in general (A. Wootten 2002;[1] as of April 2002). These range from simple diatomic molecules, like molecular hydrogen, H_2, and carbon monoxide, CO, through to the 13-atom linear carbon chain, $HC_{11}N$. In addition to C_6H_6, *ISO* has also been used to detect several other complex species in CRL 618, including C_4H_2, C_6H_2, C_2H_4, CH_3C_2H, and CH_3C_4H (Cernicharo et al. 2001a, 2001b). More surprisingly, emission from H_2O has also been detected by *ISO* (Herpin & Cernicharo 2000) despite the fact that, normally, water is detected only in oxygen-rich environments. While H_2O has also been detected in IRC +10°216 (Melnick et al. 2001), where it is explained as due to the breakup of cometary bodies, the abundance of water in CRL 618 is too large for this to be the case. Instead, it is likely that water is the result of high-temperature shock chemistry driven by the interaction of the outflow from the central star with the ambient gas. Benzene has not been detected in IRC +10°216.

We have investigated benzene formation quantitatively by using a detailed chemical kinetic model that involves 3880 reactions among 407 species consisting of the six elements: H, He, C, N, O, and S. This model has been previously used to model the chemically rich carbon star, IRC +10°216 (Millar, Herbst, & Bettens 2000). Table 1 lists the initial fractional abundances adopted at the inner radius. To describe the physical conditions in CRL 618, we have used data taken from model fits to *ISO* observations in Herpin & Cernicharo (2000). The hot (30,000 K) central star provides a UV flux of 2×10^5 times the ambient interstellar UV flux, G_0. We model the molecular gas as a shell with a temperature of 250 K at an initial inner radius of 10^{14} cm that drifts away from the central star at a velocity of 1 km s^{-1}; the low velocity simulates the presence of a long-lived reservoir of gas in the disk around CRL 618. A similar scenario

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[1] See http://www.cv.nrao.edu/~awootten/allmols.html.

TABLE 1

Adopted Initial Fractional Abundances of Parent Species with Respect to $n(H_2)$

Species	Initial Fractional Abundance
He	1.5×10^{-1}
CO	6.0×10^{-4}
C_2H_2	5.0×10^{-5}
CH_4	2.0×10^{-6}
HCN	8.0×10^{-6}
NH_3	2.0×10^{-6}
N_2	2.0×10^{-4}
CS	4.0×10^{-6}
H_2S	1.0×10^{-6}

has been proposed for the Red Rectangle by Jura, Balm, & Kahane (1995). The mass-loss rate equivalent to this gas flow is approximately $7 \times 10^{-5}\ M_{\odot}\ \mathrm{yr}^{-1}$, which gives an initial abundance of H_2 of $10^{11}\ \mathrm{cm}^{-3}$ at the inner boundary. We assume that the shell remains at constant thickness, chosen to be 3×10^{13} cm, as it moves away so that its internal density varies with radius from the star as $1/r^2$, corresponding to a $1/t^2$ law. This results in the intrinsic visual and UV extinctions also following a $1/r^2$ law. The initial visual extinction, A_V, is then around 3600 mag at a radius of 10^{14} cm.

3. RESULTS

The interstellar route to benzene formation has been studied by McEwan et al. (1999), who used laboratory measurements of three-body association reactions to infer radiative association rate coefficients involving atomic hydrogen to synthesize benzene. In CRL 618, atomic hydrogen is not particularly abundant, 1×10^{-7} relative to molecular hydrogen, and does not contribute to the formation of benzene until a distance of 10^{17} cm from the star, some 50 times further out than the peak abundance of benzene, although the C_2H_2 abundance is so low by this distance that benzene formation is inefficient.

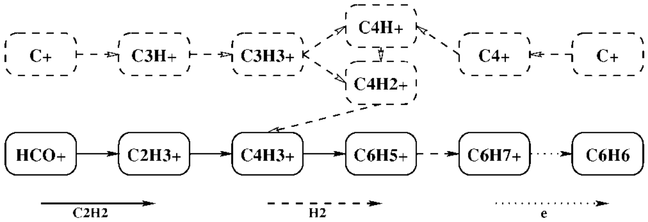

Fig. 1.—Synthesis of benzene in CRL 618. The upper chain (*dashed boxes and arrows*) shows the inefficient interstellar formation mechanism. The lower chain (*solid boxes and arrows*) shows the new circumstellar formation process discovered in CRL 618. A key to the arrows in the lower chain is given at the bottom of the figure.

We find that benzene formation under our adopted conditions for CRL 618 is much more efficient than in interstellar clouds or cool circumstellar shells around AGB stars. The synthesis relies on relatively large fractional abundances of both HCO^+ and C_2H_2. The former ion is detected only at very low levels in AGB star envelopes but is observed in PPNs in large abundances (Deguchi et al. 1990), which reflects the much greater level of ionizing radiation in PPNs. This may be due to soft X-rays, shock waves, and cosmic-ray particles. We simulate this through an enhancement of the cosmic-ray ionization rate by a factor of 100 over the standard interstellar rate. The direct ionization of H_2, followed by proton transfer between H_3^+ and CO, leads to HCO^+ production. Reaction of H_3^+ with CO is the dominant loss mechanism for this ion, so that the molecular abundances calculated are independent of the choice of the rate coefficient for the dissociative recombination of H_3^+ with electrons. Once HCO^+ is formed, it can transfer a proton to the C_2H_2 parent molecule and drive very efficient synthesis of $C_4H_3^+$, which is followed by reactions (3)–(5) to form benzene (Fig. 1). The reaction scheme can be written as

$$HCO^+ + C_2H_2 \rightarrow C_2H_3^+ + CO, \tag{1}$$

$$C_2H_3^+ + C_2H_2 \rightarrow C_4H_3^+ + H_2, \tag{2}$$

$$C_4H_3^+ + C_2H_2 \rightarrow c\text{-}C_6H_5^+ + h\nu, \tag{3}$$

$$c\text{-}C_6H_5^+ + H_2 \rightarrow c\text{-}C_6H_7^+ + h\nu, \tag{4}$$

which, when followed by dissociative reaction,

$$c\text{-}C_6H_7^+ + e \rightarrow c\text{-}C_6H_6 + H, \tag{5}$$

forms benzene, where we denote cyclic species by the prefix "*c*-." Reaction (3) has been measured in the laboratory by Scott et al. (1997) in the three-body limit and shown to produce cyclic $C_6H_5^+$. The corresponding radiative association rate coefficient has been included in models for some time. The radiative association rate coefficient for reaction (4) was determined by McEwan et al. (1999).

The model predicts a high abundance of HCO^+, with a column density of $2.0 \times 10^{11}\ \mathrm{cm}^{-2}$, which, coupled with abundant C_2H_2 (a column density of $1.1 \times 10^{17}\ \mathrm{cm}^{-2}$, at an inner radius of 2×10^{15} cm, and a factor of ∼2 lower than observed by Cernicharo et al. 2001b), ensures that our formation mechanism is very efficient. At 2×10^{15} cm, our calculated benzene column density is $7.4 \times 10^{15}\ \mathrm{cm}^{-2}$, less than 2 times larger than observed (Cernicharo et al. 2001b). Finally, we note that condensation reactions of acetylene and its derivatives drive efficient formation of the series C_nH_2. We find column densities of C_4H_2 and C_6H_2 of $1.9 \times 10^{16}\ \mathrm{cm}^{-2}$ and $1.3 \times 10^{16}\ \mathrm{cm}^{-2}$, respectively, within a factor of 4–6 of those observed (Cernicharo et al. 2001b).

Figure 2 shows the radial distribution of some relevant species, including benzene, around CRL 618. As can be seen from the figure, the fractional abundance of benzene becomes very large, $\sim 10^{-6}$, at a radius of $\sim 2 \times 10^{15}$ cm. For an expansion velocity of $1\ \mathrm{km\ s}^{-1}$, this corresponds to a timescale of around 600 yr. Figure 2 shows that the abundances of all species fall rapidly at a distance of $\sim 3.5 \times 10^{15}$ cm. This is due to the rapid increase in the UV flux that occurs when A_V is around 20 mag. For smaller distances, dust absorption ensures that the photon flux is negligible despite the fact that the unshielded flux is some 2×10^5 times greater than the interstellar flux. We note here that if we adopt an expansion velocity more typical of that in a circumstellar wind ($20\ \mathrm{km\ s}^{-1}$), the timescale for removal of benzene becomes very short, ∼30 yr, as the shell dilutes in density, and hence extinction, very rapidly. An alternative choice for the location of benzene would be in a stationary, or rotating, disk, in which the timescale becomes that at which the star evolves to higher temperature and erodes the disk by photoionization, typically 10^3 yr.

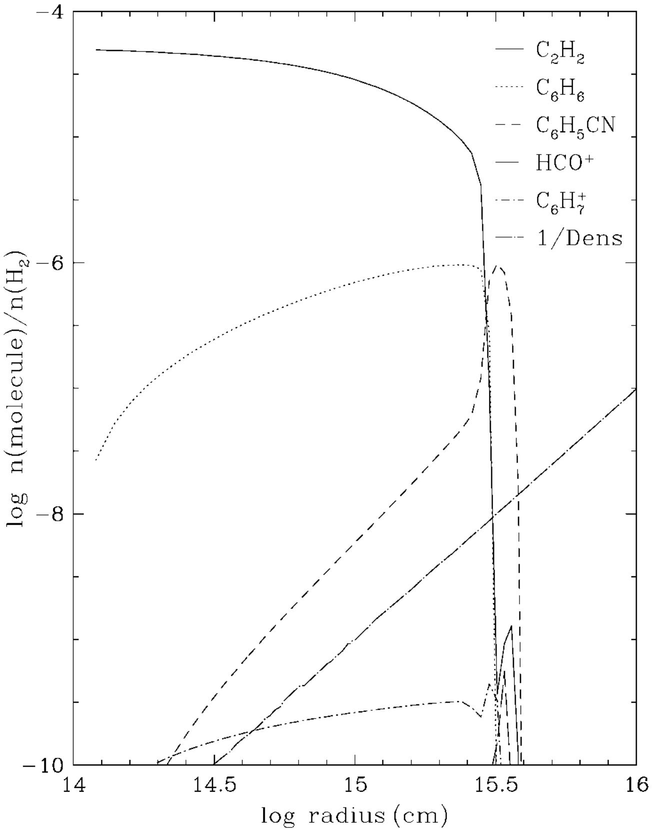

FIG. 2.—Fractional abundance of benzene and other molecules as a function of the inner radius of the shell. The straight line labeled 1/Dens shows log [1/$n(H_2)$].

4. DISCUSSION

The endpoint of PPN evolution is the formation of fully fledged PNs. These are seen to be very molecule deficient, which is in agreement with the rapid decrease in abundances shown in Figure 2 as molecules become photodissociated by the large UV photon flux. The very fact that some simple molecules are seen in PNs indicates that molecules must be shielded, most likely in small dense clumps, to survive the transition from PPNs to PNs. It is possible that some complex molecules also survive in these clumps.

The large abundances of HCO^+ observed in PPNs and young PNs led Deguchi et al. (1990) to suggest that ionization was provided by X-ray emission from the central stars. Their calculations were applied by Cox et al. (1992) to the particular case of CRL 618, and it was concluded that the central star was not hot enough. Hence, the source of ionization must be due to something other than the central star alone. One strong possibility is that CRL 618 contains a binary, with an accretion flow being the source of the ionization (Livio & Shaviv 1975). The presence of a fast bipolar outflow and disk is normally interpreted in terms of a binary, where the infall on the secondary star supplies the energy for the outflow (Bujarrabal et al. 2001).

Further evidence for complex chemistry in CRL 618 comes from the detection of infrared absorption and emission bands from carbonaceous particles. Chiar et al. (1998) have detected absorption at 3.4 μm in CRL 618. The absorption band is thought to be due to an aliphatic hydrocarbon component in interstellar dust and is normally detected in the diffuse interstellar medium. CRL 618 also shows a weak emission band at 3.3 μm, thought to be due to aromatic C−H stretch. The absorption band in CRL 618 and in the interstellar medium is very similar in shape to that found in meteoritic organic matter that has a "kerogen" structure consisting of a mixture of aliphatic and aromatic components. The formation mechanism of these complex molecules in space is not certain, but most theories to date rely on the formation of a molecule, such as benzene, with a single ring, followed by additions of C_2H_2 or C_2H and subsequent closure to form an additional ring (Frenklach & Feigelson 1989; Cherchneff, Barker, & Tielens 1992). These mechanisms use a neutral-neutral chemistry and need very high densities and temperatures in the vicinity of 1000 K to be efficient. Our calculation of a large benzene abundance indicates that the environment of CRL 618 is indeed one in which complex organic molecule formation might also be efficient. Could this synthesis be efficient in standard, oxygen-rich, interstellar clouds such as Sgr B2? Given that typical interstellar abundances of C_2H_2 are about 100 times less than those detected in carbon-rich, circumstellar environments, it appears that the interstellar abundance of benzene will be quite low.

Our finding that enhanced ionizing radiation results in a large abundance of a complex ring molecule leads to an interesting hypothesis: if benzene can be formed efficiently near regions with intense sources of ionization (such as a supernova or a low-mass star with a high X-ray production), then it could be the route to the original formation of complex organic molecules in the solar system. The presence of abundant short-lived radio nuclides (^{40}Ca, ^{26}Al, ^{60}Fe, ^{53}Mn) in the early solar system has been interpreted as due to a nearby supernova (Cameron et al. 1995). There is strong evidence for the injection of carbon-rich material into the presolar nebula (Amari et al. 2001). Furthermore, another source of acetylene in the inner disk is the combustion (evaporation) of carbonaceous grains (Finocchi, Gail, & Duschl 1997; Wehrstedt & Gail 2002), which enhances carbon locally. Under these conditions, the formation of prebiotic molecules in the forming solar system could have occurred under conditions not dissimilar from those in CRL 618. The effect of high-energy sources of ionization on the complex chemistry in proto–planetary disks should be explored along the lines discussed by Aikawa & Herbst (2001).

Finally, we note that other complex molecules might be detectable in CRL 618. As an example, benzonitrile, C_6H_5CN, is also predicted to have a high abundance, ~10^{-6}, similar to benzene. It is produced in the neutral-neutral reaction

$$CN + C_6H_6 \rightarrow C_6H_5CN + H \qquad (6)$$

with a rate coefficient of 2×10^{-10} cm^3 s^{-1} and has an electric dipole moment of 4.3 D. A fuller discussion of the chemistry of CRL 618 is in preparation.

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