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ON THE MOLECULAR COMPLEXITY OF THE HOT CORES IN ORION A: GRAIN SURFACE CHEMISTRY AS "THE LAST REFUGE OF THE SCOUNDREL"

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ABSTRACT

We have modeled the gas phase chemistry of warm molecular material around protostars that is seeded with evaporating grain mantles. We show that the release of simple molecules into the gas drives ion-molecule and neutral chemistries which can account for many of the complex O-bearing and N-bearing molecules observed in hot cores. Initial grain mantle components and secondary product molecules are identified, and the observational consequences are discussed.

Subject headings: ISM: abundances — ISM: clouds — ISM: molecules — molecular processes

1. INTRODUCTION

Warm (100–300 K) and dense ($\sim 10^6$–10^8 cm^{-3}) regions around luminous protostars show much higher abundances of certain complex molecules than quiescent dark clouds (Blake et al. 1987; Turner 1991). Moreover, strong chemical differentiation exists between different sources and even within individual sources. In particular, the Orion Hot Core contains high abundances of N-bearing molecules (i.e., NH_3, HCN, CH_3CN, CH_2CHCN, and CH_3CH_2CN), whereas the nearby Compact Ridge is rich in large O-bearing molecules (i.e., CH_3OH, $HCOOCH_3$, CH_3OCH_3, CH_2CO, HCOOH, and CH_3CHO). This molecular complexity, as well as the abundance gradients and high deuteration also observed in these warm regions, cannot be explained by gas phase chemistry alone. It is clear that the high observed abundances of ammonia (Pauls et al. 1983) and doubly deuterated formaldehyde (Turner 1990) are produced by grain surface chemistry. This has led to the notion that many, if not all, of the observed molecules are the products of surface chemistry or were originally formed in the gas at low temperatures and temporarily stored in the grain mantles. Evaporation of the mantles once the protostar is formed releases these molecules back into the gas phase (Brown, Charnley, & Millar 1988).

Three inherently different schemes for the formation of these complex molecules can be envisioned (Blake et al. 1987; Brown et al. 1988; Millar, Herbst, & Charnley 1991a). First, they might originate purely from gas phase reactions, here grain mantles merely act as a "freezer." Second, grain surfaces could play an active chemical role, facilitating the formation of ever larger molecules. Third, the release of simple grain mantle molecules might drive a chemistry in the warm gas which leads to molecule formation in situ. We will adopt the third point of view in this paper. In this, we are motivated by the notion that "grain surface chemistry is the last refuge of the scoundrel" (Walmsley 1992) and assume only that grain chemistry is responsible when all else fails.

2. MODEL

We have developed a comprehensive model for the gas-grain chemistry in warm (≥ 70 K), dense ($\geq 10^6$ cm^{-3}) cores. The details will be described elsewhere (Charnley et al. 1992). We assume that initially all heavy atoms are contained in mantle species and that the highly depleted gas, consisting of H_2, H, He, their ions, and H_3^+, is in chemical steady state. Initial gas phase abundances are obtained from simple analytical formulae (e.g., Lepp, Dalgarno, & Sternberg 1987). Initially, a mixture of simple grain mantle molecules is instantaneously injected into the gas phase and the ensuing chemistry is followed in a manner similar to the "hot phase" of the model of Brown et al. (1988). The initial mantle composition $H_2O/NH_3/CH_4/CO/CH_3OH/HCN/HNC/C_2H_2/H_2CO/C_2H_4/C_2H_6/O_2/N_2$ is a free parameter, constrained by observed hot core versus dark cloud abundances; observations of interstellar ices; and by theoretical models, in that order (Blake et al. 1987; Irvine, Goldsmith, & Hjalmarson 1987; Lacy et al. 1989, 1991; Turner 1991; Tielens 1989; Grim et al. 1991; Skinner et al. 1992; Brown et al. 1988; Brown & Charnley 1990). We adopted time-independent physical conditions similar to that of the Orion cores. For the Hot Core we assumed a hydrogen nucleon density of 2×10^7 cm^{-3} and a temperature of 200 K; for the Compact Ridge we took 2×10^6 cm^{-3} and 100 K (Blake et al. 1987). Reactions were taken from Millar et al. (1991a, b), supplemented by some neutral-neutral processes involving O and OH with simple hydrocarbons and their radicals (Tsang & Hampson 1986). Two important modifications are that we adopted a slower rate coefficient for the reaction of $CH_3OH_2^+$ with CH_3OH (Morris et al. 1991) and a faster dissociative recombination rate for H_3^+ (Canosa et al. 1991).

3. RESULTS

The chemical evolution of the Orion Compact Ridge and Hot Core models that best reproduce the observations are shown in Figures 1 and 2; abundances at one representative time in each model are compared to the observations in Table 1. The exact initial abundances of H_2O, O_2, N_2, and CO are of minor importance and set the time scale for the initial burst ($t < 10$ yr) of protonation reactions (Brown et al. 1988). Following this burst, the degree of ionization in the core is determined by the cosmic ray ionization rate, taken to be

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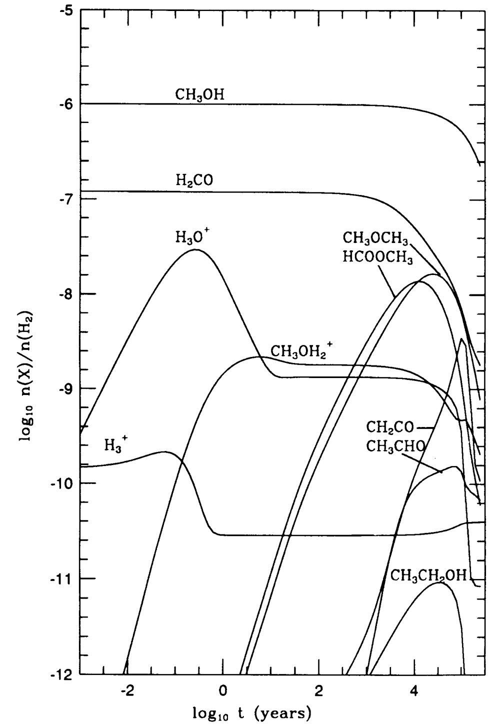

FIG. 1.—Chemical evolution in the Compact Ridge model with the input mantle composition of Table 1. The mantles were injected into the gas phase at $t = 0$.

1.3×10^{-17} s^{-1}. The two models differ fundamentally in the initial abundances of CH_3OH and NH_3, and this is reflected in the observed dominance of O- and N-bearing molecules in the Compact Ridge and Hot Core, respectively. We now discuss these two regions and the implications of the derived differences in turn.

3.1. *The Compact Ridge*

Methanol released into the gas phase can be protonated by H_3^+ and to a lesser extent by H_3O^+. Reactions of $CH_3OH_2^+$ with methanol itself and with H_2CO then lead to $CH_3OCH_4^+$ and $HCOOCH_4^+$, respectively, subsequent dissociative recombinations form dimethyl ether (CH_3OCH_3) and methyl formate ($HCOOCH_3$). Our calculations show that the observed high abundances of these two molecules are a direct consequence of the (observed) high abundances of methanol driving these reaction pathways. Protonated methanol reacts faster with H_2CO than with CH_3OH (Millar et al. 1991b; Morris et al. 1991), and this accounts for the observed comparable abundances of CH_3OCH_3 and $HCOOCH_3$ despite the large difference in the abundances of their precursor molecules injected from the dust (Table 1). Formation of $CH_3OH_2^+$ through radiative association of H_2O and CH_3^+ (Blake et al. 1987) is never important. Gas phase production of H_2CO is inefficient, and we must assume a grain mantle origin in order to explain the observed $HCOOCH_3$ abundance. The formation of CH_2CO and CH_3CHO are effectively detached from

TABLE 1

OBSERVED AND CALCULATED MOLECULAR ABUNDANCES IN THE ORION HOT CORE SOURCES

	HOT CORE			COMPACT RIDGE		
MOLECULE	Observed Abundance	Input Abundance	Theory 6.3(4) yr	Observed Abundance	Input Abundance	Theory 4.0(4) yr
CO	1.2 (−4)	1.0 (−4)	9.5 (−5)	5.0 (−5)	1.0 (−4)	9.2 (−5)
H_2O	~1.0 (−5)[a]	2.0 (−5)	1.6 (−5)	2.0 (−7) − 1.0 (−4)[b]	2.0 (−5)	1.2 (−5)
NH_3	1–10 (−6)	5.0 (−6)	1.4 (−6)	2.0 (−8)	0	6.8 (−8)
CH_4	5–50 (−8)[c]	3.0 (−7)	4.8 (−7)	...	1.0 (−7)	2.0 (−7)
HCN	3.0 (−7)	0	2.6 (−7)	2.0 (−8)	0	1.1 (−8)
HNC	1.0 (−9)[d]	0	1.9 (−9)	...	0	2.8 (−11)
CH_3CN	7.8 (−9)	0	1.4 (−9)	3.2 (−10)	0	2.6 (−10)
HC_3N	1.6 (−9)	0	5.0 (−9)	...	0	1.7 (−9)
HC_5N	...	0	1.5 (−11)	...	0	4.4 (−13)
C_2H_2	1–10 (−7)[e]	3.0 (−7)	3.1 (−7)	...	0	1.6 (−8)
C_2H_4	...	2.0 (−9)	2.1 (−9)	...	8.0 (−8)	6.5 (−8)
C_2H_6	...	2.0 (−9)	1.8 (−9)	...	1.0 (−8)	1.9 (−8)
H_2CO	2.6 (−8)	8.0 (−8)	3.2 (−8)	3.7 (−8)	1.2 (−7)	2.0 (−8)
CH_3OH	...	0	1.7 (−10)	1–10 (−7)[f]	1.0 (−6)	7.2 (−7)
CH_3OCH_3	...	0	1.3 (−15)	1.0 (−8)	0	1.5 (−8)
$HCOOCH_3$	...	0	4.4 (−12)	8.7 (−9)	0	7.7 (−9)
CH_2CO	...	0	2.7 (−11)	6.7 (−10)	0	6.4 (−10)
CH_3CHO	...	0	3.5 (−11)	≲1.7 (−10)	0	1.4 (−10)
CH_3CH_2OH	...	0	4.2 (−14)	<5.0 (−10)	0	9.2 (−12)
CN	<1.0 (−9)	0	1.3 (−11)	...	0	1.5 (−9)
H_3O^+	...	0	9.1 (−11)	1–5 (−9)[g]	0	9.8 (−10)
$CH_3OH_2^+$	...	0	3.5 (−11)	...	0	8.1 (−10)
HCO^+	<1.0 (−9)	0	1.7 (−11)	...	0	3.5 (−10)

NOTES.—All abundances taken from Blake et al. 1987 except where noted. A hyphen denotes a nondetection. $a(-b) = a \times 10^{-b}$. In both theoretical models the assumed abundance of the representative metal was 2×10^{-8}.

[a] Jacq et al. 1988.

[b] Moore, Langer, & Huguenin 1986; Wannier et al. 1991.

[c] Estimate based on the range of solid and gas phase CH_4/CO ratios detected toward star-forming regions by Lacy et al. 1991.

[d] Estimate based on HCN/HNC = 300 (Goldsmith et al. 1986).

[e] Lacy et al. 1989; Evans et al. 1991.

[f] Menten et al. 1988.

[g] Wootten et al. 1991.

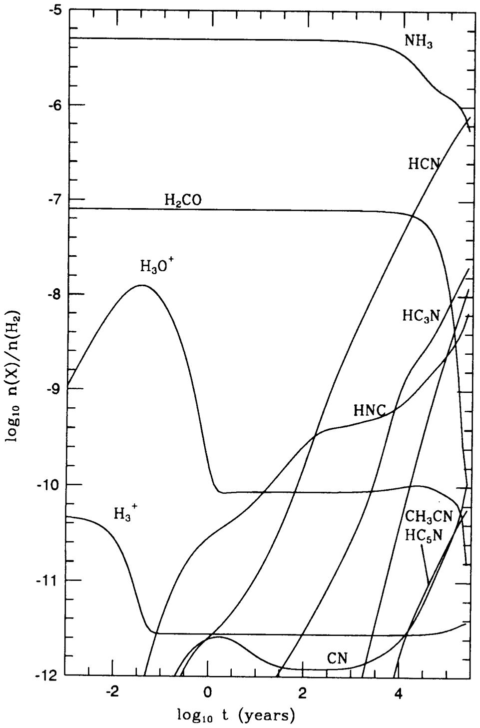

Fig. 2.—As Fig. 1 but for the Hot Core model

that of the other O-bearing molecules as they are formed directly by neutral-neutral reactions. It has been suggested that they are driven by radiative association of H_3O^+ and C_2H_2 (Millar et al. 1991a). However, even a very high initial abundance of acetylene cannot reproduce the observed abundances of these two molecules. Instead, we suggest that they result from the protonation of injected ethene and ethane ($C_2H_5^+$ and $C_2H_7^+$), followed by dissociative recombination to C_2H_3 and C_2H_5. Reactions of atomic oxygen, produced later in the core evolution, with the vinyl and ethyl radicals then form ketene and acetaldehyde respectively (Tsang & Hampson 1986). The calculated CH_2CO/CH_3CHO ratio thus reflects directly the mantle C_2H_4/C_2H_6 ratio and, if the routes are correct, these two precursors should be present in the Compact Ridge. Ethanol formation in our models is inefficient and is initiated by the slow radiative association of H_3O^+ with C_2H_4. The calculated abundance is actually in agreement with the abundance derived from observations by Blake et al. (1987). Recently, Turner (1991) has suggested that the ethanol abundance in the Compact Ridge could be as high as 10^{-6}. If correct, such a large abundance would unquestionably imply a grain surface chemistry origin according to our models which, in any case, could not reproduce the observed ethanol abundances ($\sim 10^{-8}$) observed in other hot cores such as that in W51 (Millar et al. 1988). Increasing the initial C_2H_4 abundance leads only to a modest increase in the peak ethanol abundance but greatly overproduces ketene. Nitrogen-bearing molecules (NH_3, HCN, CH_3CN) have low observed abundances in the Compact Ridge relative to the Hot Core, and our model reproduces them well (Table 1). Finally, the calculated abundance of H_3O^+ is in good agreement with the observations, and we suggest that HCO^+ and $CH_3OH_2^+$ are also observable in this source.

3.2. *The Hot Core*

The Hot Core is warmer and more dense than the Compact Ridge and so endothermic neutral reactions will proceed more rapidly; ion-molecule reactions will be less efficient due to the lower degree of ionization in the core. The high ammonia abundance from grains drives an N-rich chemistry. Both HCN and HNC can be made in situ through protonation of NH_3 by H_3^+ followed by dissociative recombination to the NH_2 radical, subsequent reaction with atomic C forms HNC. Following Pineau des Forêts, Roueff, & Flower (1990), we have assumed that the reaction of HNC with H to form HCN has an activation barrier of only 100 K. This sequence channels a significant fraction of the NH_3 released to HCN and the HCN/HNC ratio is much larger than in cold clouds (Table 1). Protonation of HCN followed by dissociative recombination leads to the formation of the cyanogen (CN) radical. Reaction of cyanogen with various hydrocarbons may drive the formation of larger nitriles. In particular, reaction with acetylene, to form HC_3N proceeds rapidly (Lichtin & Lin 1986) and the observed gas phase C_2H_2 and HC_3N abundances are consistent with this route. Likewise, CN could react rapidly with C_2H_4 in the Hot Core (Lichtin & Lin 1986), and its products may include vinyl cyanide (Herbst & Leung 1990). Similar calculations have shown that the observed CH_2CHCN abundance requires a mantle C_2H_4 abundance comparable to that observed for C_2H_2 (Charnley & Tielens 1992). Cyanogen also reacts rapidly with C_2H_6, however, for saturated hydrocarbons this route probably tends to form HCN rather than CH_3CH_2CN (Lichtin & Lin 1985). We have been unable to determine a viable route for ethyl cyanide formation, and it is possible that it, like ethanol, is formed on grain surfaces. Finally, CH_3CN formation is by radiative association of CN with CH_3, and of CH_3^+ with HCN followed by reaction with an electron. These can reproduce the observed abundance in situ but on a longer time scale than for other molecules (Fig. 1). Acetylene and formaldehyde cannot be formed in the gas phase at their observed abundances and have therefore to be injected from grain mantles. Injection of appreciable quantities of CH_3OH leads to large amounts of $HCOOCH_3$ and CH_3OCH_3, in conflict with the observations (Blake et al. 1987; Turner 1991).

3.3. *Implications*

We can separate the observed species into primary (i.e., injected grain mantle molecules) and secondary molecules (i.e., formed in situ). Among the former are CH_3OH, NH_3, C_2H_2, C_2H_4, C_2H_6, CH_4, and H_2CO. Molecules formed in situ are $HCOOCH_3$, CH_3OCH_3, CH_2CO, CH_3CHO, HCN, HC_3N, CH_2CHCN, and CH_3CN. On grain surfaces CH_3OH, H_2CO NH_3, and CH_4, are probably formed by the hydrogenation of CO, N, and C. There is no obvious grain surface route to C_2H_2, but accreted acetylene can be hydrogenated to form C_2H_4 and C_2H_6 (Tielens 1992). The presence of deuterated species such as DCN in hot cores (Mangum et al. 1991) implies that not all the HCN is in fact produced in situ but that some comes from grain surfaces. However, considering hot gas phase chemistry does give better observational agreement for HCN abundances, as well as for HNC and CH_3CN which were both overproduced in the model of Brown et al. (1988). Furthermore, deuteration in simple mantle molecules (e.g., aliphatic hydrocarbons) can be transferred to complex species by gas phase reactions and so caution should be exercised in ascribing high D/H ratios in these species purely to a mantle origin. Finally, ethanol and ethyl cyanide cannot be produced in large abundances in situ, and our models appear to require a mantle origin. Ethanol may result from hydrogenation and oxidation reactions of C_2H_2 on grain surfaces (Tielens 1992). Hydrogenation of accreted HC_3N may lead to CH_2CHCN and ultimately CH_3CH_2CN on grain surfaces (Blake et al. 1987; Tielens 1992). If this route is correct then, as the accretion chemistry of the higher cyanopolyynes is similar to that of HC_3N (Brown & Charnley 1991), these molecules would undergo similar hydrogenation sequences which terminate in *n*-alkyl cyanides, and one might expect a characteristic abundance pattern mimicking that of the cyanopolyynes in dark clouds. The presence of higher cyanopolyynes in the Hot Core has, however, yet to be demonstrated unambiguously and the amount of HC_3N accreted from the gas phase chemistry of Brown et al. (1988) would be insufficient to reproduce the observed CH_2CHCN and CH_3CH_2CN abundances (Blake et al. 1987); formation of only HC_3N in situ provides the simplest explanation of the currently available observations

3. CONCLUSIONS

The Hot Core and Compact Ridge are both sites of recent mantle evaporation and are *also* sites of active gas phase chemistries. The observed strong molecular differentiation between these two sources is explained as being primarily due to differences in the composition of the mantles evaporated in each. The Compact Ridge mantles were CH_3OH-rich but NH_3-poor and drive an *ion-molecule* chemistry, whereas the Hot Core mantles were NH_3-rich and CH_3OH-poor and initiate a predominantly *neutral* chemistry. Variations in the solid phase abundances of both molecules have been observed (Schutte, Sandford, & Tielens 1991; Graham & Chen 1991). Differences in mantle composition may reflect differences in chemical history of the gas forming the cores (Brown et al. 1988) or could be due to grain surface chemistry effects. In the spirit of this paper we discuss only the former possibility. Thus, the Hot Core may have formed earlier in the evolution of the ridge cloud when the gas was mostly atomic and surface hydrogenation led to NH_3, CH_4, and H_2O (Pauls et al. 1983; Blake et al. 1987; Brown et al. 1988). By contrast, the Compact Ridge may be the result of a later phase when simple molecules dominated the accreting gas. The gas phase was then likely dominated by CO, forming H_2CO and CH_3OH on the grain surface, as well as O_2 and unreactive N_2.

We have been able to determine plausible gas phase formation routes for many of the complex molecules observed in these regions and conclude that they are not products of grain surface chemistry. This work places constraints on grain surface reaction studies and suggests that interstellar ices may contain only specific simple molecules. We predict correlations between the abundances of "parent" mantle species, such as ammonia and methanol, and various "daughter" molecules. Recent observations show that CH_3OH and CH_3OCH_3 abundances appear to be correlated in Sgr B2 (Sutton et al. 1991). We predict the location and abundances of ethane and ethene in Orion. If ethanol is also formed on grains, then its release into the gas phase will drive an ion-molecule chemistry analogous to that of methanol. Protonated ethanol can react with methanol, ethanol, and formaldehyde (Karpas & Meot-Ner 1989) leading to methyl ethyl ether ($CH_3OCH_2CH_3$), diethyl ether ($CH_3CH_2OCH_2CH_3$) and perhaps ethyl formate ($HCOOCH_2CH_3$), respectively. The detection of these molecules in the Compact Ridge would be definitive proof for the theory proposed here of simple grain mantle molecules initiating molecular complexity in the gas phase.

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