Evaporation of ices near massive stars: models based on laboratory TPD data

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ABSTRACT

Hot cores and their precursors contain an integrated record of the physics of the collapse process in the chemistry of the ices deposited during that collapse. In this paper, we present results from a new model of the chemistry near high mass stars in which the desorption of each species in the ice mixture is described as indicated by new experimental results obtained under conditions similar to those hot cores. Our models show that provided there is a monotonic increase in the temperature of the gas and dust surrounding the protostar, the changes in the chemical evolution of each species due to differential desorption are important. The species H_2S, SO, SO_2, OCS, H_2CS, CS, NS, CH_3OH, $HCOOCH_3$, CH_2CO, C_2H_5OH show a strong time dependence that may be a useful signature of time evolution in the warm-up phase as the star moves on to the Main Sequence. This preliminary study demonstrates the consequences of incorporating reliable TPD data into chemical models.

Key words: stars: formation; ISM: abundances; ISM: clouds; ISM: molecules

1 INTRODUCTION

Conventionally, the first indirect manifestation of a young massive star is provided by the presence of 'hot cores'. Hot cores are small, dense, relatively warm, optically thick, and transient objects detected in the vicinity of newly formed massive stars. It is well-known that they exhibit a range of molecular species unlike those found in quiescent molecular clouds: in comparison, hot cores are richer in small saturated molecules and in large organic species (e.g. Walmsley and Schilke 1993). The characteristic hot core chemistry is believed to arise from the evaporation of the icy mantles that accumulated on dust grains during the collapse that led to the formation of the massive star; solid-state processing in the ice and gas-phase chemistry after evaporation also occur (cf. Millar 1993; Nomura and Millar 2004). Moreover, recent observations do indicate the existence of possible precursors of hot cores (e.g Molinari et al. 2002; Beuther et al. 2002). Thus, hot cores and their precursors may be regarded as containing an integrated record of the physics of the collapse process in the chemistry of the ices deposited during that collapse. It is the task of astrochemistry to unravel this record from the observations.

Viti & Williams (1999) noted that the duration in which the grains are warmed from very low (∼10 K) temperatures to the temperature at which H_2O ice desorbs and above is determined by the time taken for a pre-stellar core to evolve towards the Main Sequence. This time is believed from observational and theoretical studies to be fairly brief, $\sim 10^4$-10^5 y (e.g. Bernasconi & Maeder

1996, hereafter BM96), and in some contexts this 'turn-on' of the star may be regarded as instantaneous. However, in the context of hot cores, which have a duration similar to that of the turn-on time of the hot star, the relatively slow warming of the grains must be taken into account. Evidently, highly volatile species will be desorbed from the ices at early stages, while the more refractory species will only be desorbed at later stages. The chemistry of the hot cores must reflect this temperature-driven evolution, and the evolutionary chemistry should provide, in principle, a direct measure of the stellar turn-on time. Thus, hot cores contain not only a record of the collapse process but also of the ignition history of the star. The de-convolution of hot core observational data should constrain both physical processes.

The Viti & Williams study, in the absence of reliable data, made a gross simplification in the description of desorption from mixed ices; their paper emphasised that appropriate temperature programmed desorption (TPD) experiments on mixed ices under near-interstellar conditions were essential. Such definitive measurements have now been made at the University of Nottingham Surface Astrochemistry Experiment. Fraser et al. (2001) reported a TPD study of pure H_2O ice, and Collings et al. (2003a) examined the TPD of H_2O/CO ice mixtures. Both experiments provided data that is in striking contrast to the assumptions made in models of hot cores. In particular, Collings et al. showed that CO desorbed from an H_2O/CO ice mixture occurs in four temperature bands, rather than the assumed CO desorption at temperatures above about 25 K. They also found that the proportion of the CO desorbing at each phase depended on the total CO concentration and on the preparation of the sample. These laboratory results suggest that in hot

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cores the CO being injected into the gas phase from the ices should occur in four phases, rather than a single pulse.

The chemistry of interstellar ices is of course much more complex than a simple H_2O/CO ice mixture, although H_2O is always the dominant partner (Whittet 2003). Therefore, similar TPD experiments on a variety of ices have been carried out at Nottingham (Collings et al. 2004). In addition, the properties of some other species with respect to desorption have been considered. It has been found possible to categorize all species relevant to hot cores as H_2O-like (i.e. behaving as determined by Fraser et al. 2001); CO-like (as described by Collings et al. 2003a), or placed in several other intermediate categories. Thus, it is now possible to attempt to model the chemistry near high mass stars in which the desorption of each species in the ice mixture is described as indicated by experimental results obtained under conditions similar to those found in hot cores. This paper reports the results of such study.

We model the chemistry of the gas and the deposition of the ices during the collapse, and subsequently the desorption and chemistry in the gas phase after the star begins to warm the core. Our purpose is to demonstrate the consequences of incorporating reliable TPD data into chemical models. Specific sources will be modelled in later papers.

In Section 2 we describe the new TPD results. Section 3 gives descriptions of the physical and chemical aspects of the model, and the results are presented in Section 4. Section 5 gives a discussion of the results and conclusions. For simplicity, throughout the paper, we shall use the word 'hot core' to include any pre-stellar core such as those observed by Molinari et al. (2002 and references therein) which are believed to be possible hot core precursors.

2   EXPERIMENTS

In the accompanying paper, Collings et al. (2004) report results of TPD experiments for a large number of molecules relevant to hot core chemistry. Details of these experiments are not discussed here. Molecules were assigned to one of three several categories of desorption as follows: (1) CO-like; (2) H_2O-like; and (3) intermediate. The work also enables us to make inferences about likely behaviour of some species not so far studied, and in doing so we have created two further categories: (4) reactive; and (5) refractory. For each category we have used the information in Collings et al. (2004), and previous studies of the CO/H_2O system (Collings et al. 2003a,b) to estimate the fraction of a particular molecular species that is desorbed in the various temperature bands. These desorption bands are from (i) the pure species; (ii) a mono-molecular layer on H_2O ice; (iii) the amorphous to crystalline H_2O ice conversion (the 'volcano' effect); (iv) co-desorption when the H_2O ice desorbs; and (v) desorption from the bare grain surface. The fraction of the species desorbing in each of the five desorption processes is shown in Table 1, assuming a relatively thick ice layer of 0.3 μm, as used in the TPD experiments. The desorption processes are tabulated in sequence, and the quoted value expresses the fraction of the species remaining in the ice at that time that is desorbed in the process. In the layered model of ice mantles, the species CO, N_2 and O_2, are thought to be found predominantly in an outer layer non-hydrogenated (apolar) ice, separate from the water dominated inner layer of hydrogenated ice (polar). As the mantle warms from 10 K, the apolar layer is able to diffuse into the porous structure of the water ice. We are yet to accurately measure the relative concentration at which the water will become saturated, but we estimate that this occurs at roughly 0.25. Since the total concentration of CO, N_2 and O_2 in our model is

0.35–0.4 relative to water, desorption of these species from the non-hydrogenated outer layer will be relevant, and we list 35% of each as desorbed from the solid phase. Methane should only be found within the hydrogenated inner layer, and we assume that this may also be true of NO and CS. Based on the CO results of Collings et al. (2003b), about 70% of molecules of CO-like species in the hydrogenated layer will undergo mono-molecular desorption in hot core conditions, and the remainder will become trapped. The TPD results (Collings et al. 2004) suggest that trapped molecules are released in volcano and co-desorptions of equal sizes for the species initially present in the water ice layer, and with a volcano desorption twice the size of the co-desorption for the species that have diffused into the water ice. The water-like species were found to be released entirely in the co-desorption process. To the experimentally tested species we have added polar organic molecules and other hydrophilic molecules. To the intermediate category we have added untested non-polar organic species and other small molecules that we anticipate will interact with have moderate interaction with water ice. All of the intermediate species are assumed to be found in the hydrogenated ice layer. The TPD results (Collings et al. 2004), suggest that desorption will be roughly evenly split between the volcano and co-desorption events. However, for the smaller species C_2H_2, and H_2S, a small fraction ($\sim 10\%$) is able to escape and undergo mono-molecular desorption. We anticipate that HCN, HNC, NS, and HCS will also behave in this manner. The nine species we have categorised as reactive are all ions or free radicals in the gas phase. It is not clear how they will behave when adsorbed in the grain mantle at 10 K, however as the ice warms they would be expected to adopt a form quite different from their gas phase structure due to strong interactions with the water ice and other molecules. As with the water-like species, we expect that they will only escape to the gas phase in a co-desorption process. The refractory species are those such as atomic magnesium and S_2 which are likely to be stable in the mantle but are strongly adsorbed and non-volatile. We intuitively expect that they will remain in the mantle as other species, including water, desorb around them. Unless some explosive desorption mechanism operated, we anticipate that they will 'sink' through the desorbing mantle and become bound to the dust grain surface. Desorption from the dust grain surface is therefore the only relevant process for this category.

3   THE CHEMICAL AND PHYSICAL MODEL

The model employed is similar to that used in VW99 and Viti et al. (2001). For this study, we performed time-dependent single-point calculations for A_V of ~ 600 mags as derived from hot core observations. For simplicity we have not used a multi-point code, as we did in VW99. Our model is a two phase calculation: the first phase starts from a fairly diffuse (~ 300 cm^{-3}) medium in atomic form (apart from a fraction of hydrogen in H_2), and undergoes a free-fall collapse until densities typical of hot cores are reached ($\sim 10^7$ cm^{-3}). During this time, atoms and molecules from the gas freeze onto the grains and they hydrogenate where possible, as in VW99. Note that the advantage of this approach is that the ice composition is *not* assumed but it is derived by a time dependent computation of the chemical evolution of the gas/dust interaction process. Also the abundances that we derive for the high density core are directly computed from the initial cosmic abundances. The main differences here with the VW99 models are i) the initial abundances which we corrected to match the latest findings by Sofia et al (2001) and are 1.0, 0.075, 4.45$\times 10^{-4}$, 1.79$\times 10^{-4}$, 8.52$\times 10^{-5}$,

Table 1. Assignment of each molecular species into a category of desorption. The first column indicates the category, column 2 lists the species belonging to each category while columns 3-7 indicates the fraction of each species (remaining after the previous desorption) that desorbs at each desorption event. We have used italics for the experimentally tested species.

	Species	Solid at T~ 20K	Mono at E_b	Volcano	Co-des	Surface
CO-like	*CO, N$_2$, O$_2$*	0.35	0.7	0.667	1.0	0
	CS, *NO, CH$_4$*	0	0.7	0.667	1.0	0
Intermediate	HCN, HNC, *H$_2$S*, NS, HCS,*C$_2$H$_2$*	0	0.1	0.5	1.0	0
	OCS,CH$_3$CN, C$_3$H$_4$,*CO$_2$, SO$_2$*, HC$_3$N,*C$_2$H$_4$*	0	0	0.5	1.0	0
H$_2$O-like	*H$_2$O, CH$_3$OH*, SO, CH$_2$CO, C$_2$H$_5$OH,*NH$_3$*,NO$_2$, H$_2$CO,*HCOOCH*, H$_2$CS	0	0	0	1.0	0
Reactive	HS$_2$, C$_2$H, OCN, O$_2$H, C$_2$H$_5$, H$_2$CN, HNO, C$_2$, C$_2$H$_3$	0	0	0	1.0	0
Refractory	Mg, S$_2$	0	0	0	0	1.0

1.43×10^{-6}, 5.12×10^{-6}, respectively, for H, He, O, C, N, S, Mg; ii) the use of the UMIST rate 99 database (www.rate99.co.uk) rather than UMIST96; iii) the low initial density (cf. 10^4 cm^{-3} in VW99). The unusually high initial density in VW99 before collapse was employed for ease of computation. Our present models start from a more realistic low density diffuse medium and this has consequences for the final percentage of gas in the mantles. In VW99, effectively 100% of the gas species was frozen onto the grains once the final density was reached. However, in Viti et al (2001), we argued that it is possible that freeze out is never total; here we assume that 99% of the gas is frozen out, leaving 1% in the gas (a more realistic description since some gaseous CO is always observed, even in regions where no millimetre continuum is detected, see e.g. Molinari et al. 2000). This difference affects the very start of Phase 2 of our computations. These differences do not affect at all our qualitative conclusions. We also performed a model where the initial abundances and rate file used matched the VW99 for an initial comparison.

Phase 2 follows the chemical evolution of the remnant core. We simulate the effect of the presence of an infrared source in the centre of the core or in its vicinity by subjecting the core to an increase in the gas and dust temperature. The temperature reaches its maximum (~ 300K) at different times depending on the mass of the new born star (see VW99).

Phase 2 is rather different from the one in the VW99 models because of the different treatment for the increasing temperature and the evaporation from the grains. In VW99 we adopted a linear dependence of the temperature with time. For this study we have opted for a more realistic approach where we derived the temperature of the gas as a function of the luminosity (and therefore the age) of the protostar. We used the observational luminosity function of Molinari et al. (2000); in their Figure 6 the total emitted luminosity is plotted against the core mass for mass accretion rates of 10^{-5} and 10^{-4} solar masses yr^{-1}. Using this plot we correlated the luminosity, and hence the effective temperature, with the age of the accreting protostar and found that a power law fitted the data. Our major assumption was then that the temperature of the gas and dust surrounding the accreting protostar increases according to the same power law as the stellar temperature, and we fitted this so that the maximum temperature of the gas is reached at the contraction time, t$_c$, i.e the time after which hydrogen starts burning and the star reaches the ZAMS; Table 2 lists the contraction times and the volcano and co-desorption temperatures as a function of the mass of the stars. The contraction times are taken from BM96. Note, that the precise contraction time and the exact behaviour of the temperature increase are mostly irrelevant to the purpose of this study: the only necessary assumptions are that i) the contraction time of

Table 2. Contraction times (t_c) and the volcano and co-desorption temperatures as a function of the mass of the stars.

M M$_\odot$	t_c 10^6 years	Volcano Desorption Kelvin	co-desorption Kelvin
60	0.0282	92.2	103.4
25	0.0708	90.4	101.6
15	0.117	89.5	100.8
10	0.288	88.2	99.4
5	1.15	86.3	97.5

a massive protostar is comparable to chemical timescales - all the evolutionary studies of the type performed by BM96 have shown that even the most massive stars (~ 120 M$_\odot$) contract in no less than 10,000 years and ii) the temperature increases monotonically and not following a step function. It is true that the volcano and the co-desorption temperatures decrease as a function of the slowing down of the heating rate so that the lower the mass of the star, the lower the volcano and the co-desorption temperatures (see Table 2 and Collings et al. 2004); however this decrease is very small and insignificant with respect of the evaporation times.

Our new evaporation treatment is pseudo-time dependent in that we allow evaporation of a fraction of mantle species *X* (in a single step) when the temperature for a particular desorption event is reached. The temperature and fractions for each species are listed in Table 1. Note that the fractions are always expressed as fractions of the current amount and not the original.

4 RESULTS

The first task of this theoretical study is to determine whether the inclusion of the five distinct desorption events occurring during TPD of dirty ice affect significantly the abundances predicted by previous models, in particular the VW99 models. To isolate this effect we ran several models using the same initial conditions of VW99 i.e the same initial abundances (see Table 2 from VW99) and chemical database. We found that substantial differences are seen between these models and VW99. These differences are solely due to the new evaporation treatment.

We then constructed a new grid of models using the revised initial elemental abundances listed in Section 3, and the latest database UMIST99. We ran several models covering stars with masses from 5 to 60 M$_\odot$. We have taken the contraction times from BM96 as the epochs at which the temperature of the core reaches 300K. The desorption temperatures were calculated by run-
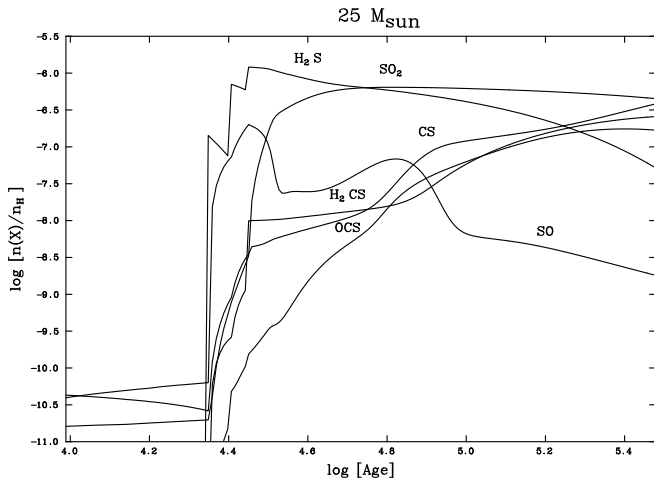
Figure 1. Fractional abundances of selected sulfur-bearing species as a function of time for a 25 $M_\odot$ star, equivalent to a contraction time of 70,000 years.
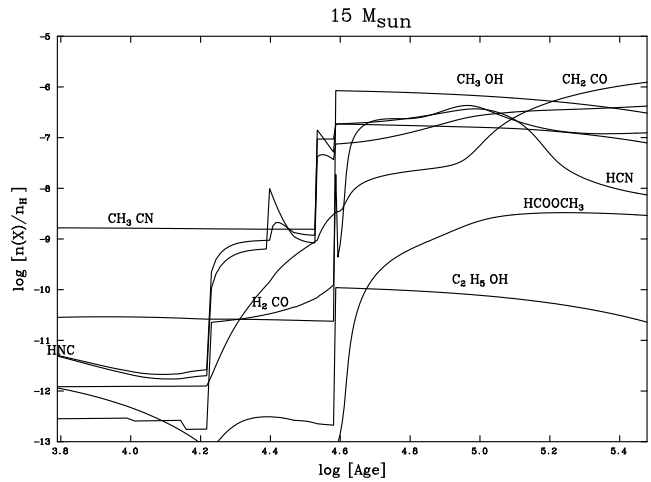

Figure 2. As in Figure 1 but for a 5 $M_\odot$ star, equivalent to a contraction time of 1.15×10^6 yrs.

Figure 3. Fractional abundances of selected large molecules as a function of time for a 15 $M_\odot$ star, equivalent to a contraction time of 70,000years.
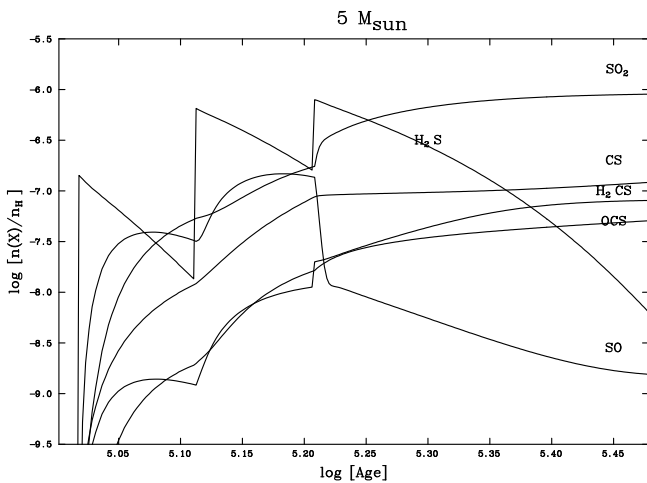
ning simulations of water ice desorption (Collings et al. 2003b) using the power law temperature profiles fitted to the stars of each mass. Figures 1-3 show the fractional abundances obtained from our computations for selected species for respectively a M = 25 $M_\odot$, M = 5 $M_\odot$, and M = 15 $M_\odot$ star.

The species that are most affected by the inclusion of the new evaporation treatment are sulfur-bearing species and the larger species. The sensitivity of sulfur-bearing species to physical and chemical variations during the lifetime of a hot cores is not surprising as previous studies have shown that sulfur-bearing species are strongly time-dependent (e.g. Hatchell et al. 1998; Viti et al. 2001, Hatchell & Viti 2002). While larger molecules, such as CH_3OH

and CH_2CO, maintain the same trends from a 5 to a 25 $M_\odot$ star, the behaviour of sulfur-bearing species depend on the heating rate and hence on the mass of the star. In particular, we find that the evaporation of H_2S at different evolutionary stages is one of the main key factor to the changes occurring in the sulfur bearing chemistry: for a 25 $M_\odot$ star the abundance of H_2S itself varies by about one order of magnitude with time; as the mass of the star decreases this difference becomes larger, up to two orders of magnitude. H_2S has two main peaks in abundance due to desorption from the volcano and co-desorption events, but each peak is followed by a quick and sharp decline due to dissociation. This fast and changing behaviour has several consequences on other sulfur bearing species; it is interesting to look at these changes in the ratios of selected sulfur bearing species e.g: for a 25 $M_\odot$ star, (i) H_2S/SO_2 is > 1 up to 50,000 years, and < 1 for older cores. (ii) H_2S/CS, H_2S/H_2CS, H_2S/OCS > 1 up to 150,000 yrs and < 1 for older cores; (iii) SO/CS, SO/H_2CS, $SO/OCS \sim 1$ up to 65,000 yrs and < 1 after that. For a 5 $M_\odot$ star, we find similar trends but much more accentuated; for example, H_2S, SO and SO_2 show similar abundances for longer periods during the earlier phases of star formation, while H_2S/SO_2 is much less than 1 after 190,000 yrs. In general H_2S decreases much more drastically with time as we move toward the lower mass regime; this is because, although the temperatures at which the evaporations occur are quite similar between the 5 and the 25 $M_\odot$ cases, the temperature increases occur more slowly for a 5 $M_\odot$ star, allowing more time for the gas-phase H_2S to be destroyed, before another H_2S evaporation 'peak' occurs. The main destruction route for H_2S is its reaction with HCO^+; the latter becomes abundant once the temperature reaches ~ 21 K and the first CO evaporation peak occurs. From these trends, it is clear that the ratio of these sulfur-bearing species can be used to investigate the evolution of the early phases of high mass star formation, and that sulfur bearing species are therefore good 'chemical clocks'.

Another set of species that can be used as evolutionary indicators are organic molecules. Figure 3 shows the time evolution for selected large species for a 15 $M_\odot$ star. From the figure, we note that large species, such as C_2H_5OH, $HCOOCH_3$ and CH_3OH, are

good indicators of old cores as these strongly bound species are abundant in the gas only at late times.

Although observationally less significant, we would also like to draw attention to other species (not shown) namely: CO varies by about 1 order of magnitude during the increase of the temperature and therefore during the formation of a high mass star but, CO being a ubiquitous species, this difference, even if detectable, may not, by itself, be indicative. Finally, we find that N_2H^+ should be present in detectable quantities in young hot cores but disappears probably within the first 15,000 years of its lifetime, when the temperature has reached $\sim 40K$; this corresponds roughly to the mono evaporation of CO (~ 40 K) and of CH_4 (~ 45 K). In fact the main destruction routes for N_2H^+ are its reactions with methane and CO. On the contrary ammonia should only be detectable in cores older than 30,000 years (for a 25 $M_\odot$). Intermediate aged high mass star formation cores should be in general nitrogen-deficient.

5 CONCLUSIONS

We have extended existing chemical models of high mass star formation cores by including the latest experimental results on desorption from grains in the evaporation of icy mantles formed in star-forming regions. We find that distinct chemical events occur at specific grain temperatures. This supports our assertion that in a comprehensive model it should be possible to use these chemical events as a chemical clock tracing the ignition of the nearby star.

We have shown that, provided there is a monotonic increase in the temperature of the gas and dust surrounding the protostar, the changes in the chemical evolution of each species due to differential desorption are important. Based on the recent TPD experimental results, the species that are most affected are: H_2S, SO, SO_2, OCS, H_2CS, CS, NS, CH_3OH, $HCOOCH_3$, CH_2CO, C_2H_5OH, and to a lesser extent CO, N_2H^+, NH_3 and HCN, HNC. Our results imply that if a large enough sample of high mass precursors objects are observed in these molecules, we would gather enough information to determine their age and therefore the evolutionary stage of the high mass star formation core.

Finally, we note that 1) effects induced by the relatively slow warming of gas near stars are more pronounced near stars of moderate mass, since the turn-on time for stars of intermediate mass is much longer than for massive stars. Observations of cores similar to hot cores are now being found for intermediate-to-low mass stars (e.g Cazaux et al. 2003); 2) the evolutionary trends found in this study depend on the temperature gradient. Hence, at the established 'hot core' stage, similar trends should be found as a function of distance from the central star, again due to a temperature gradient (e.g Nomura and Millar 2004).

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