

Organic molecules in oxygen-rich circumstellar envelopes: methanol and hydrocarbons

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ABSTRACT

The existence of anomalously high abundances of gaseous CH₄ has been invoked to explain the unexpectedly high abundances of the carbon-bearing molecules HCN and H₂CO in the outflows from O-rich red giants. We have modelled the chemistry that proceeds in the outer envelope when CH₄ is injected from the inner envelope. We find that photolysis by the interstellar radiation field drives an ion-neutral chemistry which produces several organic molecules. The calculated abundances of CH₃OH, C₂H and C₂ can be comparable to those calculated for H₂CO and HCN. Species such as C₂H₄, C₂H₂ and CH₃CN can also be abundant. A search for CH₃OH and C₂H in several O-rich outflows known to exhibit strong HCN emission is needed. As it derives entirely from the CH₄ photochain, is insensitive to the envelope temperature distribution, and has accessible transitions at millimetre wavelengths, the detection of the C₂H radical would provide further indirect support for the presence of the hypothesized methane.

Key words: molecular processes – circumstellar matter – stars: late-type.

1 INTRODUCTION

Infrared, millimetre, submillimetre and radio observations of the expanding, massive envelopes (or winds) of cool, late-type stars have revealed a rich chemical inventory (see reviews by Millar 1988, Olofsson 1988, Jura 1990 and Omont 1993). An outstanding theoretical problem in circumstellar chemistry is to account for the presence and unexpectedly high abundances of several C-bearing molecules in envelopes that are ostensibly O-rich (Olofsson 1988; Nercissian et al. 1989; Lindqvist et al. 1988, 1992; Olofsson et al. 1991). In particular, a major puzzle is the presence of HCN in many oxygen-rich sources with abundances in the range $\text{HCN}/\text{H}_2 \sim (0.04-6) \times 10^{-6}$ (Lindqvist et al. 1988, 1992; Nercissian et al. 1989; Bujarbal, Fuente & Omont 1994). On the basis of photospheric molecule formation in local thermodynamic equilibrium (LTE), oxygen-rich circumstellar envelopes (CSEs) are expected to have essentially all of their available carbon locked in CO; the excess oxygen is present in water, and hydrocarbon molecules such as HCN and CH₄ have negligible abundances (Tsuji 1973). Carbon-rich CSEs, on the other hand, have most of the available oxygen locked in CO, and the excess carbon available (mostly as C₂H₂) leads

to the formation of many C-bearing molecules in the wind (e.g. IRC + 10216: Cherchneff, Glassgold & Mamon 1993). Photochemical models of the outer regions of O-rich CSEs that rely on transferring carbon atoms from CO into HCN fail spectacularly to reproduce the observed abundances of HCN (Nejad & Millar 1988; Nercissian et al. 1989).

Hydrogen cyanide can be formed in the outer envelope by reaction of atomic N with CH₂ and CH₃, the respective photoproducts of N₂ and CH₄. Nejad & Millar (1988) postulated that these objects possess an excess of methane, which they attributed to grain surface reactions deep in the envelope, and demonstrated that inclusion of this CH₄ gave much better agreement with the observed HCN abundances. The abundance of CH₄ required to explain the HCN observations is substantial, $\text{CH}_4/\text{H}_2 \sim (0.1-1) \times 10^{-5}$. Recently, Millar & Olofsson (1993) have invoked the hypothesized methane to show that the observed abundance of formaldehyde in OH231.8+4.2 (Lindqvist et al. 1992) could be explained by reaction of CH₃ with atomic oxygen, and that H₂CO should be detectable in several other oxygen-rich envelopes. In this Letter we report theoretical results which predict that other carbon-bearing molecules can form in these envelopes.

2 CIRCUMSTELLAR CHEMISTRY DRIVEN BY METHANE

A general picture for the chemistry in these envelopes has now developed (see Jura 1990). Near the stellar photosphere, the gas is in LTE and the molecular composition is effectively determined by the C/O ratio and the temperature (Tsuji 1973). At some distance above the photosphere, dust grains condense out from the gas phase, forming silicate grains in the O-rich case. Stellar radiation pressure causes the dust to stream through the gas and drag it along to create a massive expanding envelope of gas and dust. This mechanism produces winds with terminal velocities in the range of $10\text{--}30\text{ km s}^{-1}$ (e.g. Tielens 1983). As gas and dust flow away from the star, their densities and temperatures fall until, in the outer regions of the envelope, molecules originally formed in LTE are photodissociated by interstellar UV photons; it is in this region that a rich photochemistry ensues, involving neutral-neutral and ion-neutral reactions. The approach to the chemical modelling that we employed has been described elsewhere (Millar 1988), and in this Letter we describe the organic photochemistry initiated by methane.

2.1 Photochemical model

We considered a spherically symmetric outflow with constant mass-loss rate, \dot{M}_* , and terminal expansion speed, v_∞ . We solved the chemical kinetic equations as a function of radius from some inner radius of the dust envelope, R_i , taken to be 10^{15} cm , out to some outer envelope radius, taken to be 10^{18} cm , at which point all LTE-produced species, except CO in the highest \dot{M}_* CSEs, have been photodissociated. The assumed LTE abundances relative to H_2 of H_2O , N_2 , NH_3 and CO defined at R_i were appropriate for an O-rich outflow, and were 3×10^{-4} , 5×10^{-5} , 1×10^{-6} and 2×10^{-4} , respectively (Nejad & Millar 1988). For the abundance of methane relative to H_2 at R_i , we adopted a value of 3×10^{-5} , since this reproduces the observed HCN and H_2CO abundances (Millar & Olofsson 1993). As in similar models (Nercessian et al. 1989), all refractory metals were assumed to be incorporated in dust grains, and any SiO remaining after silicate condensation was assumed to have been depleted on to cool grains (Jura & Morris 1985); sulphur chemistry was omitted (but see Section 2.2).

We included cosmic ray ionization processes and H_2 formation on grain surfaces, as well as molecular self-shielding by H_2O and CO. For the continuum photodissociation of H_2O , we split the dissociating continuum into three bands and solved for the H_2O radial distribution iteratively, as described by Mamon, Glassgold & Omont (1987). For line dissociation of CO, we adopted the 'schematic theory' of Morris & Jura (1983) with the parameters of Mamon, Glassgold & Huggins (1988) to compute the C^+ radial abundance distribution most accurately. For continuum shielding by dust, we employed the approach of Mamon et al. (1987) and used their dust shielding lengths for each species.

For the major molecular species we adopted the unshielded photodissociation and photoionization rates and shielding lengths (suitably re-scaled to \dot{M}_*) of Mamon et al. (1987) and Nercessian et al. (1989). We used an unshielded rate of $1.9 \times 10^{-9}\text{ s}^{-1}$ for N_2 photodissociation. The

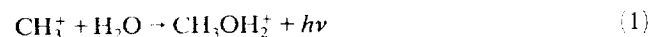
unshielded photorates for other species were taken from the compilation of Millar et al. (1991b), with additions and revisions from the work of Roberge et al. (1991) where appropriate. For neutral species not listed by either Millar et al. or Roberge et al., an unshielded photodissociation rate of $1.0 \times 10^{-9}\text{ s}^{-1}$ was assumed; this choice has a negligible effect on the results, as none of the relevant molecules (e.g. HCOOCH_3) plays a significant part in the chemistry.

The organic chemistry used has been described in detail elsewhere (Charnley, Tielens & Millar 1992, and references therein); the most important processes are identified and discussed in Section 2.2 below. We employed a gas temperature distribution of the form $T_i(R_i/r)^{0.6}$ down to 10 K where it remains constant due to grain photoelectric heating. We chose $T_i = 150\text{ K}$ for $\dot{M}_* > 10^{-6}\text{ M}_\odot\text{ yr}^{-1}$ and $T_i = 300\text{ K}$ otherwise (Millar & Olofsson 1993). These choices are designed to account roughly for the fact that the principal heating contribution to the radial temperature gradient is due to gas-grain collisions and is proportional to $(L_*/\dot{M}_*v_\infty)^{0.5}$ (Kwan & Linke 1982). The calculations presented here used a fixed expansion speed of 15 km s^{-1} .

2.2 Results

The radial distributions of organic molecules in oxygen-rich CSEs with mass-loss rates of 10^{-5} and $10^{-7}\text{ M}_\odot\text{ yr}^{-1}$ are shown in Fig. 1. The organic photochemistry that ensues in the outer envelope is due entirely to the influx of methane molecules from the inner regions. The importance of neutral-neutral reactions for O-rich envelopes has long been recognized (Scalo & Slavsky 1980), and these account for the observed HCN and H_2CO (see Section 1). However, the formation of many of the organic species in Fig. 1 is by ion-neutral reactions driven by the photon field. At a given radius in the CSE, depending upon the value of the ratio \dot{M}_*/v_∞ , the products of methane photochemistry all become abundant: CH_4 , CH_3 , CH and CH_3^+ . Rapid reactions with H_2 quickly channel any CH_3^+ and CH^+ into CH_3^+ .

The chemical importance of CH_3^+ lies in the fact that it reacts much more slowly with H_2 than do any of the CH_m^+ , and so represents a bottleneck for the ionized carbon photo-produced from CH_4 . Consequently, removal of CH_3^+ by reactions with abundant neutral molecules in the outflow, specifically H_2O and CH_4 , is competitive with CH_3^+ formation. The reaction



accounts for the methanol produced in the models. Photodestruction of CH_3OH provides an additional source of H_2CO . The radiative association of CH_3^+ with CO proceeds more slowly than that of (1) and leads to ketene (CH_3CO). Despite the large overabundance of CO relative to HCN, the high rate coefficient for radiative association of CH_3^+ with HCN offsets the lower HCN abundance attained by neutral reactions, leading to a peak methyl cyanide (CH_3CN) abundance greater than that of CH_3CO but lower than that of CH_3OH .

The molecular distributions produced by the hydrocarbon chemistry (summarized in Fig. 2) can be best understood by specifically considering the $10^{-5}\text{ M}_\odot\text{ yr}^{-1}$ model (Fig. 1b). For $r \sim 10^{16}\text{ cm}$, ethene and acetylene are formed by the pathways involving CH_3^+ with CH_4 and CH_2 (Fig. 2). Direct photodissociation of C_2H_4 is a significant source of C_2H_2

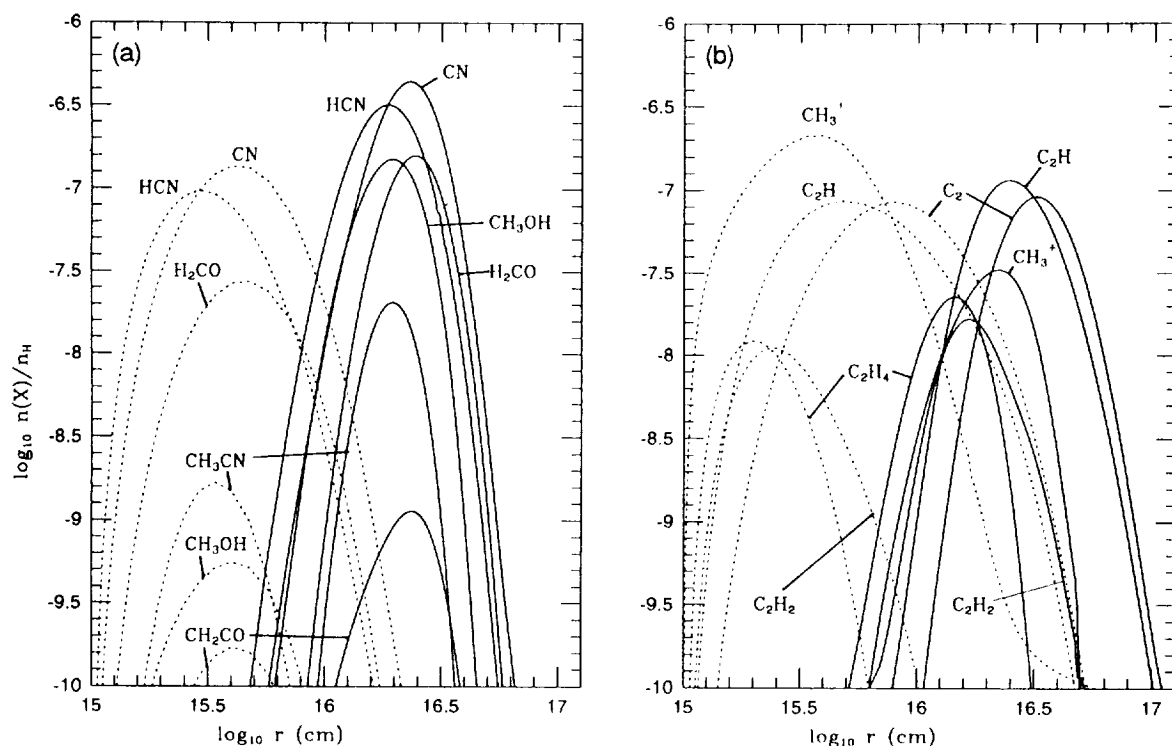


Figure 1. Radial abundance distributions of molecules formed from excess circumstellar methane: (a) oxygen-bearing and nitrogen-bearing species; (b) hydrocarbons. Models shown are for mass-loss rates of $10^{-5} M_{\odot} \text{ yr}^{-1}$ (full curves) and $10^{-7} M_{\odot} \text{ yr}^{-1}$ (dotted curves).

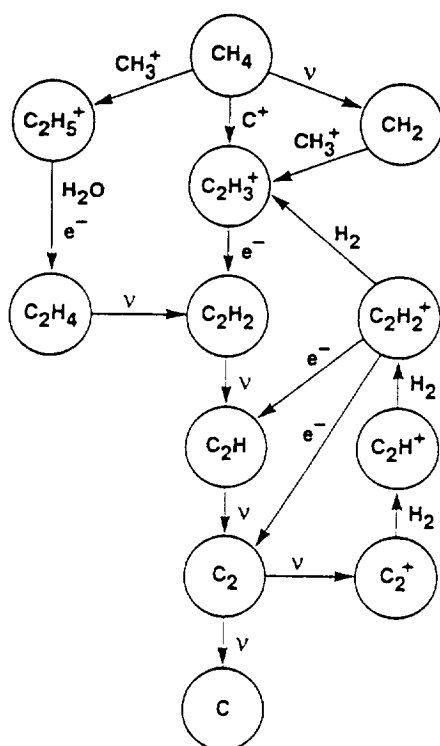


Figure 2. The circumstellar hydrocarbon chemistry driven by methane.

molecules (≈ 30 per cent) but the dominant source is dissociative recombination (of C_2H_2^+ and C_2H_3^+ ; Glassgold, Omont & Guélin 1992). At $r \sim 3 \times 10^{16}$ cm and beyond, C^+ production, the major source of electrons in these models, increases the efficiency of dissociative recombination. As C^+ recombines more slowly than CH_3^+ , reactions involving CH_3^+ become less important in the outer envelope where the hydrocarbon chemistry is driven by C^+ insertion in CH_4 , and where the chemistries of C_2H_4 and C_3H_2 are effectively decoupled. The photochemistries of the ethynyl radical (C_2H) and the carbon dimer are as shown in Fig. 2. Photo-ionization of C_2 recycles carbon back into the acetylenic photochain via rapid reactions of H_2 with C_2H_m^+ ($m = 0, 1, 2, 3$); this accounts for the high abundances of C_2H and C_2 in the outer envelope.

The mass-loss rates of the models shown in Fig. 1 span a range that includes many HCN-containing CSEs. In the model with the lower \dot{M}_* , the photochemical region is shifted to smaller radii and is less extended, relative to the higher \dot{M}_* case, since here external UV photons can penetrate further into the envelope (Nercessian et al. 1989). As the rate coefficients for radiative associations have inverse temperature dependences, the higher temperatures and lower densities in the photochemical region of the lower \dot{M}_* model suppress the radiative association of CH_3^+ with CO , H_2O and H_2 in the outflow, and lead to its higher CH_3^+ abundance. The much lower CH_3OH abundance at $10^{-7} M_{\odot} \text{ yr}^{-1}$ is due to the unfavourable physical conditions and the form of the rate

coefficient of reaction (1) appropriate in the temperature range 70–300 K (Millar, Herbst & Charnley 1991a); both factors combine to reduce the CH_3OH_2^+ production rate to about a factor of 100 less than that of the $10^{-5} M_\odot \text{ yr}^{-1}$ model. The peak abundances of the C_2 -bearing species are insensitive to the temperature distribution.

Neutral-neutral reactions have long been known to be important in these objects (Scalo & Slavsky 1980; Nejad & Millar 1988). Our calculations show that ion-neutral reactions may also be important and, as there are no conceivable neutral co-reactants that could remove ions faster than those we have included, we now consider factors that could impair their efficacy by increasing the electron density in the outer envelope. The circumstellar gas is assumed to be free of refractory metal atoms (Al, Mg, Na, Fe), and silicon monoxide is probably depleted with a high enough efficiency that photoionization of Si is not a significant source of electrons (Section 2.1). The models in Fig. 1, however, like those of Nercissian et al. (1989), neglect sulphur chemistry; if sufficiently abundant, S^+ can be a major source of electrons. In LTE, gas-phase sulphur is present as H_2S , which is too volatile to accrete on dust and so flows into the photochemical region where it is destroyed and produces electrons. As it depends on knowledge of the H/H_2 ratio and detailed modelling of the temperature structure, a comprehensive treatment of circumstellar S chemistry is beyond the scope of this paper and is deferred to a further paper (Charnley, in preparation). By considering only the H_2S photochain, an appreciation of the role of sulphur in depressing ion-molecule chemistry can be obtained. Fig. 3

shows the result of injecting sulphur with an abundance relative to H_2 of 10^{-5} (Omont et al. 1993) in the $10^{-5} M_\odot \text{ yr}^{-1}$ model of Fig. 1. Two cases are shown, distinguished by whether or not H_2S is destroyed by H atom reactions in the warm inner envelope (Scalo & Slavsky 1980). The CH_3^+ abundance is reduced by over a factor of 10, and this is reflected in lower abundances of these molecules derived from it, specifically CH_3OH . HCN and CN are unaffected. The peak C_2H abundance is reduced by only a factor of 3, owing to the fact that here the acetylenic photochain is primarily driven by C^+ which recombines relatively slowly compared to CH_3^+ . Since neutral reactions involving S and SH to form SO and SO_2 , both known to be abundant in these objects (Omont et al. 1993), were omitted, the C_2H abundances shown in Fig. 3 are probably the lowest attainable in this model.

When the amount of CH_4 injected into the outer envelope is fixed, photochemical models show that peak HCN abundances should roughly increase with increasing \dot{M}_* . Observations of O-rich envelopes (Lindqvist et al. 1992; Bujarrabal et al. 1994) show that measured peak HCN abundances vary by factors of ≈ 100 and do not correlate clearly with \dot{M}_* . In the context of our models, the HCN abundance is more sensitive to the amount of CH_4 injected, and so if C_2H also traces CH_4 , as our calculations demonstrate, then we expect its abundance and that of HCN to be correlated. Note that, to reproduce an HCN abundance of a few $\times 10^{-6}$ in TX Cam (Lindqvist et al. 1992), methane abundances that are a significant fraction of that of the available carbon are required. It remains to be seen whether

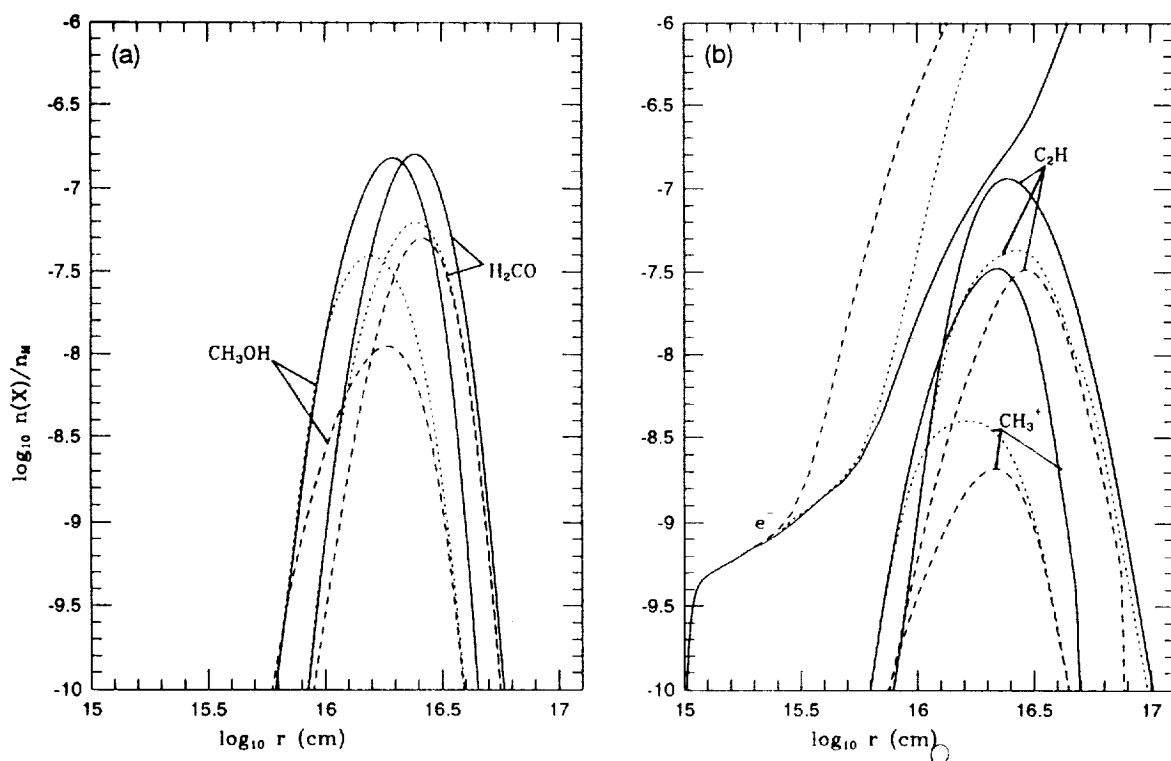


Figure 3. The effect of sulphur on the ion-molecule chemistry of key species in the $10^{-5} M_\odot \text{ yr}^{-1}$ model of Fig. 1. Cases shown are no S injected (full curves); all S injected as H_2S (dotted curves), and all S injected as atoms (dashed curves).

this CH_4 production efficiency can be realized by either of the proposed mechanisms for forming the putative methane: grain surface reactions (Nejad & Millar 1988) or UV/shock chemistry (Nercessian et al. 1989).

3 CONCLUSIONS

We have shown that circumstellar methane can initiate an *ion-molecule* chemistry in oxygen-rich envelopes that yields significant abundances of C_2H_4 , C_2H_2 , C_2H , C_2 and CH_3OH . We predict H_2CO , CH_3CN and NO also to be abundant (see Nejad & Millar 1988; Nercessian et al. 1989; Millar & Olofsson 1993). As CH_3OH and C_2H have strong transitions at millimetre wavelengths, we expect that such observations should detect these molecules in some oxygen-rich envelopes where HCN emission has already been observed. Observations of circumstellar C_2H_4 and C_2H_2 will require infrared spectroscopy (Goldhaber, Betz & Ottusch 1987; Lacy et al. 1991).

From our calculations, red giants with higher mass-loss rates appear to offer the best opportunity for detecting circumstellar methanol. However, the rates of radiative association reactions involving CH_3^+ are temperature-sensitive and so, if target CSEs have temperatures in the photochemical region that are larger than those of our model, detectable CH_3OH emission may not always accompany that of HCN . The C_2H radical is probably the best indicator of the putative methane, since it derives entirely from the CH_4 photochain and its formation is temperature-independent.

The direct detection or otherwise of CH_4 is the null test of these photochemical models, and will require observations at infrared wavelengths (Hall & Ridgeway 1978). Radio detections of the predicted organic molecules around oxygen-rich, late-type stars (e.g. TX Cam) would be further indirect support for the presence of large amounts of methane in their envelopes, and we recommend that a search for these molecules be made.

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