Episodic Explosions in Interstellar Ices

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ABSTRACT

We present a model for the formation of large organic molecules in dark clouds. The molecules are produced in the high density gas-phase that exists immediately after ice mantles are explosively sublimated. The explosions are initiated by the catastrophic recombination of trapped atomic hydrogen.

We propose that, in molecular clouds, the processes of freeze-out onto ice mantles, accumulation of radicals, explosion and then rapid (three-body) gas-phase chemistry occurs in a cyclic fashion. This can lead to a cumulative molecular enrichment of the interstellar medium.

A model of the time-dependent chemistries, based on this hypothesis, shows that significant abundances of large molecular species can be formed, although the complexity of the species is limited by the short expansion timescale in the gas, immediately following mantle explosion.

We find that this mechanism may be an important source of smaller organic species, such as methanol and formaldehyde, as well as precursors to bio-molecule formation. Most significantly, we predict the gas-phase presence of these larger molecular species in quiescent molecular clouds and not just dynamically active regions, such as hot cores. As such the mechanism that we propose complements alternative methods of large molecule formation, such as those that invoke solid-state chemistry within activated ice mantles.

Key words: astrochemistry – molecular processes – ISM: clouds – ISM: molecules

1 INTRODUCTION

A variety of laboratory evidence shows that the catastrophic recombination of hydrogen atoms and other accumulated radicals in a solid may abruptly raise the temperature of the solid to $\sim 10^3$ K. Duley & Williams (2011) proposed that for HAC dust grains in the interstellar medium, such temperatures are sufficiently high to permit the grains to radiate in the so-called Unidentified Infrared Bands (UIBs) associated with carbonaceous materials, lying between 3.3 and 11.3 $\mu$m. Recently, Cecchi–Pestellini, Duley & Williams (2012) have shown that H$_2$ molecules released from HAC grains in such abrupt temperature excursions caused by the recombination of a sufficient number of accumulated H-atoms could not only account for the populations in rotational levels of H$_2$ observed in the “hot component” of H$_2$ in diffuse clouds, but also produce amounts of CH$^+$ and OH comparable with those observed in diffuse clouds. This theory of radical recombination-driven mantle explosions is very similar to that described by Greenberg (1978) except that the mechanism for mantle explosion is the spontaneous internal recombination of trapped hydrogen atoms, rather than an external heating source.

In this paper, we consider an application of the idea of abrupt temperature excursions caused by radical recombination to dark clouds where ices have been deposited on dust grain surfaces. If the abrupt temperature excursions are of the magnitude discussed by Duley & Williams (2011) then any ices present will be abruptly converted to gas and evaporated explosively. As pointed out by Cecchi–Pestellini et al. (2010), hereafter Paper I, the density in the expanding gas can be so high that three-body reactions have the potential to create new and more complex species from the ice constituents. Here, we extend the ideas of Cecchi–Pestellini et al. (2010) to the gas formed by the exploding ices.

Interstellar ices are deposited on dust grains in dark interstellar clouds in regions where the visual extinction exceeds some critical value, typically a few visual magnitudes.

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The ices in quiescent lines of sight towards low mass stars are observed to contain H$_2$O, CO, CO$_2$, CH$_4$, NH$_3$, H$_2$CO, CH$_3$OH, OCN$^-$, and some other species of low abundance (Oberg et al. 2011). The ices may also contain radicals created from these molecules by photodissociation, where the dissociating radiation is the cosmic ray-induced radiation field (Prasad & Tarafdar 1983).

Thus, H$_2$O may give rise to OH, CH$_4$ to CH$_3$, etc., and the population of these radicals is associated with the bulk of the ice. The various reactions resulting from the accretion of atoms and molecules from the ambient gas as well as processing by ultraviolet photons and cosmic rays must always be incomplete and will, for example, lead to the presence of trapped H-atoms at weak binding sites on or near the surface. According to Duley & Williams (2011), when a critical number of these weakly bound H-atoms is accumulated, then a localised recombination of a few hydrogen atoms can trigger a chemical runaway which releases all of the chemical energy stored in the grain. This can include both the hydrogen recombination energy and the energy stored in other radicals as well as the grain substrate. This leads to a runaway explosion which abruptly heats the ice mantle and grain core to temperatures on the order of one thousand K. Duley & Williams (2011) show that the number of H-atoms required to cause this explosion is equivalent to about 5% of the total number of atoms in the grain plus mantle. We postulate that the recombination of trapped H atoms to H$_2$ drives the explosion but that the heavy, and less mobile, molecular radicals are released into the gas phase.

In the work presented here, we follow the time-dependent gas-phase chemistry in a dark interstellar cloud; we compute the deposition of ices and the accumulation of weakly bound H-atoms that are assumed to trigger the explosions when their number on a grain reaches the critical value. Thus, in this model, the frequency of the episodic temperature excursions is controlled by the cloud chemistry. When a temperature excursion occurs, the ices are assumed to be instantaneously sublimated, and three-body reactions involving radicals produce products in the very high density expanding gas. This gas is assumed to undergo a free expansion which occurs on a timescale on the order of nanoseconds; however, the density in this sublimate is so high that many collisions occur before the gas has relaxed to more normal interstellar conditions. In this picture, the episodic explosions therefore enrich the interstellar gas with the products of the three-body reactions, and the material undergoing this enrichment is accumulated during the interval between explosions. The interstellar gas may be enriched by a number of successive events, if the timescales for accumulation of ices and H-atoms (typically, on the order of one million years in canonical dark cloud conditions) are suitable. Evidently, if the interval is very short (as will occur if the H-atom abundance in the gas is high), little material can be accumulated as ices.

Our model for molecular cloud chemistry has some similarity to that described by Garrod, Widicus Weaver & Herbst (2008) to account for chemical complexity in hot cores. The accumulation of radicals within ices is adopted in both our model of chemistry in molecular clouds and that of Garrod et al. in hot cores. In our model, the radicals are released through the abrupt warming in episodic explosions, while in the Garrod et al. model of hot core chemistry the radicals are released in the slow warm-up of material in the early hot core phase.

We describe the model in Section 2. The results are presented in Section 3, and we give a discussion of the implications and make our conclusions in Section 4.

\section{The Model}

To test the hypothesis described above, we first of all constructed a simple ‘proof of concept’ model of the time-dependent chemistry. The first stage considers the chemistry (gas-phase, plus freeze-out), for moderately dense conditions (density $n = 10^3$ cm$^{-3}$, temperature $T = 10$ K, extinction $A_V = 3$) where we expect the atomic hydrogen abundance to be high, so as to promote the rapid accumulation of radicals in the ice mantles. During this phase limited surface chemistry is allowed to occur, so that full hydrogenation of C, N, O, and S-hydrides to CH$_4$, NH$_3$, H$_2$O and H$_2$S is allowed. A fraction (10\%) of the CO is allowed to react with O and OH on the surface of grains to form CO$_2$. It is further assumed that no (continuous) desorption mechanisms are operating. After a specified period ($\sim 10^4$ – $10^6$ years) the ice mantles (composed of CO, CH$_4$, NH$_3$, N$_2$, O$_2$, H$_2$O, Na, H$_2$CO, CO$_2$, HCN, HNC, HNO, H$_2$S, CS, HCS, O and OH) are released back into the gas phase. No change of temperature or density is included and no high-density chemistry is included. The cycle is then allowed to repeat.

The results from this model show that, for most species, a limit cycle is achieved after only one or two mantle explosions. Ions and unsaturated species tend not to be strongly affected by the process, but the simple saturated species (such as H$_2$O, CH$_4$ etc.) are very strongly enhanced. A few species, such as CO and CO$_2$ show a slower, more steady rise in abundance over several cycles.

We have therefore constructed a more realistic and comprehensive two-phase model which considers the time-dependent chemistry at a single point in a molecular cloud. The parameters for this model are given in Table 1. This model utilizes the LSODE integration package (Hindmarsh & Petzold 1993) and has been sub-divided to describe the two chemical phases. Phase I represents the (standard) dark cloud chemistry, with freeze-out and (limited) surface chemistry, whilst Phase II considers the chemistry in the high density, rapidly expanding gas, in the immediate vicinity of a dust grain following ice mantle sublimation.

The two phases are physically and chemically distinct from each other, but the output from each phase feeds into the other as material cycles between the two. The characteristics of the two phases are described below.

\subsection{Phase I}

The physical and chemical parameters for Phase I (as given in Table 1) are discussed below.

For the gas-grain interactions, all species are assumed to have a sticking coefficient of 1.0 and as with the simple model - and for the purpose of clarity - we suppress all continuous desorption processes. The freeze-out rates (and hence the H to H$_2$ conversion rate) are calculated self-consistently, using
Table 1. Physical parameters in the standard model - see text for description

| Parameter                        | Value        |
|----------------------------------|--------------|
| He/H                            | 0.1          |
| C/H                             | 2.6 × 10⁻⁴   |
| N/H                             | 6.1 × 10⁻⁵   |
| O/H                             | 4.6 × 10⁻⁴   |
| S/H                             | 1.0 × 10⁻⁷   |
| Na/H                            | 1.0 × 10⁻⁷   |
| Density (n₁)                    | 10⁴ cm⁻³     |
| Temperature (T₁)                 | 10 K         |
| Aᵥ                               | 3 magnitudes |
| Cosmic ray ionization rate (ζ₀) | 1.3 × 10⁻¹⁷ s⁻¹ |
| Initial abundance of H-atoms (n₀) | 1 cm⁻³ (see text) |
| H-atom non-recombination probability (pυ) | 0.1 |
| Explosion threshold abundance of H (f_H) | 0.05 |
| No. of (refractory) atoms per grain (N_g) | 10⁶ |
| Mantle radical formation rate (R_rad) | 0.01 Myr⁻¹ |
| Average grain radius (a)         | 0.0083 μm    |
| Dust surface area per H-nucleon (σ_H) | 8.0 × 10⁻⁻²¹ cm² |
| Grain albedo                     | 0.5          |
| CO → CO₂ conversion efficiency (f_CO₂) | 0.1 |
| Phase II: Initial density (n₁₁₁) | 10²⁰ cm⁻³ |
| Phase II: Initial Temperature    | 1000 K       |
| Phase II: Three-body rate coefficients (k₃B) | 10⁻²⁸ cm⁶s⁻¹ |
| Number of cycles (n_cyc.)        | 5            |

Note that we have not included the (equally likely) possibility of the formation of molecular ions in the ice mantles. This is a potentially serious omission, but since we have little idea as to the efficiencies and products we have opted not to include these processes in our model. However, we also note that molecular ions are highly reactive, so the results from this study must be regarded as a lower limit to the formation efficiencies of complex organic molecules.

It is further assumed that the hydrogen atoms so-generated are released back into the gas-phase and are not retained in the ice mantles. These radicals will be crucial in determining the efficiency of large molecule formation in Phase II, as we postulate that radical-radical three-body reactions will be much faster (by a factor of > 100×) than reactions between saturated species. We use a value of R_rad = 1% per Myear in our standard model.

In the case of atomic hydrogen we assume that a fraction (p_H) that impacts grains simply sticks as free hydrogen atoms in the ice. The remainder recombin to H₂ and is returned to the gas phase, as per standard models of interstellar clouds. In our standard model we follow Rawlings & Ketel (2012) and adopt a value of 0.1 for p_H. The timescale between mantle explosions is determined by the rate of accretion of atomic hydrogen, so the initial H abundance is an important parameter. Assuming that chemical equilibrium initially pertains in the cloud then, for typical gas-to-dust ratios, the abundance of atomic hydrogen is given by (e.g. Duley & Williams [2011])

\[ n_H = 1 \left( \frac{\zeta_0}{1.3 \times 10^{-17} \text{s}^{-1}} \right) \text{cm}^{-3} \]

There are 81 gas-phase and 25 solid-state species in the dark cloud (Phase I) chemistry which are listed in Table 2. Those given in italics are solid-state (frozen-out) species, whilst those in bold are the solid-state radicals formed in situ.

The time-dependence of the chemistry is followed until the atomic hydrogen abundance in the ices reaches some threshold value (f_H). At this point we assume that the hydrogen explosively recombines (with 100% efficiency) to H₂ and all components of the ice mantles are instantaneously heated and fully sublimated. The energy liberated has to heat the whole grain, so f_H is the fraction of H-atoms rel-

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Table 2. Chemical species in Phase I

|                  |                    |
|------------------|--------------------|
| H, H₂, H⁺, H⁻, H₂⁺, H₂⁻, He, He⁺, Na, Na⁺,  |
| C, C⁺, C⁻, CO, CO⁺, CH, CH⁺, CH₂, CH₂⁺,  |
| CH₃, CH₂O, CH₃⁺, CH₃⁻, CH₄, CH₄⁻, CH₅⁺,  |
| N, N⁺, NH, NH⁺, NH₂, NH₂⁺, NH₃, NH₃⁺, NH₄⁺,  |
| N₂, N₂⁺, N₂H⁺,  |
| O, O⁺, O₂, O₂⁻, OH, OH⁺, H₂O, H₂O⁺, H₃O⁺,  |
| H₂O⁻, H₂O₂⁻, H₄O⁺,  |
| HCO, HCO⁺, H₂CO, H₂CO₂⁺, CO₂, CO₂⁻, H₂O₂⁻,  |
| CO₂⁺, CN⁻, CNI⁻, HCN⁻, HNC⁻,  |
| NO, NO⁺, HNO⁻, HCN⁺, HCN⁻, H₂NC⁺, H₂NO⁻,  |
| HNO₂⁻, S, S⁺, HS⁺, H₂S⁺, H₃S⁺,  |
| CS, CS⁺, C₂S⁺, C₂S⁻⁺, HCS⁻, HCS⁺, H₂CS⁺,  |
| CH₄, CO, NH₃, N₂, O₂, H₂O, Na, H₂CO, CO₂,  |
| HCN, HNC⁻, HNO⁻, H₂S, C₂H₂S⁺, HCS⁻, HCS⁺,  |
| CH₃, NH₃, HCO, HS, CH₃O, CH₂OH.  |

Table 3. Chemical species in Phase II

|                  |                    |
|------------------|--------------------|
| H₂O, H, H₂, CO, CH₄, CH₃, NH₃, NH₂, OH, H₂CO, HCO,  |
| CO₂, H₂S, HS, CH₂OH, CH₃O, CH₂OH, NH₂OH, HCOOH,  |
| C₂H₆, CH₂NH₂, CH₂CH₂O, C₂H₂OH, CH₂CHO, HCONH₂,  |
| (CH₂OH)₂, CH₂OCH₂CHO, CH₂OCHN₂H₂, CH₂OCH₂O,  |
| CH₂OH, CH₂OCH₂OH.  |

Table 4. Reaction network in Phase II

| Reaction |                  |
|----------|------------------|
| OH + CH₃ | H₂O → CH₂OH     |
| OH + NH₂ | H₂O → NH₂OH     |
| OH + CH₂O | H₂O → CH₂OCH₂   |
| OH + HCO | H₂O → CH₂OCH₂   |
| CH₃ + CH₃ | H₂O → C₂H₆     |
| CH₃ + NH₂ | H₂O → CH₂NH₂    |
| CH₃ + CH₂O | H₂O → CH₂OCH₂   |
| CH₃ + HCO | H₂O → CH₂OCH₂   |
| NH₂ + CH₂OH | H₂O → CH₂OCH₂N₂H₂ |
| NH₂ + HCO | H₂O → CH₂OCH₂N₂H₂ |
| CH₂O + CH₂O | H₂O → CH₂OCH₂O   |
| CH₂O + CH₂OH | H₂O → CH₂OCH₂O   |
| CH₂OH + CH₂OH | H₂O → (CH₂O)₂   |
| CH₂OH + HCO | H₂O → CH₂OCH₂OH  |

2.2 Phase II

There are 34 chemical species in the Phase (II) high-density expanding gas as listed in Table 3. The (limited) reaction network is shown in Table 4. Both the species and the reaction network are highly uncertain and ill-determined. We speculate that the three-body reactions (for which we assume the third body to be H) are the most abundant species in the post-sublimation gas-phase) may yield obvious organics (such as C₂H₅OH and (CH₂OH)₂). Of course, other, unidentified, reaction channels/products may also exist. Other (small species) products of the reactions are not specified in Table 4. Since clear detections of sulfur-bearing species in ice mantles do not exist, we do not include any complex species/reactions which incorporate sulfur atoms. As H₂O is the dominant gas-phase constituent of the Phase II gas, we renormalise all integrations to calculate abundances relative to H₂O, rather than H nuclei.

The physical conditions in this extremely high density, rapidly expanding, gas are as described in Paper I, so that we again consider a sphere of ice, instantaneously sublimated into the gas-phase of initial radius r₀ and with an initial density (n₀) that is comparable to the solid-state number density. This gas freely expands, with spherical symmetry, into a vacuum at the sound speed v₀. Then, as described in Paper I, if r₀ is assumed to be comparable to the typical thickness of an ice mantle and v = 10⁴ cm s⁻¹, the evolution of the number density is given by

\[ n/n₀ = 1/\left(1 + 10^9t\right)^3 \]  

(1)

where t is the time in seconds. At such high densities the chemistry will be completely dominated by three-body reactions. Some of the mantle explosion energy will be released as heat and we assume that the gas has an initial temperature of ~1000 K, which may help to drive the chemistry. We follow the practice of Paper I and adopt a single value for the rate coefficient (k₃B) for all reactions which incorporates any implicit dependence on temperature. The radical-radical-H₂O reactions are expected to be faster than the radical-neutral-H₂O reactions and so we adopt larger values for k₃B than we did in Paper I. As we do not include any specific temperature-dependences of the rates, the variation of temperature with time is not a relevant parameter in our models.

We follow the chemistry in this expanding sublimated gas - which is quite distinct from the background chemistry in the surrounding (Phase I) cloud - until quasi-equilibrium and/or suppression of chemical activity due to geometrical expansion occurs. In practice, this is extremely fast - of the order of 1-10 ns (see Paper I); many orders of magnitude faster than the chemical timescale of Phase I. This necessitates a separate numerical integration and the complete switching of the chemistry and differential equations at each transition between Phases I and II.

2.3 Cycling

After 10 ns, when the Phase II chemical calculations are terminated, the abundances (calculated relative to H₂O) are
re-normalised to hydrogen and (fully) mixed back into the Phase I gas. The cycle, as described above and the duration of which is calculated self-consistently, is then repeated. For the standard model \((\zeta_0 = 1.3 \times 10^{-17} \text{s}^{-1})\) the Phase I duration is \(\sim 3.2 \times 10^5\) years and we follow the chemical evolution through 5 cycles. We use this number of cycles for two reasons: (i) The results indicate that, by then, the solution is approaching a limit cycle, and (ii) The total duration of \(\sim 1.5\) Myr is comparable to the average lifetime for a dense cloud. However, for \(\zeta_0 = 1.3 \times 10^{-16} \text{s}^{-1}, n_{\text{H}} \sim 10 \text{cm}^{-3}\) and so the inter-explosion period is reduced accordingly to \(\sim 3.2 - 4 \times 10^4\) years. We therefore run the calculation for 50 cycles, so as cover approximately the same time interval \((\sim 1.5\) Myr\) as for the standard model.

There will obviously be some optimal value for \(n_{\text{H}}\); if it is too high, then that implies that the molecular content of the gas is low and ices will not form. If it is too low, then the inter-explosion timescale becomes too long for the processes described here to be important. The importance of \(n_{\text{H}}\) in controlling mantle growth in molecular clouds may be relevant to the determination of the observed critical visual extinction for the onset of ice formation. We shall return to this question in a later publication.

Strictly speaking, we should model the gas-phase chemistry and freeze-out of the larger organic molecules created in Phase II through successive cycles to ever increasing complexity. However, we note that the chemistry is very much faster and more efficient in Phase II, so we make the simplifying assumption that the larger species (not included in the species list for Phase I) are ‘sunk’ and simply build up in successive cycles, not taking part in the gas-phase chemistry, and not being converted into larger species. By contrast, simple saturated species (such as CH\(_3\) and NH\(_3\)) are allowed to re-cycle with a full gas-phase chemistry, freeze-out and sublimation.

3 RESULTS

At first sight it may seem that there are an unmanageably large number of free parameters in the model, but in reality many of these are degenerate and in effect the chemical complexity will largely be defined by two ratios:

(i) In Phase I; the ratio of the accretion to the inter-explosion timescales, and

(ii) In Phase II; the ratio of the three-body chemistry to the expansion timescales

In the discussion below, we therefore only investigate the sensitivities to four parameters; the density in Phase I \((n_1)\), the cosmic ray ionization rate \((\zeta_0)\), the density in Phase II \((n_{1f})\) and the rate of formation of radicals in the ice mantle \((R_{\text{rad}})\). Other parameters, such as the assumed universal three-body reaction rate \((k_{3B})\), have obvious linear effects on the large species formation efficiencies (subject to saturation limits).

The model described above is complex; yielding abundances as a function of time for both the quiescent phase (Phase I) and the sublimation phase (Phase II) for each of the cycles of quiescence and explosion. We present the results in two forms: (i) as graphical representations of the time-dependence of (key) species in the two phases - results from all cycles being shown on one plot, and (ii) as tabulated abundances of species in Phase I.

Figures 1 and 2 show the abundances of selected species in Phases I and II respectively. The different curves in each frame depict the results from different cycles. The time-dependences in Phase II, shown in Fig 2 are simple and as expected; molecular abundances build up very rapidly until saturation (exhaustion of the reactants) and/or geometrical dilution become important (typically within 1 ns). From Fig 1 it is immediately apparent that, in Phase I, there is considerable variation of the abundances with time, partly due to the gas-phase chemistry, but mainly as a result of the freeze-out of species onto dust grains. Interstellar clouds will consist of an incoherent ensemble of material in various stages of cycling between the gas-phase and the frozen-out states. Bearing these two facts in mind it is therefore apparent that to make a sensible comparison with observations we need to calculate the time-averaged values of the abundances. For those species where we calculate the full time-dependence of the abundances the time-averaged values can be easily obtained. For the larger species produced in Phase II, whose gas-phase chemistry we do not follow, we use a simple analytical approximation.

On the assumption that freeze-out is the only process that affects the abundances of these species in Phase I, the rate of change of abundance of species \(i\) is simply:

\[ \dot{n}_i = -k_in_i \]

where \(k_i\) is the freeze-out rate for species \(i\) and \(n\) is the density. Simple integration then yields, for the average fractional abundance:

\[ \langle x_i \rangle = \frac{X_i(0)}{k_in} \left[ 1 - e^{-k_i n t} \right] \]

where \(X_i(0)\) is the fractional abundance of species \(i\) at the beginning of Phase I and \(t\) is the duration of the phase. This approach therefore makes allowance for the statistical ensemble of explosion cycles, but does not include the effects of sequential enrichment of the gas through successive explosions. Whilst some species will approach a limit cycle, others will be constantly supplied by successive explosions and a cumulative build-up of the explosion products will occur. To quantify these effects we have studied the (time-averaged) abundances in a sequence of cycles - see Table 3 below.

We also note that other destruction processes may need to be considered. In the case of the larger organic molecules, protonation followed by dissociative recombination may be an effective loss mechanism (e.g. Buckle et al. 2002). We can make a simple, empirically-based, estimate for the efficiency of this process as follows: Assume physical parameters as for our standard model and a fractional ionization of \(\sim 10^{-8} - 10^{-7}\), as appropriate for a molecular cloud. As an upper limit, if we further assume that the abundance of the protonating reactant is equal to the ionization fraction and that the reaction rate coefficient is \(\sim 10^{-9} \text{cm}^3\text{s}^{-1}\) then the upper limit to the protonation (and loss) rate implies a destruction timescale of \(\sim 3 \times 10^4 - 3 \times 10^5\) years. To check this approximation we have run a simple model of a static molecular cloud with a full gas-phase chemistry. The initial abundance of CH\(_3\)OH is set high \((\sim 10^{-7})\). The model confirms that the CH\(_3\)OH decays on these timescales.
These values are comparable to the time interval between explosions. By comparison, in our standard model, the freeze-out timescale for CH$_3$OH is $\sim 2 \times 10^5$ years. We therefore conclude that chemical destruction of the larger molecules is possibly significant, inhibiting the (time-averaged) abundances by a factor of $\sim 2 - 5$, although this effect would be reduced significantly if the period between explosions were shorter.

We present the results from 10 model runs. Model 1 is the standard model, which uses the parameter values given in Table 1. The variations to these parameter values used in the other models are given in Table 5. 

Tables 6, 7 and 8 give the (Phase I) time-averaged abundances for selected species calculated as described above. Note that the only species in these tables that are not created exclusively in the explosions are NH$_3$, H$_2$O, H$_2$CO and H$_2$S. These are all formed in both the gas and the solid-state. In the absence of explosions, all other species would have a zero gas-phase abundance and, since we suppress continuous desorption in our models, the smaller species would also just freeze-out within 1 Myr. Table 6 shows results for the standard model (model 1) in the form of the (average) abundances of selected species in each of the five cycles. Several conclusions can be drawn from this table: The small (Phase I) gas-phase species approach a limit cycle - with only small cycle-to-cycle variations after 4 or 5 cycles. The same applies to the smaller species produced in the explosion chemistry (eg. CH$_3$OH, C$_2$H$_6$) which reach abundances of $\sim 10^{-9} - 10^{-7}$. The larger species (eg. CH$_3$OHNH$_2$, C$_2$H$_5$OH) have smaller abundances ($\sim 10^{-13} - 10^{-10}$) but these steadily grow as each cycle adds more to the ‘reservoir’ of the larger species.

Tables 7 and 8 show the sensitivity of the results to variations in the free parameters. The results from models 2-4 are a little surprising at first sight; increasing the (Phase I) density drives a faster and more efficient chemistry, so that the abundances are somewhat enhanced for model 2 ($n_I = 10^6$ cm$^{-3}$). However at higher densities (in models 3 and 4), as might be applicable to hot core environments, the abundances are notably suppressed - especially for the larger species; model 4 yields the lowest abundances of any of the models. This is simply a result of the rapid freeze-out at high densities so that, although the abundances at the beginning of Phase I are higher, the time-averaged abundances in Phase I are much lower. Increasing the cosmic ray ionization rate ($\zeta$) - model 5 - again yields relatively small enhancements relative to model 1 (by factors of $< 2 - 6$) for most species, whilst some are inhibited. However, increasing both $\zeta$ and $n_I$ (model 6) results in substantial abundance enhancements, especially for the larger species which in some cases (eg. CH$_3$OCH$_3$) are by more than three orders of magnitude. Part of the explanation for this is that higher ionization rates result in larger atomic hydrogen abundances and hence shorter inter-explosion periods. This, in turn, means that the gas-phase depletion factors are lower.

Models 7 and 8 investigate the effects of a higher density in Phase II ($n_{II}$). In model 8 the density in Phase I is also increased. In the case of model 7 the chemistry of the Phase I species is barely affected, whilst the species formed in the explosions are enhanced by small factors (typically $< 2$). Model 8 exhibits a similar behaviour to models 2-4 in that the higher Phase I density and shorter freeze-out timescales result in lower abundances. Models 9 & 10 investigate the effects of increasing the radical formation rate ($R_{rad}$) - model 5 - again yields relatively small enhancements, especially for the larger species which in some cases (eg. CH$_3$COCH$_3$) are by more than three orders of magnitude. Part of the explanation for this is that higher ionization rates result in larger atomic hydrogen abundances and hence shorter inter-explosion periods. This, in turn, means that the gas-phase depletion factors are lower.

4 DISCUSSION AND CONCLUSIONS

The results show that, despite the large number of poorly-constrained free parameters, the results are fairly insensitive within the range of values that we have investigated. Significant enhancements of the abundances of large molecular species are obtained in the cases of a combination of an elevated cosmic ray ionization together with a high gas-phase density, or when then the rate of formation of radicals in the ices is increased.

It is interesting to compare the predictions of our dark cloud model with observations. However, in so doing, it is
important to note that a direct comparison is not possible; a major conclusion of our study and result from the model is that we predict the presence of appreciable abundances of large molecules in dark clouds. So far, it has only been possible to detect these species towards hot core sources. Never the less, despite the very different physical conditions, our models are able to reproduce the hot core abundances for all species except for the largest ones, e.g. acetamide (HCONH$_2$) and glycolaldehyde (CH$_2$OHCHO); However we note that acetamide has only been observed towards the Galactic Centre whilst glycolaldehyde has been detected towards the Galactic Center and one hot core only, hence the observed abundances may not be typical.

Our model is general and not specific to any one source.
However, although we defer specific modelling and a detailed comparison with the dark cloud source TMC-1 (CP) to a future study, we can make some rough comparisons. Some of the species given in these tables (NH$_3$, H$_2$O, H$_2$CO, H$_2$S, CH$_3$OH, HCOOH and CH$_3$CHO) have been observed in TMC-1 (CP) and their abundances have been determined by Smith, Herbst & Chang (2004). These abundances are generally in very good agreement with our models, with the notable exception of methanol (CH$_3$OH) which in most of our models is apparently over-produced by a factor of up to $\sim 100$. However, there are two reasons why this is probably not discrepant: (i) there is considerable flexibility/uncertainty in the physical parameters (given in Table 1) which determine the efficiency of the formation of

Figure 2. Logarithmic fractional abundances (relative to H$_2$O) of selected species as a function of time in Phase II. Results are shown, overlaid, for each of the five cycles: 1-solid line, 2-dashed line, 3-dot-dashed line, 4-wide-dotted line, 5-close-dotted line.
complex molecules, and (ii) as described in the previous section, we have probably underestimated the loss rate for large molecules in the quiescent phase (Phase I). Our model also over-produces water. However, the clumps in TMC-1 are known to have substructure (Peng et al. 1998) which means that ultraviolet penetration into CP is easier than it would be in a uniform region - as we have assumed. So, we would expect that the time-averaged H$_2$O abundance should be lower than the values we have computed for the non-specific case. In addition, we also note that the efficiency of the surface reaction converting O to H$_2$O is required by observations to be high, but is undetermined. We have assumed a value of 100% but a factor of a few less than this would still be compatible with the observed strengths of the water ice features. Looking ahead, we expect that the predicted presence of hot-core type molecules within molecular clouds are at levels that can be detected with new facilities, such as ALMA.

As it stands, the model is largely hypothetical. We have been able to give reasonable estimates for the key parameters. However, we require further experimental study of the explosion mechanism. In addition, we need confirmation of the viability of the proposed three-body reaction pathways.
and quantification of the reaction rates. However, several conclusions can already be drawn from this study:

- From our results it can be seen that our model predicts the presence of detectable (observationally verifiable) gas-phase abundances of ‘large species’ in molecular clouds. However, the mechanism that we describe has a limiting effect on the size of molecules that can be made, because of the very short time available for rapid 3-body reactions to take place.

- Our model also suggest that there could be significant amounts of undetectable molecules, such as C\textsubscript{3}H\textsubscript{6}, present in dark clouds. If so, these species - which tend to be ignored in chemical networks - may also play a role in the formation of observed larger species, through ordinary gas phase ion-molecule reactions. For example, a reaction sequence involving C\textsubscript{2}H\textsubscript{2} and CH/\textsubscript{2}CH radicals can lead to the formation of benzene (C\textsubscript{6}H\textsubscript{6}) in dark cloud environments [Jones et al. 2011].

- In recent years, spectral line surveys of dark cores, such as those of TMC-1, have revealed a surprising repertoire of complex molecules and large carbon chain species including propylene (CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}). This latter species, expected in hot cores rather than in dark clouds, has been detected in TMC-1 [Marcelino et al. 2007] but not in Orion. In general, other more common species, such as HNCO and CH\textsubscript{2}OH, are surprisingly abundant in some dark cores. Pure gas-phase models at low temperatures (~10 K) cannot reproduce their abundances and grain surface reactions on icy mantles are often invoked. However, it is not clear what mechanisms are responsible for the release of icy mantles in cold cores; it is unlikely that non-thermal desorption alone would suffice and the presence of shocks inducing explosive injection of grain mantles has been suggested in the past (e.g. Snyder 2006). Our model provides a novel mechanism for the production of large complex molecules in cold dark clouds.

- Methanol (CH\textsubscript{3}OH) and formaldehyde (H\textsubscript{2}CO) are found in ices in quiescent regions. In our model these species are synthesised in the gas phase following the ice mantle explosions, are ejected and subsequently frozen onto the grains in the next cycle. This is different from the conventional picture in which they are made by the hydrogenation of CO in the ice. Although we allow for the partial conversion of CO to CO\textsubscript{2} we have deliberately suppressed the solid-state conversion of CO to CH\textsubscript{2}OH in our models, so as to clearly separate the significance of our mechanism from the conventional channel. We find that both processes may be effective.

- The composition of the ice mantles and the nature of gas-grain interactions differ from previous models. We have postulated an alternative desorption mechanism which should be considered alongside other desorption processes. Our model predicts that the ices will probably be more chemically complex than previously recognised. Moreover, the chemical processing is cumulative, so that we expect the the chemical complexity of ices in molecular clouds to grow in time.

- The presence of trace metal elements, such as Na, in the hot sublimated gas together with OH radicals may lead to the formation of NaOH. NaOH has a large dipole moment, a rotational constant of \( B_0 \sim 12.57 \text{ GHz} \) and an observationally detectable rotational spectrum [Pearson & Trueblood 1973].

- The chemical network that we employ in the high density phase (Phase II) is highly speculative, probably incomplete, and somewhat pessimistic in that it only involves reactions with H\textsubscript{2}O as a passive third body: i.e. one that stabilizes associating species, but does not chemically react with them. Our results should therefore be considered as lower limits to the large molecule formation efficiencies. We can speculate, for example, that the abundant species CO (which is technically a radical) could be involved as an active third body in which it chemically combines with the other reactants. If, for example, these were NH\textsubscript{2} and CH\textsubscript{2}OH radicals then it may be possible to form a large molecule, such as glycine (NH\textsubscript{2}CH\textsubscript{2}COOH), in a single step process.

- The model may provide a mechanism for the formation of larger molecules, of biochemical importance, in molecular clouds. If we consider C\textsubscript{2}H\textsubscript{2}O\textsubscript{2}, then three isomers of this molecule are detected in hot cores; acetic acid (CH\textsubscript{3}COOH), methyl formate (HCOOCH\textsubscript{3}) and glycolaldehyde (CH\textsubscript{2}OHCHO). No detections of these species have been made in molecular clouds. However, in hot cores, acetic acid and glycolaldehyde are only detected rarely (such as in Sgr B2(N) and W51), whilst methyl formate is more abundant and is observed in many sources. Thus, for example, the relative abundances of (acetic acid):(glycolaldehyde):(methyl formate) are \( \sim 1:1:26 \) in Sgr B2(N). This is consistent with the observation that interstellar molecules with a C-O-C backbone structure are preferred over those with a C-C-O structure [Hollis, Lovas & Jewell 2000].

Our model only specifically identifies glycolaldehyde as a reaction product. It is possible that methyl formate could be formed as a result of a three-body reaction involving the radicals CH\textsubscript{3}O and HCO. However, even if this assumption is made, then the model predicts methyl formate abundances that are less than those of glycolaldehyde. There are three possible explanations for this apparent discrepancy: (i) The physical and chemical conditions in hot cores are very different to molecular clouds, so that molecular ratios determined from hot core observations may not apply, (ii) as is highly likely to be the case, our Phase II reaction network is neither fully accurate, nor complete and/or (iii) alternative mechanisms may be operating which produce the methyl formate. Indeed a variety of mechanisms have been proposed for methyl formate formation, including the solid-state reaction of methanol and CO in cosmic-ray irradiated ices [Modica & Palumbo 2010, Occhiogrosso et al. 2011], the solid-state reaction of formic acid and methanol (Hollis et al. 2000) and gas-phase reaction of methanol and formaldehyde in hot cores [Caselli, Hasegawa & Herbst 1993].

Looking at the structure of these three isomers we see that methyl formate, glycolaldehyde and acetic acid have a central O-atom (ether group), methylene group and carbonyl group respectively. As we do not have atomic oxygen in our Phase II chemistry it is therefore perhaps not surprising that methyl formate is not produced in our model.

If we go on to speculate about the possible formation of larger bio-molecules then we should note that methyl formate is less important that the other two (C-C-O structure) isomers; glycolaldehyde is the simplest sugar, whilst acetic acid is only an NH\textsubscript{2} group away from the simplest amino acid, glycine (NH\textsubscript{2}CH\textsubscript{2}COOH). Indeed, it is highly likely that the main synthesis channels for glycine involve acetic
acid so that it may be something of an essential pre-cursor to bio-molecule formation (Snyder 2006).

Whilst acetic acid is not specifically included in our reaction scheme, it is a perfectly feasible product of the reactants that are present in the high density phase (Phase II) of our model - indeed more so than methyl formate. It is also worth noting that our model does produce formic acid (HCOOH) with typical fractional abundances of $\sim 10^{-10} - 5 \times 10^{-9}$. Formic acid is also believed to be a significant species in glycine synthesis (Snyder 2006). An alternative mechanism for the formation of complex organic molecules was proposed by Sorrell (2001) in which radicals are created in ice mantles by UV photolysis. In that model, the grains are heated by grain-grain collisions and the radicals react with each other in the mantles. Chemical explosions release the complex organics, including glycine and glycolaldehyde into the gas-phase. There is no reason why the mechanism that we are proposing and that of Garrod, Widicus Weaver & Herbst (2008) should not be both possible and may indeed complement each other.

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