

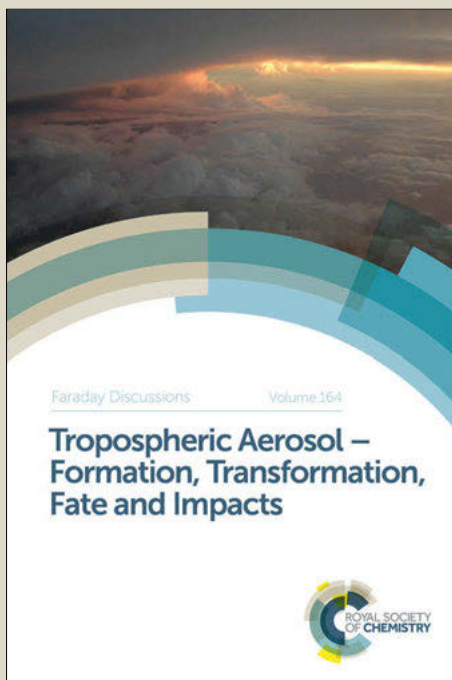
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The Formation of Glycine and other Complex Organic Molecules in Exploding Ice Mantles

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Abstract

Complex Organic Molecules (COMs), such as propylene (CH_3CHCH_2) and the isomers of $\text{C}_2\text{H}_4\text{O}_2$ are detected in cold molecular clouds (such as TMC-1) with high fractional abundances [18]. The formation mechanism for these species is the subject of intense speculation - as is the possibility of the formation of simple amino acids, such as glycine ($\text{NH}_2\text{CH}_2\text{COOH}$). At typical dark cloud densities, normal interstellar gas-phase chemistries are inefficient, whilst surface chemistry is at best ill defined and does not easily reproduce the observed abundance ratios in the gas-phase. Whatever mechanism(s) is/are operating it/they must be both efficient at converting a significant fraction of the available carbon budget into COMs, and capable of efficiently returning the COMs to the gas-phase.

In our previous studies we proposed a complementary, alternative, mechanism; in which medium- and large-sized molecules are formed by three-body gas kinetic reactions in the warm *high density gas-phase*. This environment exists, for a very short period of time, subsequent to the total sublimation of grain ice mantles in transient co-desorption events. In order to drive the process, rapid and efficient mantle sublimation is required and we have proposed that ice mantle ‘explosions’ can be driven by the catastrophic recombination of trapped hydrogen atoms, and other radicals, in the ice. Repeated cycles of freeze-out and explosion can thus lead to a cumulative molecular enrichment of the interstellar medium. Using existing studies we have based our chemical network on simple radical addition, subject to enthalpy and valency restrictions.

In this work we have extended the chemistry to include the formation pathways of glycine and other large molecular species that are detected in molecular clouds. We find that the mechanism is capable of explaining the observed molecular abundances and complexity in these sources.

We find that the proposed mechanism is easily capable of explaining the large abundances of all three isomers of $\text{C}_2\text{H}_4\text{O}_2$ that are observationally inferred for star-forming regions. However, the model currently does not provide an obvious explanation for the predominance of methyl formate, suggesting that some refinement to our (very simplistic) chemistry is necessary.

The model also predicts the production of glycine at a (lower) abundance level that is consistent with its marginal detection in astrophysical sources.

Key words: astrochemistry - ISM: molecules - ISM: clouds

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1 Introduction

Organic molecules containing more than a few carbon atoms, known collectively as Complex Organic Molecules (or COMs) are found in a wide variety of interstellar astrophysical environments - from dynamically active, star-forming, regions, to quiescent molecular clouds. Unlike many of the smaller molecules that have been identified in molecular clouds, which are often exotic unsaturated radicals, detected COMs include organic species that are well known in the laboratory (e.g. alcohols, acids, esters, ketones, saturated and unsaturated hydrocarbons, simple sugars etc.). However, the mechanisms by which they are formed remains largely unknown. Simple bimolecular reactions between neutral species and/or between ions and neutrals (that are driven by ultraviolet radiation and ionization by cosmic rays) are known to be efficient for the formation of the smaller species, but cannot explain the observed abundances of COMs.

It is believed that many of the COMs are formed on the surface of dust grains, in ice mantles, via solid-state reactions that are perhaps catalysed by the presence of ultraviolet photons and/or thermal processing in star-forming regions. However, even these mechanisms fail to reproduce some of the observed abundances. Notable examples of instances where the models struggle are in predicting; (a) the presence of significant quantities of propylene (CH_3CHCH_2), (b) the abundances and ratios of the three isomers of $\text{C}_2\text{H}_4\text{O}_2$; glycolaldehyde (CH_2OHCHO), methyl formate (HCOOCH_3) and acetic acid (CH_3COOH), and (c) the possible presence of the simplest amino acid, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$).

The three isomers of $\text{C}_2\text{H}_4\text{O}_2$ have all been detected in star-forming regions, but - to date - no detections of these species have been made in molecular clouds. However, where detected, methyl formate is found to be much more abundant than the other isomers. For example, the relative abundances of (acetic acid):(glycolaldehyde):(methyl formate) in one well-studied source (Sgr B2(N)) are $\sim 1:4:26$. 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 [16]. In the context of ‘large molecule chemistry’, methyl formate is considered to be less important than the other two (C-C-O structure) isomers; glycolaldehyde is the simplest sugar, whilst acetic acid is probably involved in the main synthesis channels for the simplest amino acid, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), so that it may be an important pre-cursor to bio-molecule formation [27].

In this paper we review the results that we have obtained from an alternative scenario, based on proposed gas-phase reactions that may occur in the high-density gas subsequent to catastrophic ice mantle sublimation. We then present and discuss an extension to the model that is capable of providing plausible explanations for (b) and (c) above - noting, for example, that our previous reaction scheme only included the glycolaldehyde isomer of $\text{C}_2\text{H}_4\text{O}_2$.

In Section 2 we describe the fundamental hypothesis that forms the basis for our studies; that the ice mantles on dust grains can be catastrophically sublimated and that a rapid and efficient three-body chemistry between radicals can take place in the gas-phase. Section 3 gives an extended summary of our previous work and provides the context for the new work presented in this paper. In section 4 we describe how the chemistry has been extended, being driven by the inclusion of additional ice mantle species, so as to describe the formation of glycine, the isomers of $\text{C}_2\text{H}_4\text{O}_2$ and other COMs. Section 5 describes the physical and chemical model. Our computational model and results are presented in section 6 and our conclusions discussed in section 7.

2 Explosive Chemistry in Sublimating Ice Mantles

Laboratory experiments involving the slow warming of chemically-mixed ices [8] demonstrate that desorption occurs in several distinct and narrow temperature bands, of which the most important to our studies is the so-called co-desorption band. This band is when the major component of the ice, H_2O , desorbs and carries with it all other species.

This understanding of desorption has been shown to be consistent with current observations of so-called ‘hot cores’. These are the ‘remnants’ of the natal molecular envelopes out of which high mass stars form. They are heated by the young protostar and the ice mantles sublimate. By transferring molecular material back into the gas-phase, they effectively reveal the composition of the ice mantles. The reasonable assumption is made that the formation of a hot core is a time-dependent process [29]. In a typical hot core the material is relatively warm (~ 200 K) and is exceptionally rich in molecules - some of which are hydrogen-poor - such as vinyl cyanide CH_2CHCN , ethyl cyanide $\text{CH}_3\text{CH}_2\text{CN}$, methyl formate HCOOCH_3 , dimethyl ether $(\text{CH}_3)_2\text{O}$, acetone $(\text{CH}_3)_2\text{CO}$, acetic acid CH_3COOH , and ethanol $\text{CH}_3\text{CH}_2\text{OH}$ (see, e.g. [27]). None of these species is readily formed in standard interstellar gas-phase chemistries. The conventional wisdom is therefore that source of these relatively complex species is solid-state chemistry occurring in the ice mantles on dust grains. Highly detailed computational models by Herbst, Garrod, and their collaborators (e.g. [11]) have investigated the chemistry that may arise from the creation of (photolytically or cosmic-ray generated) mobile radicals within the ices. Their models predict a rich and relatively complex chemistry. These species are subsequently returned to the gas-phase when the ice mantles are (thermally) sublimated.

At the same time, 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. For abrupt temperature excursions of this magnitude any ices that are present will be completely converted to gas and sublimated explosively.

In this paper, we develop and extend our proposal that COMs may be formed in the high-density gas-phase that pertains immediately after the ice mantle on a dust grain is catastrophically desorbed (‘explodes’). In this model, hydrogen atoms are accreted from the gas-phase and accumulate in the ices until a critical hydrogen atom density is reached, whereupon a runaway explosion occurs [10]. This process 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 energy released due to phase changes in the grain substrate. The theory of radical recombination-driven mantle explosions is very similar to that described by [14] except that the mechanism for mantle explosion is the spontaneous internal recombination of trapped hydrogen atoms, rather than an external heating source. Unlike the laboratory situation, there is a large excess of hydrogen in the interstellar medium. Hydrogen-ice bonding energies are of the order of ~ 1000 K and ices typically possess a high density of binding sites. It therefore seems highly plausible that any explosion will be hydrogen-driven, although other radicals can and will contribute. Note that as this mechanism does *not* require the presence of an external heating source, it may therefore be as applicable to quiescent dark clouds as it is to dynamically active regions.

It was shown by [10] 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. An instantaneous conversion from solid to gas would create a gas with a number density similar to that of the solid, i.e. about 10^{23} cm^{-3} . This is unlikely, but it is nevertheless possible that the density is initially extremely high, if only for a very short period of time. In our models we postulate that three-body reactions occurring in this extremely dense and fairly warm gas (with a temperature that is sufficiently high to overcome any activation barriers) can create molecules of considerable complexity. The reactants

are the radicals that are produced in the ices by the action of cosmic-rays and UV photons.

The sublimated gas is subsequently 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. Ideas of a similar kind (but operating on much longer timescales) were first explored by [9] who suggested that amino acids, peptides, and a variety of organometallic compounds could be created from evaporating ices confined within cavities inside aggregate grains.

3 Summary of the Results from Our Previous Models

In [7, Paper I] we presented the basic model, and considered the gas-phase reactions that occur between the primary (saturated) constituents of the ice mantles, once released into the gas-phase. In that study there was no attempt to identify the nature of the products of the reactions - the purpose was to establish whether or not the proposed mechanism is viable; i.e. that it results in significant abundances of COMs.

The chemistry that we adopted was entirely hypothetical, since there is no information available about three-body gas phase chemistry at extremely high number densities. We considered various types of possible three-body reactions. For these, one normally considers the third body as being chemically inert, but whose purpose is to collisionally stabilise the excited product of the reaction. However, we also postulated reactions in which all three species are chemically active. Whilst some of the product species can be formed in a single-stage reaction, many require two stages, involving intermediate species after the first stage.

The physical model is very simple and idealised: we consider a situation in which a sphere of ice is instantaneously sublimated into the gas-phase. This gas then is assumed to freely expand into a vacuum at some fraction, ϵ , of the sound speed v_s . The parameter ϵ makes allowance for real (non-spherical) grain morphologies, and/or the effects of trapping in cavities. Unhindered spherical expansion corresponds to $\epsilon = 1$.

If the sphere of gas has an initial radius r_0 and density n_0 then, by mass conservation, at any time t after mantle sublimation, the density n is given by

$$\frac{n}{n_0} = \frac{1}{(1 + 10^9 \epsilon t)^3} \quad (1)$$

where we have assumed that r_0 is comparable to the typical thickness of an ice mantle ($r_0 = 10^{-5}$ cm), and the local sound speed $v_s = 10^4$ cm s⁻¹. At the instant of sublimation, the gas density (n_0) may be comparable to the density in the solid-state.

On inspection of the results from that model, we found that the most significant of the free parameters are the initial density (n_0) and the value(s) of the rate coefficients (k_{3B}). There is, however, a wide range of the (n_0, k_{3B}) parameter space which results in the formation of significant abundances of COMs. If activation barriers can be overcome, then the chemistry will be fast and efficient.

Observational studies (e.g. [1],[2]) emphasise that detected molecules (such as amino acetonitrile, NH₂CH₂CN, and ethyl formate, C₂H₅OCHO) tend to be hydrogen-poor, which is consistent with

the mechanism that we postulate; H-atoms will be ejected in the bond-breaking and bond-making processes of three-body chemistry.

In [24, Paper II] we took a more holistic and stochastic view of the process, by developing a much more complex model of a population of grains that successively cycle through phases of ice mantle accretion, explosion and mixing of the chemically rich gas into the ISM. This can lead to a cumulative molecular enrichment of the interstellar medium and allowed us to obtain more realistic, time-averaged abundances. We also postulated a more specific reaction scheme (involving both one-stage and two-stage formation processes) for identifiable reaction products; many of which have been clearly detected in the interstellar medium.

Importantly, we addressed a limitation of Paper I, which only considered reactions between (saturated) primary ice components. In this, and subsequent work, we recognised that reactions between radicals are likely to be much more important and significant to the chemical evolution of the exploding mantles. Thus, an inspection of databases for known three-body reactions (e.g. [30]) shows that the rate coefficients for reactions between radicals, may be quite large ($> 10^{-26} \text{ cm}^6\text{s}^{-1}$), as compared to reactions involving saturated species (for which $k \sim 10^{-33} - 10^{-31} \text{ cm}^6\text{s}^{-1}$). To try and produce a self-consistent chemistry, we assumed that any saturated molecules produced in either stage are unreactive and that only the radicals are capable of undergoing further stages of association.

In the quiescent phase, we followed the dark cloud gas-phase and freeze-out chemistry of some 81 gas-phase and 25 solid-state species, assuming that full hydration of atoms and simple hydrides to CH_4 , NH_3 , H_2O and H_2S occurs on grain surfaces. During this phase we assumed that reactive radicals are created in the ice mantles due to the action of impinging cosmic rays. We note that there may be contributions both from direct cosmic ray impact and photolysis by the cosmic ray induced radiation field [22]. This is a cumulative effect and we assume that it is limited to the stripping of a single hydrogen atom from saturated species. Thus, H_2O 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 relative abundance of the radical to the parent saturated species will therefore be proportional to the cosmic ray ionization rate and the period of exposure. The time-dependence of the chemistry was followed, together with the deposition of ices and the accumulation of weakly bound H-atoms, 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 H_2 and all components of the ice mantles are instantaneously heated and fully sublimated.

In the explosion phase we considered the chemistry in the high density, rapidly expanding gas, in the immediate vicinity of a dust grain following ice mantle sublimation. As explained above, the radical-radical- H_2O reactions are expected to be faster than the radical-neutral- H_2O reactions and so we adopted larger values for k_{3B} than we did in Paper I.

We then followed the chemical evolution through a number (typically 5) of cycles, resulting in a total duration of ~ 1.5 Myr, which is comparable to the average lifetime for a dense cloud. In those cases where the choice of parameters leads to shorter inter-explosion times, we cycled the chemistry through a larger number of explosions. The frequency of the episodic temperature excursions is controlled by the cloud chemistry, so that there will be some optimal value for n_H ; if it is too high and the molecular content of the gas is low, then this implies efficient desorption/dissociation is taking place, which will not be conducive to the formation of ices. If it is too low, then the inter-explosion timescale becomes too long for the processes described here to be important.

As described above, this model comprises two phases for each cycle. Phase I models the (standard) dark cloud chemistry, with freeze-out and (limited) surface chemistry, whilst Phase II models the chemistry in the high density, rapidly expanding gas, in the immediate vicinity of a dust grain

Table 1: Parameter values used in the models described in Paper II. See text for details.

Model	Parameter values
1	standard
2	$n_I=10^5 \text{ cm}^{-3}$, $A_v=10$
3	$n_I=10^6 \text{ cm}^{-3}$, $A_v=10$
4	$n_I=10^7 \text{ cm}^{-3}$, $A_v=10$
5	$\zeta=1.3 \times 10^{-16} \text{ s}^{-1}$, $n_{H,0}=10 \text{ cm}^{-3}$, $n_{cyc.}=50$
6	$\zeta=1.3 \times 10^{-16} \text{ s}^{-1}$, $n_I=10^5 \text{ cm}^{-3}$, $n_{H,0}=10 \text{ cm}^{-3}$, $A_v=10$, $n_{cyc.}=50$

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.

In our standard model (Model 1), the temperature, density and extinction in the dark cloud phase (Phase I) are $n_I = 10^4 \text{ cm}^{-3}$, $T_I = 10 \text{ K}$, and $A_v = 3$ magnitudes, respectively. The cosmic-ray ionization rate of H_2 is $\zeta = 1.3 \times 10^{-17} \text{ s}^{-1}$ and the initial atomic hydrogen density $n_{H,0} = 1.0 \text{ cm}^{-3}$. The initial density and temperature in the explosion phase (Phase II) are $n_{II} = 10^{20} \text{ cm}^{-3}$ and $T_{II} = 1000 \text{ K}$, respectively. The ‘universal’ three-body reaction rate-coefficient is set at $k_{3B} = 10^{-28} \text{ cm}^6 \text{ s}^{-1}$ and the chemistry is cycled through 5 explosions ($n_{cyc.} = 5$). The variations to these parameter values used in the other models are given in Table 1. Results from these models are illustrated in Table 2, which gives the time-averaged abundances of selected species and illustrates the sensitivity of the results to variations in the free parameters.

Although there are a large number of poorly-constrained free parameters in the model, the results are found not to be strongly sensitive to the values used. Key results from the model included the prediction of (i) the presence of detectable gas-phase abundances of COMs in cold molecular clouds, (ii) significant abundances of undetectable molecules, such as C_2H_6 , which may play a role in the formation of other larger species, that are observed, and (iii) a mechanism for the formation of larger molecules, of biochemical importance, in molecular clouds.

We found that this mechanism may be an important source of precursors to bio-molecule formation as well as smaller organic species, such as methanol and formaldehyde. However, some caution is necessary here; our models would seem to predict excessively high gas-phase abundances of methanol which could imply that we have overestimated either the CH_4 abundance in the ices, or the rate for the $\text{CH}_4 + \text{OH}$ association. Never the less, the most unique prediction of our model was the gas-phase presence of these larger molecular species in quiescent molecular clouds and not just dynamically active regions, such as hot cores. This is not predicted by the standard solid-state chemistries, which require a physical mechanism to return the chemically enriched ices mantles to the gas-phase. The detection of COMs in quiescent clouds would therefore give strong observational support for the proposed mechanism.

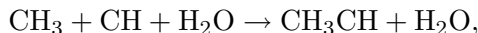
In [25, Paper III], we retained and expanded the chemistry of Paper II, but reverted to the simpler one-grain physical model of paper I to study the specific issue of propylene formation.

Propylene, CH_3CHCH_2 , has been detected in dense gas towards the cyanopolyne peak of the low mass star-forming region TMC-1 with a substantial fractional abundance of $\sim 2 \times 10^{-9}$ relative to hydrogen [18]. Detailed modelling studies ([15],[17]) suggest that propylene cannot be readily formed by conventional interstellar gas phase chemistry.

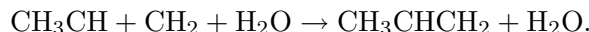
Table 2: Results from Paper II: Time-averaged fractional abundances of selected species in the final cycle for models 1-6. The nomenclature $a(b)$ implies a value of $a \times 10^b$.

Species	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
NH ₃	6.3(-8)	1.9(-6)	3.3(-7)	3.5(-8)	1.1(-7)	5.0(-8)
H ₂ O	4.1(-6)	1.6(-5)	1.6(-6)	1.6(-7)	7.3(-6)	1.2(-5)
H ₂ CO	1.9(-9)	2.5(-8)	4.5(-10)	2.4(-11)	1.0(-9)	1.8(-9)
H ₂ S	6.4(-10)	4.3(-9)	5.2(-10)	5.2(-11)	7.9(-10)	4.3(-9)
CH ₃ OH	1.6(-7)	5.5(-8)	5.5(-9)	5.5(-10)	3.2(-7)	8.7(-7)
NH ₂ OH	2.9(-8)	1.3(-8)	1.7(-9)	1.7(-10)	9.2(-8)	3.9(-8)
HCOOH	1.3(-10)	7.7(-11)	1.3(-12)	6.9(-14)	4.7(-11)	4.7(-9)
C ₂ H ₆	4.9(-8)	2.1(-8)	2.1(-9)	2.1(-10)	9.9(-8)	2.2(-7)
CH ₃ NH ₂	7.5(-9)	4.7(-9)	6.3(-10)	6.5(-11)	1.3(-8)	1.2(-8)
CH ₃ CH ₃ O	1.5(-11)	2.2(-11)	2.3(-12)	2.2(-13)	4.4(-11)	2.0(-9)
C ₂ H ₅ OH	1.5(-11)	2.2(-11)	2.3(-12)	2.2(-13)	4.4(-11)	2.0(-9)
CH ₃ CHO	1.4(-11)	2.9(-11)	4.8(-13)	2.6(-14)	6.6(-12)	1.1(-9)
HCONH ₂	2.8(-12)	6.3(-12)	1.4(-13)	8.1(-15)	9.1(-13)	1.9(-11)
(CH ₂ OH) ₂	1.8(-13)	3.6(-14)	3.5(-15)	3.5(-16)	8.5(-13)	2.1(-10)
CH ₂ OHCHO	6.5(-14)	4.3(-14)	7.1(-16)	3.7(-17)	1.6(-14)	6.8(-12)
CH ₂ OHNH ₂	5.7(-12)	4.9(-12)	6.7(-13)	6.9(-14)	3.3(-11)	7.2(-11)
CH ₃ OCH ₃ O	1.8(-13)	3.6(-14)	3.5(-15)	3.5(-16)	8.5(-13)	2.1(-10)
CH ₃ OOH	2.6(-10)	5.1(-11)	5.1(-12)	5.0(-13)	1.6(-9)	2.1(-8)
CH ₃ OCH ₂ OH	1.5(-13)	2.7(-14)	2.7(-15)	2.6(-16)	8.3(-13)	1.8(-10)

We again proposed formation by simple two-stage radical addition;



followed by



Although hypothetical, there is some laboratory evidence to justify that this type of reaction scheme is viable (e.g. [20]).

In Table 3 we give the final (asymptotic) abundances for propylene as a function of two free parameters; the fraction of the ice that is converted to radicals (F_{rad}) and the value of the product of the three-body reaction rate coefficient with the square of the initial, post-explosion density ($k_{3B}n_0^2$). In these calculations, the gas is allowed to expand freely subsequent to the ice mantle sublimation.

With this assumption, the free parameters are found to be the ice composition, the branching ratios for radical production, F_{rad} and $k_{3B}n_0^2$.

The efficiency of the conversion of the radicals trapped in the ice to complex organic molecules is effectively determined by the ratio of the dynamical (geometrical dilution) timescale to the chemical timescale and, as can be seen from Table 3, a saturation limit is seen to apply to those situations where $t_{chem} \ll t_{dyn}$; in which case a robust limiting value for the propylene abundance (relative to H₂O) of $Y_{sat.} \sim 1.9 \times 10^{-6}$ is obtained. Thus, provided 0.1 percent or more of the ice is converted to radicals and the product of the reaction rate coefficients with the square of the initial, post-sublimation, gas density is $> 10^{14} \text{ s}^{-1}$, the abundances of the COMs may approach saturation levels. We found that the value of this saturation limit is primarily dependent on the chemical initial conditions (i.e. the

Table 3: Results from Paper III: log of the final abundances (relative to H₂O) for propylene (CH₃CHCH₂).

Log ₁₀ ($k_{3B}n_0^2$)	Log ₁₀ F _{rad}				
	-4.00	-3.50	-3.00	-2.50	-2.00
10.0	-16.86	-15.36	-13.86	-12.37	-10.87
11.0	-14.86	-13.37	-11.87	-10.39	-8.94
12.0	-12.87	-11.39	-9.94	-8.57	-7.34
13.0	-10.94	-9.57	-8.34	-7.29	-6.39
14.0	-9.34	-8.29	-7.39	-6.60	-5.90
15.0	-8.39	-7.60	-6.90	-6.28	-5.73
16.0	-7.90	-7.28	-6.73	-6.22	-5.72
17.0	-7.73	-7.22	-6.72	-6.22	-5.72
18.0	-7.72	-7.22	-6.72	-6.22	-5.72

ice mantle composition and the degree of processing to radicals), and is essentially independent of the physical parameters.

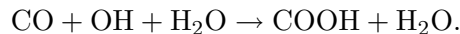
Using these results we estimated an optimal injection rate for propylene into a dense cloud core like those seen in TMC-1. Comparing this timescale to that for the destruction of propylene by gas-phase chemistry in the molecular cloud, we used a simple argument to estimate the time-averaged abundance of propylene that could result from this mechanism: $X_{prop.} \sim 2 \times 10^{-10} - 2 \times 10^{-9}$. This is comparable to the observationally inferred value in TMC-1.

We therefore found that rather special conditions may be required to produce the observationally inferred values of $X_{prop.}$. The dependence on the abundance of atomic carbon and oxygen in the gas-phase, as well as the properties (such as the temperature) of the dust grains may help to explain why propylene is detected in TMC-1, but not in other sources, such as Orion-KL.

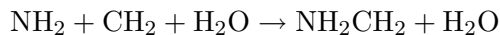
4 Extending the Chemistry

In this section we discuss how we can extend our model to describe possible formation routes for glycine and the isomers of C₂H₄O₂, via the high density radical association scheme.

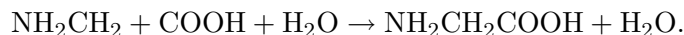
One possible way of forming glycine in such a high density regime would be via a three-stage process involving four radicals. The first step would form COOH by simple association of CO and OH:



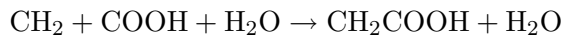
Then:



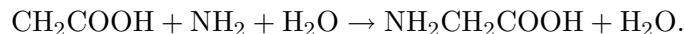
followed by



Or, alternatively,

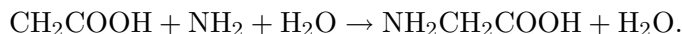


followed by

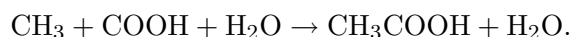
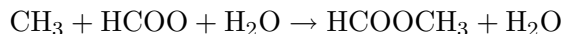
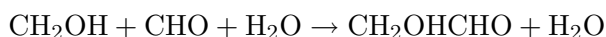


However, it is unlikely that these mechanisms can produce glycine with the requisite efficiency: In our previous studies we limited the chemical network to reactions between radicals of matching valency, on the grounds that unsaturated product species would be rapidly converted into more complex molecules. In those studies, we did not wish to investigate the formation of species more complex than propylene, so that was a satisfactory approximation. It is exactly those reactions involving radicals formed in the second stage to form more complex species, such as glycine, that is central to this formation mechanism. Thus, consideration of all possible reactions (and also including CO) would lead to a network of over 1400 reactions and a substantial enhancement in the number of chemical species. The combined effects of requiring three stages for the formation of glycine, plus the fact that the distribution of C, N and O would be over a much larger number of products implies that the process would only yield a small fractional abundance of glycine.

However, recent observations of hot core sources implies that a much simpler, one-stage process, may be viable: Specifically, formic acid (HCOOH), glycolaldehyde (CH₂OHCHO), methyl formate (HCOOCH₃), and acetic acid (CH₃COOH) are seen to be present in at least some hot core environments ([31],[3],[26]). Whilst not providing conclusive proof of the fact this would strongly suggest that they (and their associated radicals) are also present in the ice mantles, thus enriching the variety of molecules present in interstellar ices. If so, then the first two stages of the glycine mechanism described could be bypassed, due to the likely presence of the COOH and CH₂COOH radicals in the sublimated gas. Glycine could then be formed by just one single-stage reaction:



Similar, one-step reactions could also lead to the formation of glycolaldehyde (CH₂OHCHO), methyl formate (HCOOCH₃) and the re-formation of acetic acid (CH₃COOH):



In our previous studies we assumed that the dust ice mantles were composed of H₂O, CH₄, NH₃, H₂CO and CH₃OH. The primary radicals in the first-stage chemistry were the photolysis products of these species, resulting from the abstraction of a hydrogen atom: OH, CH₃, CH₂, CH, NH₂, NH, CHO, CH₃O. and CH₂OH.

Here we now assume that since formic acid (HCOOH) and acetic acid (CH₃COOH) are also present in the ice then the following additional photolytically generated radicals would also be present: COOH, CH₂COOH, CH₃COO and HCOO. To implement this we have augmented the chemistry of our previous models (first stage only) to include the reactions between these additional radicals and our original set (given above).

With these additions, a set of 46 possible additional reactions involving 47 possible additional species could result. The additional species are given in Table 4 and the additional reactions are listed in Table 5. With these augmentations to the propylene chemistry, the chemistry consists of a total of 185 reactions between 165 species.

The inclusion of these extra species introduces some new variables to the model; the fractional abundances of HCOOH and CH₃COOH (relative to water) in the canonical ice mantle and the branching ratios for the formation of the radicals by photolysis;

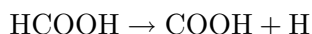
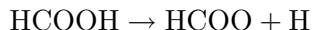
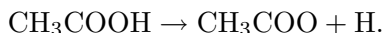
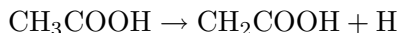


Table 4: Extra chemical species

COOH	CO(OH) ₂	CH ₂ COOH	CH ₂ OHCOOH	CH ₃ COO
CH ₃ COOOH	HCOO	HCOOOH	CH ₃ COOH	C ₂ H ₅ COOH
CH ₃ COOCH ₃	HCOOCH ₃	(CH ₂) ₂ COOH	CH ₃ COOCH ₂	HCOOCH ₂
CHCOOH	CH ₂ CHCOOH	CH ₃ COOCH	HCOOCH	NH ₂ COOH
CH ₂ NH ₂ COOH	CH ₃ COONH ₂	HCOONH ₂	NHCOOH	CH ₂ NHCOOH
CH ₃ COONH	HCOONH	CHOCOOH	CH ₂ CHOCOOH	CH ₃ COOCHO
HCOOCH ₃ O	CH ₃ OCOOH	CH ₂ CH ₃ OCOOH	CH ₃ COOCH ₃ O	CH ₂ CH ₂ OHCOOH
CH ₃ COOCH ₂ OH	HCOOCH ₂ OH	(COOH) ₂	CH ₂ (COOH) ₂	CH ₃ COOCOCH ₂ OH
HCOOCOCH ₂ OH	(CH ₂ COOH) ₂	CH ₃ COOCH ₂ COOH	CH ₂ (HCOO)COOH	(CH ₃ COO) ₂
CH ₃ COOHCOO	(HCOO) ₂			



and



In our models we assume that the HCOOH and CH₃COOH solid-state abundances, relative to H₂O, lie in the range of 0.001-1%, consistent with observational constraints. For the branching ratios, we assume that there is no preferred channel in either case - i.e. the ratios are 0.5 for each branch. These values, as well as the values of the other parameters in our model, are given in Table 6.

5 The Physical and chemical model

5.1 Physical model of the explosion

In this study, we are looking for a proof-of-concept result, rather than accurate quantitative predictions for the abundances of the COMs that we are investigating. We therefore employ the simple physical model of a single grain explosion that was used in papers I and III, rather than complex multi-phase cyclic model described in paper II - which would not be justified, bearing in mind the speculative nature of our extension to the chemistry.

As stated above, we assume that a purely gas-phase chemistry occurs in the high density gas that is produced as a result of the sudden, and complete, sublimation of the ice mantle. The cause of that process is not the subject of this paper - but it could be an externally driven sudden heating event, or result from the catastrophic recombination of radicals trapped in the ices and/or phase changes within the substrate. In either case we simply note that any sudden and efficient desorption process is potentially capable of driving the three-body gas-phase chemistry that we describe above. As in papers I and III we again consider an idealised situation in which a sphere of ice is instantaneously sublimated into the gas-phase.

5.2 Chemistry produced from exploding ices

On empirical grounds - based on observations along lines of sight towards low mass stars - we assume that ice consists mainly of H₂O, CO, CO₂, CH₄, NH₃, H₂CO, CH₃OH (e.g. [21], together with the recently-identified additions of HCOOH and CH₃COOH. Other species (such as OCN⁻), which are

Table 5: Reactions added to the propene chemistry. These are all three-body reactions, with H₂O as the third reactant. The products of the first 12 reactions are all radicals with a valency of 1 or 2.

No.	Reactant 1	Reactant 2	Product	name
1	NH	COOH	NHCOOH	
2	NH	CH ₂ COOH	CH ₂ NHCOOH	
3	NH	CH ₃ COO	CH ₃ COONH	
4	NH	HCOO	HCOONH	
5	CH ₂	COOH	CH ₂ COOH	
6	CH ₂	CH ₂ COOH	(CH ₂) ₂ COOH	
7	CH ₂	CH ₃ COO	CH ₃ COOCH ₂	
8	CH ₂	HCOO	HCOOCH ₂	
9	CH	COOH	CHCOOH	
10	CH	CH ₂ COOH	CH ₂ CHCOOH	
11	CH	CH ₃ COO	CH ₃ COOCH	
12	CH	HCOO	HCOOCH	
13	NH ₂	COOH	NH ₂ COOH	Carbamic acid
14	NH ₂	CH ₂ COOH	CH ₂ NH ₂ COOH	Glycine
15	NH ₂	CH ₃ COO	CH ₃ COONH ₂	
26	NH ₂	HCOO	HCOONH ₂	
17	OH	COOH	CO(OH) ₂	
18	OH	CH ₂ COOH	CH ₂ OHCOOH	
19	OH	CH ₃ COO	CH ₃ COOOH	
20	OH	HCOO	HCOOOH	
21	CH ₃	COOH	CH ₃ COOH	Acetic acid
22	CH ₃	CH ₂ COOH	C ₂ H ₅ COOH	Propionic acid
23	CH ₃	CH ₃ COO	CH ₃ COOCH ₃	Methyl acetate
24	CH ₃	HCOO	HCOOCH ₃	Methyl formate
25	CHO	COOH	CHOCO OH	
26	CHO	CH ₂ COOH	CH ₂ CHOCO OH	
27	CHO	CH ₃ COO	CH ₃ COOCHO	
28	CHO	HCOO	HCOOCH ₃ O	
29	CH ₃ O	COOH	CH ₃ OCO OH	
30	CH ₃ O	CH ₂ COOH	CH ₂ CH ₃ OCO OH	
31	CH ₃ O	CH ₃ COO	CH ₃ COOCH ₃ O	
32	CH ₃ O	HCOO	HCOOCH ₃ O	
33	CH ₂ OH	COOH	CH ₂ OHCO OH	
34	CH ₂ OH	CH ₂ COOH	CH ₂ CH ₂ OHCO OH	
35	CH ₂ OH	CH ₃ COO	CH ₃ COOCH ₂ OH	
36	CH ₂ OH	HCOO	HCOOCH ₂ OH	
37	COOH	COOH	(COOH) ₂	Oxalic acid
38	COOH	CH ₂ COOH	CH ₂ (COOH) ₂	
39	COOH	CH ₃ O	CH ₃ COOCO OH	
40	COOH	HCOO	HCOOCO OH	
41	CH ₂ COOH	CH ₂ COOH	(CH ₂ COOH) ₂	
42	CH ₂ COOH	CH ₃ COO	CH ₃ COOCH ₂ CO OH	
43	CH ₂ COOH	HCOO	CH ₂ (HCOO)CO OH	
44	CH ₃ COO	CH ₃ COO	(CH ₃ COO) ₂	
45	CH ₃ COO	HCOO	CH ₃ COOHCOO	
46	HCOO	HCOO	(HCOO) ₂	

Table 6: Physical and chemical parameters defining the explosion. Where variable, the values used in our standard model are given in square brackets. See text for further description.

Parameter	Value
CH ₄ /H ₂ O(ice)	0.04
NH ₃ /H ₂ O(ice)	0.01
H ₂ CO/H ₂ O(ice)	0.03
CH ₃ OH/H ₂ O(ice)	0.03
HCOOH/H ₂ O(ice)	0.0001-0.01 [0.001]
CH ₃ COOH/H ₂ O(ice)	0.0001-0.01 [0.001]
Fraction converted into radicals (F_{rad})	0.01-1% [1%]
Initial density (n_0)	$10^{19} - 10^{23} \text{ cm}^{-3}$ [10^{22}]
Three-body rate coefficients (k_{3B})	$10^{-32} - 10^{-26} \text{ cm}^6\text{s}^{-1}$ [10^{-28}]
Trapping parameter (ϵ)	0.1-1.0 [1.0]
Molecule \rightarrow radicals	branching ratio
H ₂ O \rightarrow OH	0.5
CH ₄ \rightarrow CH ₃ , CH ₂ , CH	0.33,0.33,0.33
NH ₃ \rightarrow NH ₂ , NH	0.5,0.5
H ₂ CO \rightarrow CHO	0.5
CH ₃ OH \rightarrow CH ₃ O, OH, CH ₃ , CH ₂ OH	0.1,0.2,0.2,0.5
HCOOH \rightarrow COOH, HCOO	0.5,0.5
CH ₃ COOH \rightarrow CH ₂ COOH, CH ₃ COO	0.5,0.5

not relevant to our reaction scheme, may also be present - but at much lower abundance levels. In addition, we also do not include CO₂, which although it has a typical relative abundance of 21%, is tightly bound and probably unreactive in the assumed conditions.

The relative abundances of the ice mantle constituents show significant variations along different lines of sight, (e.g. [13],[4]) which reflect the different physical and chemical conditions when the ices were formed. These are key free parameters in the model and we speculate that they are a major factor in observed variations in the abundances of COMs. In our standard model, the canonical values for the ice abundances that we have used are based on a variety of observational studies (e.g. [5]) and are given in Table 6.

The chemistry that we propose is driven by the presence of radicals. Following previous studies we assume that molecules in the ice mantles are subject to photodissociation driven by the secondary radiation field that is generated by cosmic ray ionization and excitation of ambient H₂ [22].

As in previous studies, we assume that the process of radical production is limited to the stripping of just one hydrogen atom per molecule. Thus, H₂O may give rise to OH, CH₄ to CH₃, etc., and the population of these radicals is associated with the bulk of the ice. We omit from the photodissociation products the atoms such as O, C, and N on the grounds that the overabundance of hydrogen will tend to enhance the hydrogenation. Hot hydrogen atoms in the explosion will tend to establish a population of hydrides.

In paper II we argued that an upper limit for the fraction of mantle species that has been photodissociated is of the order of 1%. So, as in Paper III we have considered a (realistic) range of $F_{rad} = 0.01 - 1\%$. Of course, the products and branching ratios for these photolysis reactions are highly uncertain. We have followed the practice of our previous studies and used values (given in Table 6) that are consistent with laboratory and theoretical determinations. As described in our basic model, it is assumed that these radicals are trapped within the ices until ‘mobilised’ when an

explosion occurs.

As the ice composition is dominated by H₂O and, to a lesser extent, by CO we again assume that the third body in the three-body reactions is usually H₂O, although we have also included some reactions where CO is the (chemically passive) third body.

The rate coefficients for these various reactions are entirely hypothetical as no detailed information is available for any of the reactions in our list. As with previous studies and for the sake of simplicity, we assume that all reactions have the same basic rate coefficients (k_{3B}). By referring to existing databases of three-body reactions (e.g. RATE12, [19]) it is evident that for saturated species, most of the values of k_{3B} for the reactions lie in the range $10^{-27} - 10^{-32}$ cm⁶ s⁻¹, but they are significantly larger for reactions involving radicals.

At the densities that we are considering, the chemistry is completely dominated by three-body reactions. We therefore do not include any two-body, photochemical or cosmic-ray induced reactions in our chemical network. Also, we note that there are no clear observations of sulfur-bearing species in ice mantles and so we do not include any complex sulfur-bearing species.

The first stage of our updated radical addition chemistry considered here involves association between the thirteen radical species identified in Table 6. Note that ~99% of the molecules from the ices are not involved, except to provide third bodies stabilising the products. The first stage generates a set of associations, giving products that are either molecules (formed when the initial radicals have equal valences) or radicals (formed where the initial radicals have unequal valences). The product molecules are often familiar, including some of the extra species in Tables 4 and 5 and many of them are detected interstellar species. It is assumed that these product molecules take no further part in the radical chemistry. However, product radicals from the first stage may undergo further stages of association. Just as in the first stage, associations in the second stage may give rise either to saturated molecules or to new radicals. The new radicals may, if the expansion timescale permits, give rise to a further stage of chemistry.

6 Computational Models and Results

As with our models of propylene formation, we have developed two different types of models to investigate the efficiency of the formation of the isomers of C₂H₄O₂ and glycine via the proposed mechanism:

1. Model A; which uses a single set of parameters to determine the time-dependence of the chemistry.
2. Model B; which performs a grid of calculations and determines the final (asymptotic) abundance of a selected species (e.g. glycine) as a function of variations in several free parameters.

The numerical calculation of the time-dependences of the chemical species utilises the LSODE integration package. As the chemical rate coefficients are taken to be the same, the chemical timescales in the model are similar and the differential equations that describe the time-dependencies of the abundances are not numerically stiff.

We also follow the practice of Papers I-III and adopt a single value for the rate coefficient (k_{3B}) for all reactions. This incorporates any implicit dependence on the temperature. Our previous work (e.g. Paper II) has shown that the temperature-dependence of the rate coefficients is relatively

unimportant, although at high temperatures the chemistry would tend to yield a thermochemical equilibrium composition. An inspection of databases for known three-body reactions (e.g. [30]) reveals that for reactions between radicals, the rate coefficients can be quite large ($> 10^{-26} \text{ cm}^6\text{s}^{-1}$), whereas for reactions involving saturated species they may be significantly smaller ($\sim 10^{-33} - 10^{-31} \text{ cm}^6\text{s}^{-1}$). Although we do not include the latter, we have considered values of k_{3B} that cover the range $10^{-32} - 10^{-26} \text{ cm}^6\text{s}^{-1}$.

Table 6 specifies the other parameters and the range of values that we have investigated in our studies. The first part gives the composition of the ice, with abundances relative to the dominant component; H_2O . The second part gives the physical characteristics of the explosion phase, and the third part identifies the radicals produced in the ices, together with the branching ratios.

An example of the results that are obtained from Model A are presented in Figure 1 and Table 7.

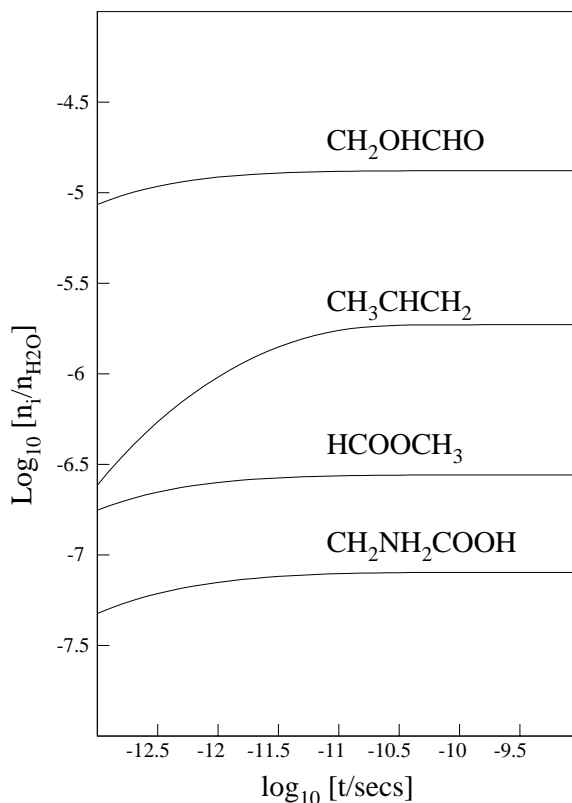


Figure 1: Example of the results obtained from the Model A, showing the time-dependencies of methyl formate (HCOOCH_3), glycolaldehyde (CH_2OHCHO), propylene (CH_3CHCH_2) and glycine ($\text{NH}_2\text{CH}_2\text{COOH}$).

In paper I we very roughly estimated the expected timescale for significant conversion of reactant species by three-body reactions into complex organics on the assumptions that (i) there are no significant activation energy barriers to the reactions in question, and (ii) the reactions are generally constructive. This was found to be of the order of $\sim 10^{-13} - 10^{-12}\text{s}$. This is very rapid indeed and is typically much shorter than the dynamical timescale. In this case, the details of the expansion and cooling of the gas are of minimal relevance; essentially the chemistry takes place very shortly after the sublimation of the ice mantles when the gas density is highest; the relative abundances of the product molecules are then “frozen in” to the flow. These results are confirmed in Figure 1 which shows results that are obtained from our ‘standard’ model in which the initial density (n_0) is 10^{22}cm^{-3} , the ‘universal’ rate coefficient (k_{3B}) is $10^{-28}\text{cm}^6\text{s}^{-1}$, and the HCOOH and CH_3COOH

Table 7: Example of the final abundances (relative to H₂O) for selected species obtained from Model A. The nomenclature $a(b)$ implies a value of $a \times 10^b$.

Species	Abundance	Species	Abundance
CH ₃ NH ₂	2.5(-6)	CH ₃ OCH ₃	1.5(-6)
C ₂ H ₅ OH	6.2(-6)	CH ₂ OHCHO	1.3(-5)
CH ₃ CHCH ₂	1.9(-6)	CH ₃ COOH	2.8(-7)
C ₂ H ₅ COOH	2.9(-7)	CH ₃ COOCH ₃	2.8(-7)
HCOOCH ₃	2.8(-7)	CH ₂ CHCOOH	2.6(-7)
NH ₂ COOH	7.4(-8)	CH ₂ NH ₂ COOH	7.9(-8)
HCOONH	7.9(-8)	(COOH) ₂	1.0(-8)

abundances in the ice are both 0.1%.

Table 7 gives the final (asymptotic) abundances relative to H₂O (for selected species) obtained from the same model. As in Paper II, we see that the modelled abundances are all quite large, showing that effective conversion of carbon to COMs is taking place. Note, however, that these abundances are relative to H₂O and so need to be scaled down by a factor of the H₂O abundance relative to hydrogen ($\sim 10^{-4}$) to obtain something like a mean gas-phase abundance. It should also be remembered that these results were obtained for a single ice mantle explosion event and so cannot be compared directly to values determined from observations. To do that requires a knowledge of the frequency of the explosions and how the chemistry evolves in the ISM in the inter-explosion periods. In most cases, the gas-phase chemistry of these species is very poorly understood. An approximate estimate of the time-averaged abundances could be estimated from assumptions about the explosion frequency and the destruction channels/rates, but that is beyond the scope of this paper and is probably not justified by the crudeness of our assumptions about the chemistry.

As in previous studies, we can see from Table 6 that there are several free parameters in the model; most importantly, the ice composition, the branching ratios for radical production, the fraction of the ice that is converted to radicals (F_{rad}), the density (n_0), the rate-coefficients (k_{3B}) and the trapping parameter (ϵ).

To show how the modelled abundances depend on these various parameters, we show in Table 8 examples of the results obtained from Model B. For this particular calculation, the ‘universal’ rate coefficient is $10^{-27}\text{cm}^6\text{s}^{-1}$, and the HCOOH and CH₃COOH abundances in the ice are both 0.1%. The initial gas density (n_0) and the fractional conversion to radicals in the ice (F_{rad}) are left as free parameters.

Despite the limitations mentioned above, we can see from this table that (a) significant abundances of glycine are predicted, that are comparable to observationally inferred limits, and (b) the ‘saturation’ effect that was seen in the case of the propylene chemistry that was the subject of Paper III is clearly apparent here as well. Thus, in Table 8: the abundance levels (of glycine) in the bottom half of that table show obvious evidence of saturation. Since this regime of the (F_{rad}, n_0) parameter space is quite feasible, it would seem reasonable to believe that, in the model that we postulate, abundances of propylene and other COMs may be expected to be in this saturation limit. A similar conclusion can be made for the isomers of C₂H₄O₂.

As with propylene, the abundances of these COMs are therefore very insensitive to the physical parameters (such as n_0 and k_{3B}). Also, we again find that the saturation levels are defined by the ice composition, and not the physical characteristics of the mantle explosion.

Table 8: Example of the results obtained from Model B: log of the final abundances (relative to H₂O) for glycine (NH₂CH₂COOH) as a function of the initial gas density (n_0) and the fractional conversion to radicals in the ice (F_{rad}).

Log ₁₀ (n_0^2)	Log ₁₀ F_{rad}				
	-4.00	-3.50	-3.00	-2.50	-2.00
19.0	-12.30	-11.30	-10.31	-9.32	-8.35
19.5	-11.31	-10.32	-9.35	-8.43	-7.61
20.0	-10.35	-9.43	-8.61	-7.89	-7.25
20.5	-9.61	-8.89	-8.25	-7.67	-7.13
21.0	-9.25	-8.67	-8.13	-7.61	-7.10
21.5	-9.13	-8.61	-8.10	-7.60	-7.10
22.0	-9.10	-8.60	-8.10	-7.60	-7.10

We find obvious near-linear dependences on the efficiency of radical formation F_{rad} and, for methyl formate, acetic acid and glycine - a similar dependence on the ice abundances of formic acid and acetic acid. This is for obvious reasons - the formation channels for these species all involve the radicals produced from the acids.

Glycolaldehyde, on the other hand, has unrelated formation channels and so is insensitive to the abundances of the acids in the ice.

7 Discussion and conclusions

In our model of high density gas-phase radical association we find that - in optimal conditions and after exploring the full volume of parameter space that we have defined - glycine can attain a ‘saturation’ abundance of $\sim 10^{-6}$ relative to H₂O. This corresponds to $\sim 10^{-10}$ relative to hydrogen in the fully-mixed gas-phase and is comparable to the observationally inferred limits.

In the case of glycolaldehyde, the saturation limit abundance (relative to H₂O) is large ($\sim 10^{-4} - 10^{-5}$) and is insensitive to the free parameters, other than the fractional conversion to radicals in the ice (F_{rad}). The modelled abundances of the other isomers of C₂H₄O₂ are also typically large ($\sim 10^{-6} - 10^{-8}$) and are consistent with their clear detection in astrophysical sources, even if - for the examples that we have shown - the abundance ratios for the isomers do not match observations. Methyl formate and acetic acid are both sensitive to the proportion of the acid radicals in the ices, so that variation in these values can explain the observed variations in the HCOOCH₃ :CH₂OHCHO and CH₃COOH:CH₂OHCHO ratios.

However, in our reaction scheme, both methyl formate and acetic acid are formed from radicals created by the dissociation of formic acid in the ice (HCOO and COOH respectively). As the branching ratio for these radicals is taken to be 50 : 50 (and in any case is unlikely to be variable) our model fails to reproduce variations in the HCOOCH₃ :CH₃COOH ratio. The most likely explanation for this is that our reaction scheme is incomplete, although other factors may also be important.

Although speculative, our model is based on plausible assumptions. We again note that a ‘normal’ gas-phase chemistry is unable to explain the observed abundances of COMs, and a viable alternative mechanism for their formation is required. This has to be both highly efficient at converting carbon to COMs, and - if it is assumed that they are formed from material contained in dust ice mantles - the COMs must be efficiently transmitted to the gas-phase. Our proposed ‘explosion chemistry’

is completed on extremely short timescales. The products of this chemistry may not be directly observed, but are injected into the dense gas of a molecular cloud core. Observational effects are therefore not necessarily defined by the explosion chemistry, but are determined by the injection and subsequent chemistry in the dark cloud.

As we have noted in our previous studies, there are clearly a large number of simplifications and approximations in our model; the reaction network that we have adopted - and the specific extensions to model the chemistry of glycine and the isomers of $C_2H_4O_2$ - are very speculative, if plausible. The adoption of a single value for the three-body reaction rate coefficients is a major simplification. In reality there could be large differences between the rate coefficients which would result in strong variations in the formation efficiencies and abundance ratios. In addition, we do not know the branching ratios in the ice photolysis reactions, nor do we have very strong constraints on the relative abundances of the ice constituents (which may vary from place to place). But at least this seems to suggest that there is a way forward to providing a viable mechanism for the formation of glycine and for understanding the relative abundances of the isomers of CH_2OHCHO in cold clouds. The model provides a possible explanation for certain observationally-inferred abundance anomalies in the interstellar medium. In particular, we have proposed a mechanism that can provide a chemical link between the three isomers of $C_2H_4O_2$, and that can explain some of the variations in the ratios of their abundances towards different sources.

Finally, we note that several alternative mechanisms have been proposed for the formation of COMs; In the models of [28], radicals are created in ice mantles by UV photolysis. It is then assumed that the grains are heated by grain-grain collisions and the radicals react with each other *in the mantles*. Chemical explosions release the COMs, including glycine and glycolaldehyde into the gas-phase. Specific mechanisms have also been postulated for the formation of methyl formate, including the solid-state reaction of methanol and CO in cosmic-ray irradiated ices, the solid-state reaction of formic acid and methanol [16] and the gas-phase reaction of methanol and formaldehyde in hot cores [6]. In addition, [12] has investigated glycine formation in the solid-state, following a similar radical reaction mechanism to that which we propose is operating in the gas-phase. There is no reason why the mechanism that we are proposing and some, or all, of these alternatives should not also be possible and may indeed complement each other.

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