The Formation of COMs in Explosions - and their Destruction

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Abstract

The method(s) by which complex organic molecules are formed is a subject of much debate. Specifically, if it is assumed that they are formed through gas-grain interactions, then it is necessary to identify a mechanism that is both efficient at forming the molecules and return them to the gas phase in quiescent clouds. In this paper we review the recent models that are based on the catastrophic recombination of radicals, stored in ice, that leads to an explosion of the ice mantles and a vigorous high density radical-radical association chemistry. We identify the strengths and weaknesses of the models in recent applications. Finally we address the often overlooked issue of COM destruction channels and argue that our poor knowledge of the chemical destruction mechanisms is undermining the diagnostic power of COM studies.

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Introduction

In the context of the interstellar medium, Complex Organic Molecules are defined as carbon-bearing molecules containing six or more atoms[1]. Whilst our undestanding of the chemistry of simple molecular species has reached some maturity, the study of the astrochemistry of COM formation and destruction is relatively new, and quite incomplete.

Since the earliest studies of astrochemistry, it has always been recognised that the formation of large molecules in interstellar environments is difficult: the low densities and ease of destruction by ions and the interstellar radiation field act to limit size and complexity. However, COMs are now widely detected in numerous astrophysical environments, both dynamically active and quiescent and, in many cases, have inferred abundances that significantly exceed the predictions of gas-phase chemical networks.

This has led to the realisation that solid-state chemistry must play a pivotal role in the formation of COMs. Generally speaking, the main theories of COM formation are based on:

- solid-state reactions on the surface (or even in the bulk) of the dust ice mantles (e.g.[2,3]), or
- gas-phase reactions between species released from the ice grains (e.g.[4,5]).

The presence of COMs in cold, quiescent, regions - such as dark molecular clouds (e.g.[6]) - poses an additional problem; if COMs are formed in, or on, ices or from molecular precursors deriving from those ices, then an efficient mechanism is required for the desorption of those species from the ices into the gas-phase.

An alternative picture was given by (7) who postulated that the ultraviolet photolysis of dust grain ice mantles could result in the build up a population of molecular free radicals and stored chemical energy. This energy could be released in catastrophic recombination (‘explosion’) leading to a total disruption of the grain material, thus providing a viable non-thermal desorption mechanism. The idea was further developed[8] as a means not just of maintaining a balance between the gas-phase and solid-state molecular components, but - via radical-radical diffusion and recombination - as a solid-state production channel for the complex organic molecules that are seen in the gas phase.

This theoretical model was subsequently supported by laboratory studies; in their groundbreaking experiment (9) simulated the conditions in an interstellar cloud by irradiating ice samples with vacuum ultraviolet. This was found to lead to the formation of a population of free radicals, followed by the release of the trapped chemical energy in ice mantle explosions. These experiments showed that if the heat capacity/conductivity of the substrate was too high then the thermal runaway would be quenched, so that the grains had to be raised to a temperature of $\sim$27K to trigger an explosion, with a deduced radical concentration of $\sim 2-3\%$.

Subsequent experimental studies (e.g.[10]) have shown that the irradiation of simple molecular ices with ultraviolet light can lead to the formation of COMs as well as species such as CO_2 and H_2CO, and these various experimental studies formed the basis of the first models of gas-phase and gas-grain chemistry which included accretion, surface diffusion and reaction, reaction driven ejection of molecules and mantle explosions[11]. However, (9) remains as the the only (published) experimental verification of the explosion mechanism.

These studies also speculated as to what (external) process could raise the grain temperature to the threshold value and trigger the explosion. In their original study, (9) postulated that, in interstellar medium conditions, this triggering could be effected by grain-grain collisions in a turbulent medium, although (12) showed that impulsive heating by cosmic rays could raise the temperature of the grains sufficiently so as to be an effective triggering mechanism.

This idea has been revisited in recent years by a variant that considered gas-phase COM formation in the material sublimated from the ice mantles. The idea was originally investigated (in a more quiescent, non-explosive, scenario) by (13) who suggested that COMs could be formed in gases trapped within cavities inside grains.

This motivated a model of COM-enrichment by ice mantle explosions[14] whose main features are: (i) the accumulation of chemical energy within the grain core and ice mantle. As well as the primary (saturated species) constituents the ices will also contain other radicals, that are adsorbed and cumulatively produced by irradiation from the cosmic ray induced radiation field and by ionization and dissociation induced by the cosmic rays themselves. These radicals will be associated with the bulk of the ice mantles; (ii) at some stage, perhaps when a critical concentration of radicals is obtained, or perhaps as a result of some external heating process, or maybe a phase change within the substrate, the trapped radicals are 'mobilised' and a runaway recombination occurs. This liberates all of the trapped chemical energy that is stored in the grains and leads to an ice mantle 'explosion'. This results in (iii) the total, instantaneous sublimation of the entire ice mantle, whilst raising the temperature of the sublimate to very high values. This then leads to (iv); a vigorous and rapid gas-phase chemistry in the sublimate. A scenario was then postulated[14] in which the episodic explosions result in the cumulative enrichment of COMs in the interstellar gas, which build up through a number of successive cycles.

In recent years this picture has been further modified by relaxing the usual assumption that hydrogen atom diffusion (by quantum-mechanical tunnelling) is so efficient that hydrogen atom retention is unlikely. The motivation for this line of enquiry is derived from experimental studies (as yet unpublished) that show strong evidence for the accumulation and spontaneous episodic recombination of hydrogen atoms described above, as well as detailed theoretical studies of hydrogen trapping in ices and the grain cores.

It was pointed out by (15) that the hydrogenated amorphous carbon (HAC) on grains can contain as much as 60% of atomic hydrogen. Whilst much of this is bound in hydrocarbon structures, as much as 30-50% may not be chemically bound and instead is present as atoms trapped at interstitial and weakly bonded internal sites[16]. Indeed, it is highly likely that grains may acquire both trapped hydrogen atoms as well as atoms that are loosely bound in dangling bonds when grains are exposed to a flux of atomic hydrogen appropriate to conditions in an interstellar cloud[17,18].

Calculations of the total energy acquired by a grain, for nominal heat capacities, show that for interstellar grains in the canonical size range of 50-1000Å, temperatures of $\sim$1000 K can be reached if stored energy of $\sim$12 kJ mole^{-1} is suddenly released. The exothermicity of the hydrogen atom recombination reaction is 436 kJ mole^{-1}, so this corresponds to a required total hydrogen atom abundance of approximately 5.5% within the grain[15]. Sufficient energy must be liberated to heat the whole grain, so this fraction is relative to the mantle plus core. Clearly, a much lower concentration of radicals would be required to raise the grain temperature to ∼100K, which would be sufficient to initiate radical recombination, but at the (not unrealistic) level of 5%, the recombination of hydrogen atoms would trigger a chain reaction and a thermal runaway - that has the potential to create additional radicals - would ensue. The process could even be assisted by other chemical changes, such as the crystallization of amorphous carbon which could itself trigger crystallization of the underlying silicate core[19].

Thus, in our subsequent studies[20–24] we considered the specific mechanism of catastrophic hydrogen atom recombination as the energy source for the explosions, but we emphasise that almost *any* sudden desorption mechanism could drive the sort of chemistry that we describe below.

As with the earlier model of (14) it was again proposed that the explosions could be *internally* triggered, by the accumulation of a critical abundance of unrecombined hydrogen atoms (relative to the entire dust mass) and that the explosion would create an additional population of chemically reactive radicals which can form COMs (and other molecules) in the high-density post-sublimation *gas-phase*.

The sublimated gas will initially have a density that is comparable to that of the solid state ices, but rapidly falls off as the gas expands (and cools) into the surrounding medium. These conditions - the presence of radicals in a hot and very dense gas, following the explosive sublimation - are then highly conducive to an efficient and extremely rapid three-body gas-phase chemistry. Due to the extremely high densities, and the rapidity of the sublimation and expansion, the timescales for the chemistry, as well as for the expansion and (adiabatic) cooling of the gas are all of the order of nanoseconds.

Although the gas-phase chemistry in the interstellar medium tends to be dominated by reactions between saturated species and radicals, associative reactions between radicals have been known to be efficient, provided the resulting complexes can stabilise radiatively or by collisions in three-body reactions[25].

In fact, the rate coefficients for associations between radicals in three-body reactions are typically much larger than for reactions involving saturated species (e.g.[26]). This is important, as it implies that the conditions that are conducive to three-body reactions taking place in the sublimate facilitate a type of reaction that is not favoured in standard two-body gas-phase chemistries.

The structure of the rest of this paper is as follows; in the following section we discuss the application of the explosion scenario to a generic model for dark clouds[20]. The application to a region of enhanced cosmic ray ionization rate is summarised in the section on the Central Molecular Zone[23], and the following sections describe extension of the model[21,22] to consider propylene, glycine and the isomers of $C_2H_4O_2$, and the successes and failures of the model in explaining the abundances of COMs in the dark cloud TMC-1[24]. The final two sections present new work which highlight some of the weaknesses of current COM modelling efforts; the use of inaccurate reaction data, and the lack of inclusion of important COM destruction mechanisms.

A model for generic dark clouds

The presence of COMs in apparently quiescent dark clouds is especially problematic in the context of traditional models of COM formation, either in or on ice mantles, or in the gas-phase following mantle desorption in that effective mechanisms are required for *both* COM formation *and* desorption into the gas-phase.

Building on the earlier studies (theoretical and experimental) of ice mantle explosions we envisage that the process could strongly enhance the presence of COMs in two ways:

1. Passively; the explosion process simply providing a mechanism for the release of (preformed) COMs from the ice mantles into the gas phase, or
2. Actively; where the conditions in the gas from the sublimated ice mantles (temperature, density, excitation etc.) are conducive to a vigorous chemistry resulting in the formation of COMs from the primary constituents of the ices.

Our studies have tended to concentrate on the latter of these, although it is possible that the passive mechanism may be more relevant in the Central Molecular Zone - the compact, molecular-rich ring-like structure surrounding the Galactic Center (see below).

The model

To test these ideas, a model was developed to represent a generic quiescent dark cloud without being specific to any one source[20]. We considered the chemistry in a two-phase model: for most of the time, the chemistry is characterised by a standard dark cloud gas-grain chemistry. Once a critical concentration of hydrogen atoms (which we take to be $\sim 5\%$, following (15)) builds up on a grain then, as described above, catastrophic recombination occurs, the ice mantle is sublimated, with the gas strongly enriched in radicals and raised to high temperatures and densities. The sublimated gas is then subject to a very rapid gas-phase chemistry, and the cycle repeats.

The dark cloud phase

During the quiescent phase we simply assume that the chemistry evolves with gas-phase reactions, freeze-out and (continuous) desorption taking place, together with a (highly simplified) surface chemistry; mostly leading to the hydrogenation of accreted species, but also allowing for the conversion of CO to CO_2 by reaction with O or OH etc. The conditions are assumed to be 'typical' for dark clouds.

Freeze-out rates (and hence the rate of conversion of H to H_2, plus the rate of accumulation of H atom radicals in the ices) depend on the dust characteristics which are important parameters in the models. These freeze-out rates and hence the all-important ice mantle composition were determined self-consistently. Similarly, the model calculates the build up of photon-generated and cosmic ray-generated radicals in the ices. For the quiescent gas and dust associated with low mass star-forming regions, the ices are mainly comprised of H_2O, CO, CO_2, CH_4, NH_3, H_2CO, CH_3OH and OCN^-. Any reported observations of sulfur-bearing species in the ices are ambiguous so we chose not to include sulfur chemistry in any of the models described below.

However, cosmic rays as well as cosmic-ray induced photons can penetrate the ices and create radicals. In the models it was assumed that this process was limited to the stripping of a single hydrogen atom from the saturated species. This generates a source of radicals and stored chemical energy. Thus, in the early studies[14], the only radicals produced are: OH, CH_3, NH_2, HCO, CH_2OH and CH_3O. CO was treated as being chemically passive in all models. A shortcoming of this reasoning was that it did not include the possibility of the formation of molecular ions by the same process, which could have a major contribution to the post-sublimation chemistry.

On the assumption that a small fraction (5-10%) of accreting atomic hydrogen is *not* converted to H_2, the abundance of H builds up until it reaches some threshold value.

The explosion phase

At that point catastrophic recombination to form H_2 occurs, the stored chemical energy is released and the entire ice mantle is instantaneously sublimated. During this explosion, some of the energy will be released as heat (and luminescence[9]) and the gas temperature will be elevated to 1000K. The sublimated gas will also have an extremely high initial density that is comparable to that in the solid-state ice. The sublimate then expands freely into the surrounding environment at the local sound speed. The model considers the simple free expansion of a spherical volume of gas.

If the initial radius and density of the sublimate are r_0 and n_0, respectively, then mass conservation implies that the density, n, at any time t is given by

$$\frac{n}{n_0} = \left(\frac{r_0}{r_0 + \varepsilon v_s t}\right)^3 .$$

where v_s is the expansion speed and ε an expansion inhibition factor that makes allowance for deviations from perfectly free, spherically symmetric, expansion as would be appropriate if the outflow is impeded by morphological effects or trapping in pores or cavities[14]. In most of our models we have considered a representative case in which r_0 is assumed to be comparable to the typical thickness of an ice mantle ($r_0 = 10^{-5}$ cm), and $v = 10^4\ \mathrm{cm\,s^{-1}}$ implying a dynamical (dilution) timesacle of the order of nanoseconds. If the gas is temperature is as high as 1000K, then the sound speed in water vapour would be larger than this ($\sim 0.7\text{kms}^{-1}$), but the ices may be somewhat thicker than 0.1μm, so these figures must be seen as representative. In any case the results are not critically dependent on these values.

During this phase a very rapid three-body gas-phase chemistry takes place (with H_2O, the dominant ice mantle component, as the collisionally stabilising third-body). This chemistry allows for the association of radicals with other radicals (with matching valences) to form saturated molecular COMs, as well as other, more simple, molecules - and occurs on a timescale of typically 1-10ns; dictated by chemical saturation and/or geometrical dilution of the gas. Examples of the types of reactions are;

$$\mathrm{CH_3 + CH_2OH + H_2O \rightarrow C_2H_5OH + H_2O}$$

and

$$\mathrm{NH_2 + HCO + H_2O \rightarrow HCONH_2 + H_2O.}$$

In the early models the number of chemical species in the explosion phase was limited to 34. However, even for these, the chemical reaction routes are largely conjectural and ill-determined. A major simplifying assumption was made that the reaction rate co-efficient is the same for all of the association/condensation three body reactions. This is as an important free parameter in the model and is assumed to have a value between $10^{-31} - 10^{-28}\text{cm}^6\text{s}^{-1}$, but it should be noted that the top end of this range is probably more relevant for radical-radical-H_2O reactions than it is for radical-neutral-H_2O reactions. Making this assumption does, however, mean that it is not possible to draw meaningful quantitative conclusions (e.g. concerning the abundance ratios of different molecular species) from the study.

Cycling and stochastic averaging

It is assumed that the gas, very chemically enriched by the explosion-driven chemistry, is mixed back into the dark cloud gas, with a high mixing efficiency. The cycle is then allowed to repeat. The duration of each cycle is determined by a variety of factors, including the cosmic ray ionization rate, the atomic hydrogen atom abundance (and hence the chemistry and the initial conditions), the gas density and temperature, the assumed hydrogen atom 'non-recombination probability' and the threshold abundance of hydrogen atoms required to trigger an explosion etc. It follows that there will be an optimal value for the gas-phase hydrogen atom density; if it is too low, the period between explosions is too long for chemical enrichment to be significant, whilst if it is too high then the implication would be that desorption is fast and the grains will not have large ice mantles. Using typical values of the parameters for a dark cloud, cycle periods of $\sim 10^4$-10^6 years are predicted.

Obviously this discussion has been limited to the evolution of a single dust grain. Real interstellar clouds will consist of an incoherent ensemble of dust grains in varying stages of the dark cloud-explosion cycle. So, to obtain representative values of the mean, stochastic, abundances in the cloud it is necessary to calculate the time-averaged abundances during a cycle.

Little attention was paid to the destruction mechanisms for COMs in this model, with simple freeze-out specified as the main loss mechanism, so that they tend to steadily increase from cycle to cycle. We return to this shortcoming in the final section of this article.

The Results

It was found that, for the smaller species, a limit cycle was achieved after 4 or 5 explosion cycles; thereafter the abundances do not change very significantly in subsequent cycles. For the larger COMs, it takes a little longer for the abundances to build up - but never the less is achieved on timescales that are shorter than the typical mean dark cloud lifetime of $\sim 10^6 - 10^7$ years. Significant abundances of COMs were predicted, although it was found that the complexity of the COMs so-produced is limited by the short expansion timescale and the dilution of the carbon budget amongst many species.

In general, the chemical complexity is determined by (i) the ratio of the accretion timescale to the cycle duration timescale, and (ii) the ratio of the chemical to the expansion timescales in the explosion phase. Results from an example model (where the cosmic ray ionization rate $\zeta = 1.3 \times 10^{-16}\mathrm{s}^{-1}$, the dark cloud density $n = 10^5\mathrm{cm}^{-3}$, the extinction A_v=10 magnitudes, and the model goes through 50 cycles, equivalent to a cloud lifetime of 1.5Myr) are shown in Table 1 (Taken from Table 7 of (20)) and show how large abundances of various COMs are obtained for this particular combination of parameters. It should, however, be noted that there are a number of ill-constrained free parameters in these models; including the dust grain size distribution, the cosmic ray spectrum and flux and the dynamics of the gas expansion following the explosion. Consequently, it must be recognised that there are significant uncertainties in the quantitative results of the models.

Table 1: Time-averaged fractional abundances of selected species in the final cycle for a model of a generic dark cloud. The nomenclature *a(b)* implies a value of $a \times 10^b$. From Rawlings et al. 2013a.

Species	Abundance	Species	Abundance	Species	Abundance
NH_3	5.0(-8)	HCOOH	4.7(-9)	$(CH_2OH)_2$	2.1(-10)
H_2O	1.2(-5)	C_2H_6	2.2(-7)	CH_2OHCHO	6.8(-12)
H_2CO	1.8(-9)	CH_3NH_2	1.2(-8)	CH_2OHNH_2	7.2(-11)
H_2S	4.3(-9)	CH_3CH_3O	2.0(-9)	CH_3OCH_3O	2.1(-10)
CH_3OH	8.7(-7)	C_2H_5OH	2.0(-9)	CH_3OOH	2.1(-8)
NH_2OH	3.9(-8)	CH_3CHO	1.1(-9)	CH_3OCH_2OH	1.8(-10)

The Central Molecular Zone

Previous (non-explosion) chemical models of the CMZ

An interesting place to study COMs is the Central Molecular Zone (CMZ) in the Galactic Center (GC) a ring like structure surrounding the very central region of the Galaxy with an inner radius of 1.5 pc (~30 arcsec). The GC is located at a distance from the Sun of ~ 8.4 kpc[27]. The physical conditions in the CMZ are extreme because it hosts an Active Galactic Nucleus (AGN) but it is also close to a massive star cluster with a total stellar mass of $\sim 10^6$ $M_\odot$[28]. Although star formation near the central black hole is difficult to explain it is believed that these massive stars may have indeed formed in situ, although the possibility that they formed further away from the black hole and migrated inward has also been proposed[29]. The CMZ is composed of molecular and atomic gas[30]. The presence of both an AGN and star formation makes the CMZ an *extreme* environment in terms of energetics and excitation conditions. The uniqueness of this environment therefore makes it an ideal laboratory to study chemical complexity.

The molecular inventory of the CMZ has been mapped in many standard dense gas tracers such as CO, CS, and HCN (e.g.[31−33]) as well as other species such as CN, SiO, H_2CO, HC_3N[34]. Recently, an unbiassed line survey in the CMZ of the 3 mm wavelength range was conducted by (35), with 30 species detected, including 10 rare isotopomers. Some of the detected species are believed to be produced in the gas phase (e.g. CO, CS, HCO^+, HCN, N_2H^+), while others such as SiO, NH_3, CH_3OH and complex organic molecules (e.g. CH_3CHO, CH_2OHCHO, $HCOOCH_3$, $(CH_2OH)_2$) appear to require grain surface chemistry for their formation. In particular, methanol (CH_3OH) was found to be widespread in the CMZ with a fractional abundance of 10^{-9}-10^{-7} with respect to H_2[36]. The distribution of the methanol is not restricted to where the star formation may be taking place. More importantly the detection of COMs that are commonly believed to be formed on the surface of grains is somewhat puzzling because the dust temperature and the gas temperature are uncoupled[37−39], with the dust temperature being $\sim$ 30 K (e.g.[40]), whilst the gas temperature is uniformly higher than 60 K (e.g.[39]) and possibly as high as 500 K in the most diffuse regions (< 100 cm^{-3})[41]). We must then ask; how do the COMs sublimate?

Several processes have been put forward as the possible mechanism responsible for sublimation, including shocks, UV photons and cosmic rays.

The discovery of widespread excited methanol was reported by (36). Its high abundance was explained by invoking cosmic ray induced photodesorption from the grain mantles driven by the enhanced cosmic ray flux. A chemical model was used to show that methanol abundances of $10^{-8} - 10^{-7}$ could indeed be obtained on a chemical timescale of 10^4-10^5 years. However, this model relied on the assumption that efficient mantle desorption is entirely a consequence of the high cosmic ray flux. (33) pointed out that the abundance of molecules in the CMZ will in fact be influenced by a variety of complex phenomena, and they explored the possibility that some of the molecular enhancements are in fact due to shock chemistry and sputtering. However, they found that shocks can only explain the molecular inventory in the CMZ on very short timescales ($\sim$ 1000 years).

The explosion model in the context of the CMZ

In (23) we explored an alternative scenario. As in the models for the dark clouds described above, we considered the possibility that COMs may be produced in the ultra-high-density gas phase immediately after the episodic explosions of grain mantles. Most studies show that in the CMZ the cosmic ray ionisation rate is very high and this has several consequences for the explosion model: (i) the rate of radical production in the ices will be enhanced, (ii) the rate of non-thermal desorption of species from ice mantles will be enhanced, perhaps to the level where ices are inhibited, (iii) the abundance of hydrogen atoms will be enhanced which, with the enhanced radical production rate, will lead to a much shorter explosion cycling timescale, but also (iv) the destruction timescale for COMs will also be much shorter.

Considering these competing factors, (23) limited the study to the determination of the formation channels and abundances of the simplest COM, methanol, and found that a good agreement between the predicted abundances and the observations is reached via the explosion mechanism. The repetition of the explosions can also explain the widespread presence of methanol on scales of a few hundred parsecs. However, in this particular case, it was found that the explosion mechanism has a passive role, and is only needed to provide an efficient desorption mechanism for methanol from the grains; whereas the dominant mechanism for the formation of methanol in the CMZ seems to be via grain surface formation through the hydrogenation of CO.

Propylene, Glycine and the isomers of $C_2H_4O_2$

The earlier explosion models were further extended to consider the possibility of the formation of (a) propylene[21] (CH_3CHCH_2), (b) glycine (NH_2CH_2COOH), and (c) the three astrophysically important isomers of $C_2H_4O_2$ (glycolaldehyde, methyl formate and acetic acid)[22] in a similar dark cloud environment to that modelled in the generic dark cloud model described above. Propylene (or propene) is detected in quiescent molecular clouds (such as towards the cyanopolyyne peak of TMC1) with high fractional abundances ($\sim 2 \times 10^{-9}$)[42] but is seemingly absent in high mass star-forming regions, such as Orion KL. There has also been a claim for a tentative detection of glycine[43], the simplest amino acid, whose astrobiological importance is obvious. The formation routes of these molecules is the subject of intense speculation and, so far, no viable gas-phase mechanisms have been identified (e.g.[44–45], and the section below)

All of these molecules are larger than the relatively simple COMs described in the previous sections and so a somewhat more complicated formation mechanism is required. Rather than being formed in a single-step radical-radical association as described above, it was proposed that the molecules are formed in a two-stage process.

The earlier studies only considered the association of radicals with equal valences, yielding saturated molecules as products. These saturated molecules are treated as being chemically inert. To extend this to ‘stage two’ associations, reactions between species with unequal valences, yielding radicals that could react again to form larger species (both saturated molecules and radicals) was also considered. This could, of course, be extended to a third stage of associations, yielding even larger COMs, but this has so far not been considered in the models.

In addition, whilst it had previously been assumed that the combined chemical effects of the explosions and irradiation by cosmic rays and photons would be limited to the abstraction of a single hydrogen atom (e.g. yielding CH_3 from CH_4) this was broadened to include the formation of other radicals as well (so $CH_4 \rightarrow CH_3$, CH_2 and CH, $NH_3 \rightarrow NH_2$ and NH, $CH_3OH \rightarrow CH_3O$, OH, CH_3 and CH_2OH etc.). The proposed two-step formation process for propylene is then:

$$\mathrm{CH_3 + CH \rightarrow CH_3CH},$$

followed by

$$\mathrm{CH_3CH + CH_2 \rightarrow CH_3CHCH_2}.$$

(Note that in these reactions, as well as the ones given below, we have omitted the third body reactant, H_2O, for the sake of clarity). For these calculations, the simple model was adopted; following the evolution of one grain through accretion, explosion and gas mixing, without the additional complexities of the cycling scenario being included. So, unlike the cyclic models, these models used canonical values for the composition of the ice (see Table 1 of (21)), but considered variations from these as an important free parameter.

For a typical simulation (in which the initial, post sublimation, density is $10^{22}\mathrm{cm}^{-3}$,the gas is allowed to expand freely and the 'universal' rate coefficient is set at $10^{-29}\mathrm{cm}^6\mathrm{s}^{-1}$) the results from the model indicate that propene, and other molecules (such as dimethyl ether, ethanol and acetaldehyde) can be formed efficiently - achieving abundances of $> 10^{-6}$ relative to H_2O in the expanding gas (see Table 3 of (21)), implying that the conversion of carbon to COMs is quite efficient. The results from the modelling also showed that the propylene abundance typically saturated on a chemical timescale of $\sim$1-10ns, shorter than the dynamical (expansion) timescale of the gas, leading to a gas-phase fractional abundance (relative to H_2O, in the sublimated gas) of

$$Y_{sat.} \sim 1.9 \times 10^{-6} \left(\frac{F_{rad}}{1\%}\right) \left(\frac{x(CH_4)}{4\%}\right)^{2.2} \left(\frac{f_{OH}}{50\%}\right)^{-0.5} \tag{1}$$

In this expression, $x(CH_4)$ is the fractional abundance of CH_4, relative to H_2O in the ice and f_{OH} is the fraction of the radicals produced from the photodissociation of H_2O that are in the form of OH. F_{rad} is the fraction of the molecules in the ice that is converted into radicals ($\sim 0.01 - 1\%$). The dependence on f_{OH} derives from the fact that the reactions leading to COM growth will often be in competition with (destructive) reactions involving OH, the most abundant radical.

Note, therefore, that the abundance of propylene is mainly determined by chemical initial conditions and is *independent* of the rate coefficients for the radical association reactions. Using this result, it was then possible to determine a value for the equilibrium abundance of propylene in a dark cloud by balancing an injection rate (deduced from the saturation limit above and the interval between explosions) with a loss rate - based on freeze-out and chemical destruction mechanisms. The main loss mechanisms included reactions with H_3^+, C, CN and O. The last of these is important[46], but is not included in the UdFA database. This, order of magnitude estimate, yields an abundance for propylene of $2 \times 10^{-10} - 2 \times 10^{-9}$ in broad agreement with the observationally inferred value for TMC-1.

As the abundance of propylene that is produced in the explosions is primarily dependent on the assumptions made about the composition of the ice, we can further speculate that the fact that propylene is detected in some sources, whilst not in others, may simply be a consequence of variations in the ice compositions. Those variations could themselves derive from the chemical age of the cloud (e.g. a younger cloud might be expected to contain more atomic carbon than an older cloud, leading to a larger CH_4:CO ratio in the ices). It is also possible that the presence of shocks in the Orion KL region may liberate more atomic oxygen, and hence enhance the loss rate for propylene.

Considering glycine; two alternative two-stage routes are possible:-

$$\mathrm{CO} + \mathrm{OH} \rightarrow \mathrm{COOH},$$

$$\mathrm{NH_2} + \mathrm{CH_2} \rightarrow \mathrm{NH_2CH_2},$$

$$\mathrm{NH_2CH_2} + \mathrm{COOH} \rightarrow \mathrm{NH_2CH_2COOH}.$$

Or,

$$\mathrm{CH_2} + \mathrm{COOH} \rightarrow \mathrm{CH_2COOH},$$

$$CH_2COOH + NH_2 \rightarrow NH_2CH_2COOH.$$

However, in general, the multi-stage association process described above for propylene will yield smaller abundances from one stage to the next; partly because these become second (or third) order effects, and partly because of the huge expansion of possible reactions and product species.

But the efficiency of these reactions is likely to be very limited. Instead, we note that species of some complexity, such as formic acid (HCOOH), glycolaldehyde (CH_2OHCHO), methyl formate ($HCOOH_3$) and acetic acid (CH_3COOH) have been detected in hot core sources (e.g.[47,48]) so that their presence in ice mantles is likely. This, in turn, implies that radicals derived from these species may be present in the sublimate; generated by the actions of cosmic rays, photons, and the explosion itself. Thus, it was speculated that the presence of the CH_2COOH radical, produced from acetic acid in the explosions, can allow glycine formation by a single-step process, as given by the last reaction above.

A similar 'first stage bypass' allows for the formation of the three isomers of $C_2H_4O_2$: glycolaldehyde (CH_2OHCHO), methyl formate ($HCOOCH_3$) and acetic acid (CH_3COOH). Here, the presence of formic acid (HCOOH) allows for the formation of HCOO and COOH radicals in the ice mantle explosions. Together with the CHO radical, derived from formaldehyde (H_2CO), radical association reactions can also be proposed for the single-step formation of the three isomers:

$$CH_2OH + CHO \rightarrow CH_2OHCHO$$

$$CH_3 + HCOO \rightarrow HCOOCH_3$$

$$CH_3 + COOH \rightarrow CH_3COOH.$$

These three COMs have been observed in numerous sources and there is considerable speculation as to what can be inferred about the chemical and physical conditions in the emitting gas from the abundance ratios of these species.

Of course, these reactions are quite speculative and the rate coefficients are unquantified, so it is currently impossible to make detailed predictions of the abundance ratios from the explosion model.

As with the model for propylene, large abundances of glycine and also the isomers of $C_2H_4O_2$ are predicted and the effective conversion of carbon to COMs is apparent. Similarly, there is evidence that, like propylene, for most of the range of parameter space that was considered, the abundances are in the saturation limit and so are insensitive to the physical parameters, such as the initial density and assumed reaction rates. In optimal conditions, the glycine abundance can be as high as 10^{-6} relative to H_2O in the sublimate - corresponding to a fractional abundance of 10^{-10} relative to hydrogen in the cloud; comparable to observationally inferred values. In the case of glycolaldehyde, even larger abundances can be obtained. As with propylene, the efficiency of the chemistry as well as the relative abundances of the products (and, specifically, the ratios of the abundances of the isomers) are essentially determined by the ice composition - in this case, the relative proportions of the acid radicals in the ices.

COMs in TMC-1: Explosions or Diffusion ?

Ultimately a comprehensive model for TMC-1 that succeeds in fitting all the observations is needed. Moreover, it is important that the explosion model is contextualized with other more commonly invoked mechanisms. In (24) the explosion mechanism was implemented in a time dependent gas-grain chemical model, UCLCHEM[49]. The aim of this study was to reproduce the abundances of all of the observed species in TMC-1. Among the observed species of interest to this article are the following COMs: CH_3OH, CH_3CHO, $HCOOCH_3$, CH_3OCH_3 and CH_2CHCH_3 whose observationally inferred abundance values are taken from (50). This study also included two important updates: (i) the inclusion of laboratory and theoretical data to discriminate between viable and non-viable reaction pathways, and to include rate coefficient data, where available, and (ii) the realisation that the earlier studies had failed to recognise that, at the densities being considered, the three-body reactions are in the saturation limit. That is to say that we can assume that every association between two species is collisionally stabilised before it can dissociate, or undergo another reaction - in which case the density of the third body, collsionally stabilising partner, does not enter into the numerical formulation of the rate of the formation of the product species.

With these additions, (24) found that the inclusion of explosion chemistry in UCLCHEM, leading to a regular enrichment of the gas phase when the explosion occurs in the mantle, would still lead to a good fit to the simple molecular species in TMC-1. However it could not reproduce the observed abundances of all of the COMs. In particular, the COMS that form efficiently on the grains were over-reproduced (e.g. CH_3OH and CH_3CHO), while others such as CH_3OCH_3 and CH_3CHCH_2 are under-produced. These low abundances are due to the combined effects of the low efficiency of some of the reactions during the explosions, the short explosion timescales and the small abundances of some of the parent species. However one should note that the rates of most reactions as well as the explosion dynamics and cycling timescale are in fact rather unknown. Moreover this work showed that the chemical diffusion mechanism also falls well short of reproducing most of the COMs observed in a dark cloud environment such as TMC-1. So, for the time being, the problem remains: we still do not have a dominant mechanism of COM formation that can account for the observed chemical complexity in cold environments where thermal sublimation is not efficient.

Propylene: an incomplete network?

Investigations into the formation and destructions of complex organic molecules have to be done with extreme care. In the following sections we investigate two major pitfalls in our understanding of the chemistry of COMs in interstellar conditions: (i) the effects of the inclusion of ‘inherited’ spurious reaction data, and (ii) the absence of major chemical destruction channels.

The first of these becomes particularly apparent when there appears to be a missing link between the observational detection of a complex molecule in the gas-phase and the theoretical channel for the formation of the molecule in the interstellar conditions where it is observed. Propylene is an example of such a situation: being detected so far only in cold environments (e.g.[42]). It is puzzling how environments such as the Orion KL hot core, where temperatures are of the order of 300 K and gas densities $\sim 10^{6-7}$ cm^{-3}, seem either to suppress its formation or to encourage its destruction. More importantly if it is produced via a solid-state formation route, then the sublimation of icy mantles in Orion KL would have led to a prominent observational signature. In fact the Orion hot core is well known for its abundance of organic molecules, many with similar structures to propylene. For instance methylacetyle or propyne, CH_3CCH[51], and propenal, CH_2CHCHO[52]. The fact that no explanation so far exists to account for the observation of propylene may be indicative of significant gaps in our understanding of cloud chemistry and led us to look into the possibility that it is indeed formed in the gas phase.

Using a model of the time dependent gas-grain chemistry we ran a large grid with the aim of determining the conditions and reaction pathways likely to produce propylene in the interstellar medium and the dependency of this production on the physical conditions. Our simulation was of a diffuse medium collapsing to become a dark molecular cloud with a density similar to that of TMC-1. The reaction set used was based on the UMIST 12 database[26] but was augmented with further reaction pathways from the KIDA database[53]. We were able to determine which reactions were contributing to the formation and destruction of propylene at each point during the simulation. We found that there were 4 distinct time periods in the evolution of the abundance of propylene.

In the first phase, when the cloud is forming from a lower density medium, propylene production is due to the photodissociation of $CH_2CHCHCH_2$, although by the end of this phase (which lasts $\sim 4\times10^{6}$ years) neutral-neutral reactions between CH and CH_3CH_3 account for 20% of propylene production. In this phase the propylene reaches a peak fractional abundance of 2×10^{-10}. The second phase lasts until $\sim 5.5\times10^{6}$ years and is characterised by a rapid decline in the abundance of propylene; by some 2 orders of magnitude. In the third phase the abundance recovers to $\sim 1.5\times10^{-10}$. Propylene formation in this phase is mainly due to the ion-neutral reaction between $C_3H_7^+$ and NH_3 which takes over from the neutral-neutral process that was previously dominant.

The last phase, in which the density is constant and lasts up to 10^7 years, sees a dramatic fall in the abundance to levels that are at least an order of magnitude below what is observationally inferred for TMC-1.

In general most models show these two abundance peaks. The first peak is due to the photodissociation reaction mentioned above and it occurs at very low densities, which had not been previously investigated. There is a wide range in the densities present in TMC-1, and the regions between clumps of denser matter may be in this density regime. Hence, at first glance, this may indicate that the propylene emission may originate from relatively young gas in TMC-1 or else from the low density inter-clump gas.

However after a careful investigation into the formation pathways for propylene it was found that the reaction that produced the first peak at low densities was in fact a spurious addition to *all* of the chemical networks. Propylene is in fact not a significant branching product of the photodissociation of $CH_2CHCHCH_2$. We therefore concluded that the first propylene abundance peak at low densities is most likely an artefact and should not be taken to diagnose the physical conditions in the emitting gas. This demonstrates neatly and somewhat brutally the dangers of using a collection of third party reaction data without verifying each reaction in detail first. Whilst this is always true, it is especially pertinent in the case of the COM chemistry, which is particularly ill-defined.

The destruction of COMs

In most studies of the chemistry of interstellar COMs, considerable attention has been paid to the various possible formation channels, whilst the destruction mechanisms have not been considered in nearly so much detail. However, we must remember that many of these COMs are well-known in the laboratory or even industrial context and have well-studied chemistries, albeit for very different physical conditions (temperatures and densities) than those that pertain in the ISM. So, in many cases, the chemistry of COMs is much more empirically well-constrained than the somewhat more conjectural reaction pathways that are adopted in insterstellar chemical networks. So far there has been no concerted effort in importing much of this considerable body of empirical data into astrochemical models. Thus, whilst the astrochemical databases include a handful of destruction channels involving common molecular ions, destruction by neutral radicals is largely ignored.

In this section we do not attempt to incorporate a comprehensive update of all chemical destruction channels for all COMs present in existing astrochemical databases. Rather we consider a small subset of oxidation reactions (by O and OH) acting on the COMs that were the subject of the study by (24): methanol (CH_3OH), acetaldehyde (CH_3CHO), methyl formate ($HCOOCH_3$), dimethyl ether (CH_3OCH_3), and propene (CH_3CHCH_2) and determine what effects the inclusion of these reactions has on the abundances and the abundance ratios of these well-known COMs.

Reactions of COMs with the most abundant molecular ions (H_3^+ and HCO^+) as well as He^+ are usually cited as the most significant loss channels. The reactions with H_3^+ and HCO^+ usually result in proton transfer, followed by dissociative recombination. Reactions with He^+ tend to lead to dissociative charge exchange and fragmentation.

In a recent paper, laboratory measurements of the reactions of dimethyl ether (CH_3OCH_3O) and methyl formate ($HCOOCH_3$) with He^+ ions were presented[54], along with a review of the available data for reactions with H_3^+ and HCO^+. For reactions with He^+ it was found that the products, branching ratios and reaction rates are all significantly different to what is reported in the UDfA and KIDA databases, whilst important differences exist between the UDfA and KIDA data for the reactions with H_3^+ and HCO^+. The total rate coefficients (in Table 3 of that paper) for the reactions of He^+ with dimethyl ether and methyl formate (including all product branches) were determined to be 1.38×10^{-9} $(T/300)^{0.295}cm^3s^{-1}$ and 1.38×10^{-9} $(T/300)^{0.241}cm^3s^{-1}$ respectively. The destruction rates by H_3^+ are given as 4.64×10^{-9} $(T/300)^{-0.5}cm^3s^{-1}$ and 4.1×10^{-9} $(T/300)^{-0.5}cm^3s^{-1}$ respectively, and those for destruction by HCO^+ are given as 2.1×10^{-9} $(T/300)^{-0.5}cm^3s^{-1}$ and 2.9×10^{-9} $(T/300)^{-0.5}cm^3s^{-1}$ respectively. Thus, even for these well-known destruction channels, there is considerable uncertainty, which has significant implications for the predicted abundances for COMs.

However, there are other major destruction channels that have seemingly been overlooked;

perhaps most significantly, reactions with neutral radicals and atomic species, such as C, CH, O and OH. Many of these are known from laboratory studies to be efficient.

An inspection of the UDfA reaction database shows that, apart from photodestruction by the interstellar radiation field (both direct and cosmic-ray induced) the only loss channels for dimethyl ether, methyl formate and acetaldehyde are reactions with the ions He^+, H_3^+, H_3O^+, HCO^+ and CH_3^+, plus O_2^+ for dimethyl ether and C^+, S_2^+ for acetaldehyde. There are 25 destruction reagents listed for methanol, but of these 22 are atomic or molecular ions and there is only one reaction involving a neutral radical (CH). By contrast, 16 destruction reagents are listed for propylene, including seven neutral radicals (C, CH, CN, C_2, C_2H, C_4H and OH). No photoionization reactions are given for either methyl formate or propylene, despite the fact that both species have ionization potentials below the Lyman cut-off ($\sim$10.8eV and $\sim$9.7eV, respectively).

Dimethyl ether is known to react with OH to form methyl formate in atmospheric conditions, whilst methyl formate itself reacts with OH at interstellar temperatures[55]. Even methanol is susceptible to oxidation by atomic oxygen. Aldehydes are generally very chemically reactive (e.g. with HCN and NH_3) and are easy to oxidise. To illustrate the potential importance of these reactions, we note that in the study of COMs in the CMZ described above the, previously neglected, destruction of glycolaldehyde (CH_2OHCHO) by OH was included[56] with a rate coefficient of 7.2×10^{-12}cm^{3}s^{-1}. The inclusion of this destruction channel was found to have a strong limiting effect on the abundance of glycolaldehyde.

To investigate the possible effects of the inclusion of these destruction reactions, involving O and OH, we have simply included the following reactions in our network:

$$CH_3OH + OH \rightarrow H_2CO + H_2O + H$$

$$HCOOCH_3 + OH \rightarrow HCOOH + CH_3O$$

$$CH_3OCH_3 + OH \rightarrow HCOOCH_3 + H_2 + H$$

$$CH_3CHO + OH \rightarrow CH_3COOH + H$$

$$CH_3OH + O \rightarrow HCOOH + H_2$$

$$HCOOCH_3 + O \rightarrow HCOOH + H_2CO$$

$$CH_3OCH_3 + O \rightarrow HCOOCH_3 + H_2$$

$$CH_3CHO + O \rightarrow CH_2COOH + H$$

$$CH_3CHCH_2 + O \rightarrow CH_3CHO + CH_2.$$

For this simple sensitivity analysis we do not pay detailed attention to the products and/or branching ratios, rather we recognise that the reactions between the products are likely to occur in each case, albeit with unknown rate dynamics. This is, of course, very simplistic and incomplete (reactions with other simple radicals, such as C, C^+ or CH, are also likely to be important) but serves to give an idea of the implications of the omission a full set of destruction channels.

We have investigated the significance of these reactions, using a very conservative generic rate co-efficient of 10^{-12} cm^3s^{-1} for each of these reactions. The model that we used for this (UCLCHEM) is as described above: we consider the time-dependent chemistry of a single point (nominally at the centre of a dark cloud) that undergoes isothermal (10K) free-fall collapse from a density of 10^2 cm^{-3} to 2×10^4 cm^{-3} and then (after about 4-5 Myrs) remains at constant density. For the purpose of this study, a standard surface diffusion chemistry (i.e. through the Langmuir Hinshelwood mechanism) is used to describe the (barrierless) formation of COMs on the ices. In this model the COMs are desorbed into the gas phase by the enthalpy of formation[57].

Examples of the results are shown in Figures 1 and 2 (without and with the extra destruction reactions included, respectively) which show the time evolution of the fractional abundances of several COMs (relative to hydrogen, in the cloud). These figures indicate that, even with the cautious values that we have adopted for the rate coefficients, the effects on the chemistry are very significant. The reactions and rate coefficients are too arbitrary to be able to draw any specific conclusions from this simple sensitivity study but it is certainly worth noting, for example, that the effective conversion of some CH_3CHO to CH_3COOH strongly enhances the abundance of CH_3COOH in this model.

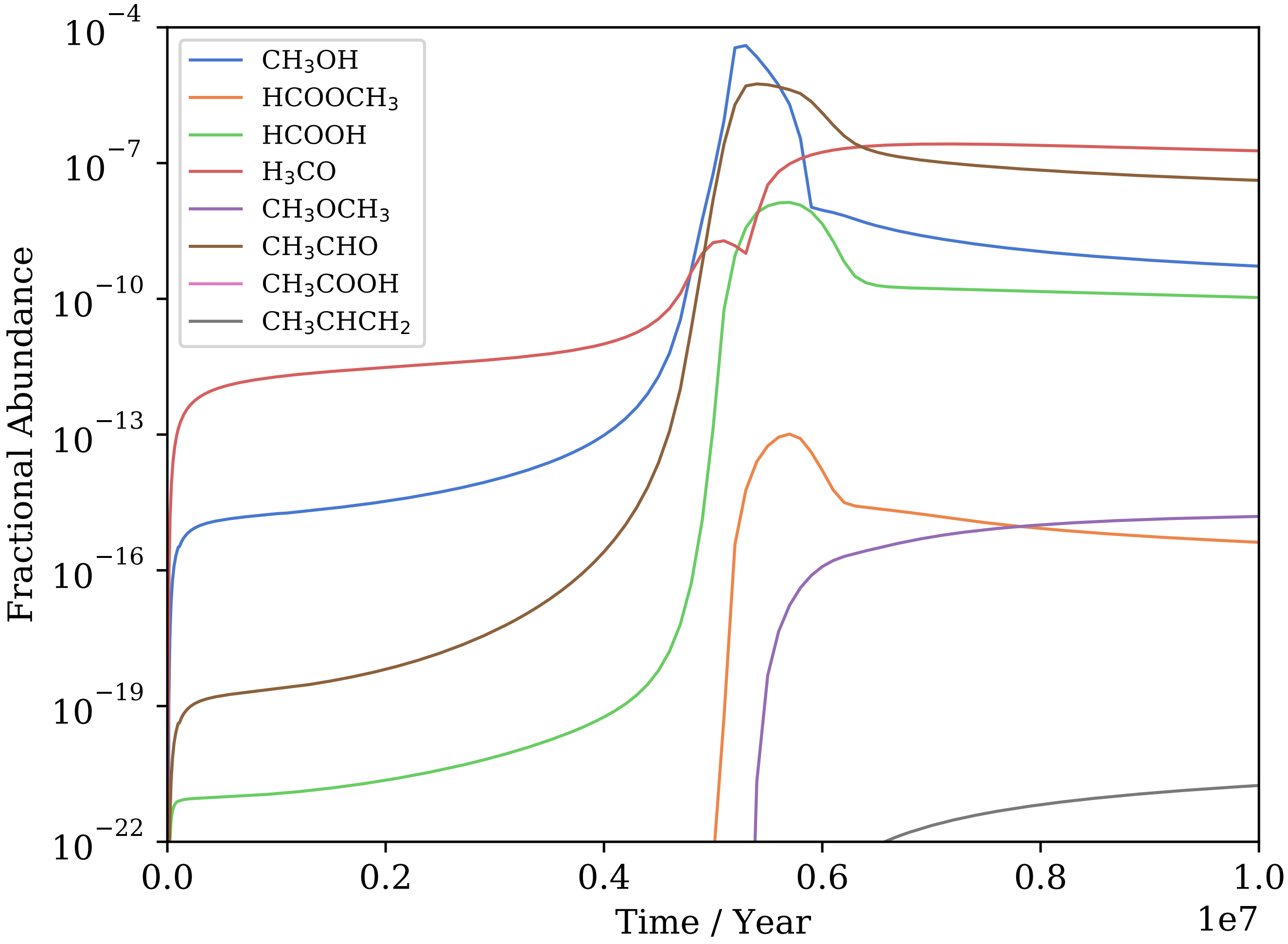

Figure 1: Results from the surface diffusion model - without additional destruction reactions.

This is a very preliminary study, and the chemical pathways that we have included are obviously narrowly selected and the destruction network for the COMs is very far from complete. However, what is very clear is the fact that the inclusion of a small subset of possible destruction reactions has very significant effects on the abundances and abundance ratios of various COMs. We therefore caution the reader to beware of over-interpreting the results of current astrochemical models of COMs.

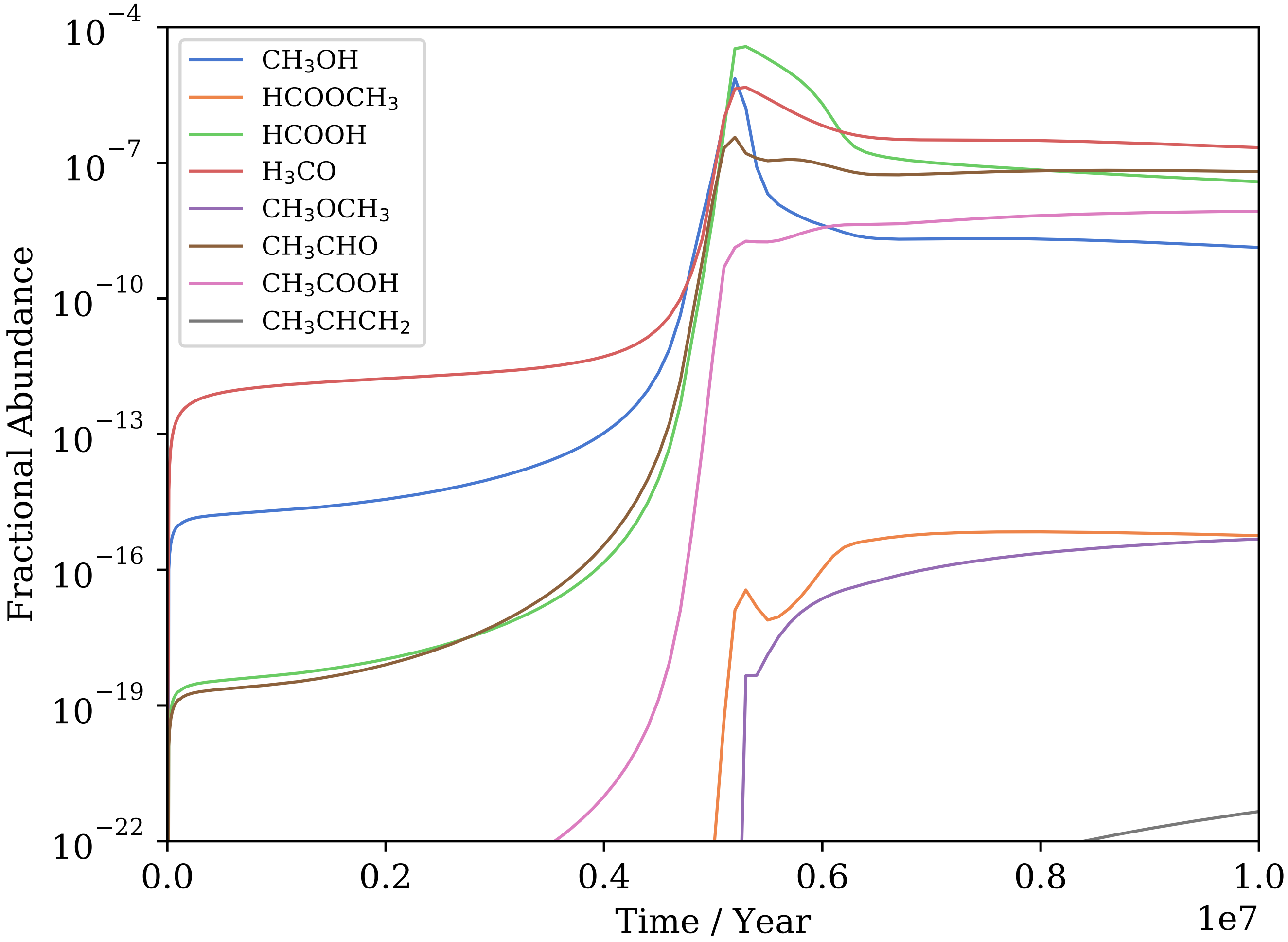

Figure 2: The same model with the new reactions. A generic rate coefficient of 10^{-12} cm^3s^{-1} is used in these calculations.

Conclusions

There are a number of general conclusions that may be drawn from these studies. Here we briefly lists the successes and failures of the models:

- The ice mantle explosions provide a mechanism by which the gas-phase chemistry of molecular clouds can be enriched, either passively (by effecting efficicient desorption of COMS present in ice mantles), or actively (by promoting a high density gas-phase chemistry). The model provides a unique method for complex molecule formation *and* return from ices into the gas phase.

- The mechanism allows the association of neutral radicals with other neutral radicals, which is otherwise prohibited in the gas phase. If operating efficiently, it is capable of explaining the observed abundances of many COMs in a variety of astrophysical environments.

- The model can explain the observed abundance of propylene, although the mechanism must be working efficiently. That efficiency is mainly determined by the ice composition and is not strongly dependent on the (unknown) rate coefficients for the association reactions nor the physical characteristics of the explosion.

- The model can explain why some sources are rich in propylene, whilst others are not; the primary cause being the composition of the ices, which are determined by the physical conditions and chemical age of the cloud.

- The models are capable of producing significant abundances of glycine and the isomers of $C_2H_4O_2$. They also suggest a possible chemical link between the three isomers and a cause for the variations in their abundances ratios.

- The model gives a plausible explanation for the high abundances of methanol seen in the Central Molecular Zone as a result of the (chemically passive) desorption of ice mantles.

- We have applied the mechanism to the specific source of TMC-1, utilizing the UCLCHEM code and partly correcting the chemical data with accurate laboratory and theoretical data. The results imply that, for this specific environment, the explosion mechanism may not be as significant as previously thought, although there are still considerable uncertainties in the chemical network. Similarly, it is also worth noting that the models imply that the standard grain diffusion model also fails to explain the observed abundances of COMs in cold dark clouds.

- Our understanding of the chemical destruction mechanisms for COMs is very incomplete. We have tested the sensitivity of a standard diffusion model for COM production to the assumed destruction chemistry by including a small set of neutral radical oxidation reactions, with a very conservative estimate of the rate coefficients. We have found that very significant variations in the abundances of COMs may result.

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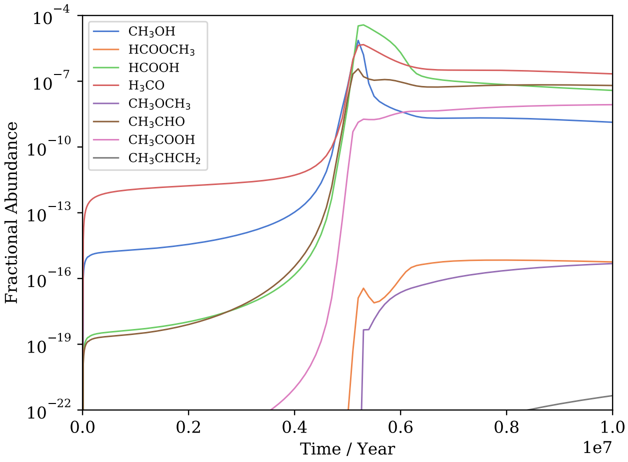

CH$_3$OH
HCOOCH$_3$
HCOOH
H$_3$CO
CH$_3$OCH$_3$
CH$_3$CHO
CH$_3$COOH
CH$_3$CHCH$_2$
Fractional Abundance
10^{-4}
10^{-7}
10^{-10}
10^{-13}
10^{-16}
10^{-19}
10^{-22}
0.0
0.2
0.4
0.6
0.8
1.0
1e7
Time / Year