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UV photolysis, organic molecules in young disks, and the origin of meteoritic amino acids

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ABSTRACT

The origin of complex organic molecules such as amino acids and their precursors found in meteorites and comets is unknown. Previous studies have accounted for the complex organic inventory of the Solar System by aqueous chemistry on warm meteoritic parent bodies, or by accretion of organics formed in the interstellar medium. This paper proposes a third possibility: that complex organics were created *in situ* by ultraviolet light from nearby O/B stars irradiating ices already in the Sun's protoplanetary disk. If the Sun was born in a dense cluster near UV-bright stars, the flux hitting the disk from external stars could be many orders of magnitude higher than that from the Sun alone. Such photolysis of ices in the laboratory can rapidly produce amino acid precursors and other complex organic molecules. I present a simple model coupling grain growth and UV exposure in a young circumstellar disk. It is shown that the production may be sufficient to create the Solar System's entire complex organic inventory within 10⁶ yr. Subsequent aqueous alteration on meteoritic parent bodies is not ruled out.

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1. Introduction

The early Solar System was replete with complex organic molecules, which can be seen today in preserved ancient bodies such as meteorites and comets. Upwards of 100 different amino acids have been detected on chondritic meteorites such as Murchison, Allende and Orguiel. Many of these have no known natural terrestrial occurrence (Ehrenfreund et al., 2001b), and are believed to be of extra-terrestrial origin. Comets and the interstellar medium (ISM) are also rich inventories of complex organic molecules, including amino acid precursors (Snyder, 2006). Amino acids and other complex organics have implications for the origins of life on Earth, so understanding their formation and history is an area of great interest. If these molecules are formed and distributed easily in a variety of disks and conditions, then pre-biotic compounds may be common throughout distant planetary systems.

Of the complex organics in the Solar System, amino acids are particularly interesting to study. These compounds are necessary for life, and may have been biotic precursors on Earth. Carbonaceous chondrites are typically 5% or more carbon by mass, most of which is in aromatic polymers and thousands of other pre-biotic organic compounds (Schmitt-Kopplin et al., 2010; Hayatsu and Anders, 1981). Laboratory studies have found Murchison to have some 10–30 ppm by mass in identified amino acids (Shock and Schulte, 1990). The simplest amino acid (glycine, NH₂CH₂COOH) has recently been detected in comets, but so far has eluded

detection in the ISM (Elsila et al., 2009; Snyder, 2006; Kuan et al., 2003). Potential amino precursors such as formic acid (HCOOH) have been detected in comets but not the interstellar medium (Hollis et al., 2003; Bockelee-Morvan et al., 2000). However, amino acids in ice form in the interstellar medium (ISM) would be more stable but harder to detect than their corresponding gas forms in comets (Ehrenfreund et al., 2001a; Chyba et al., 1990), so it is likely that they exist in the ISM but have not yet been detected.

The origin of these molecules is unknown. Two broad explanations exist for the amino acids in our Solar System. First, they may be produced endogenically, by chemical synthesis within the Solar System itself. A variety of energy sources for this exist, including infall heating, radiogenic heating, lightning, and shocks. For the amino acids present on meteoritic parent bodies, the best-studied endogenic process is Strecker synthesis. This is a method by which amino acids are formed in aqueous environments, such as the warm sub-surface aquifers that could have been present on asteroids as they were heated by ²⁶Al and other radionuclides during their first few Myr (Ehrenfreund et al., 2001b). Amino acids are produced in the laboratory by this process, and sufficient ²⁶Al existed to heat parent bodies to liquid water temperatures (McSween et al., 2002). However, a serious problem exists with this model. Isotopic measurements of the chondritic amino acids consistently show deuterium *enhancements* of $\delta D = 600-2000\%$, while measurements of the water in these same bodies show deuterium depletions of roughly 100%. In situ synthesis of aminos does not preferentially change the D/H ratio, so this argues that the water and organics come from distinct sources (Lerner, 1997).





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Second, the molecules may have been inherited *exogenically* from the interstellar medium which formed the solar nebula. The ISM is known to be rich in complex chemistry, with over 150 different gas-phase species detected to date in molecular clouds (Herbst and van Dishoeck, 2009). Amino acids have not been detected in the ISM, but sugars, alcohols, polycyclic aromatic hydrocarbons (PAHs), and other complex molecules have been. The formation of these compounds in the ISM is thought to be due to a combination of processes, including gas phase, gas-grain, and UV-grain reactions. Once molecules are formed, stable compounds can be incorporated into young disks as new YSOs condense out of the ISM. This pathway is supported by measurements showing the organic composition of comets and the ISM to be quite similar (Bockelee-Morvan et al., 2000; Irvine et al., 2000).

Laboratory results have shown that simple ices can be turned into a zoo of amino acids and other complex organics simply by the presence of UV flux followed by a warming stage (Nuevo et al., 2008, 2007; Bernstein et al., 2002; Munoz Caro et al., 2002). Though these studies are performed at fluxes higher than the ISM, their total photon dosages are comparable to the current problem. Amino acids similar to those seen in meteorites are created. Moreover, chemical reactions (including photolysis) which occur at cold temperatures <70 K can preferentially increase D/H because deuterium's higher mass allows it to bond more readily than H at low temperatures. D/H enrichments are seen throughout the ISM, and the D/H enrichments in amino acids suggests that they too have a low-temperature origin compared with the water in meteorite parent bodies (Sandford et al., 2001). Continued UV exposure may sometimes destroy the same large molecules the UV created earlier, but for a proper range of timescales and fluxes, cold-temperature photolysis of ices may be a more plausible pathway to forming the meteoritic amino acids than warm aqueous synthesis.

The ISM formation model is not without problems. First, the high optical depth within dense molecular clouds blocks nearly all external UV light. The only source of UV within the clouds is that caused by cosmic rays interacting with gas in the clouds, resulting in a UV flux of 10^{-4} – 10^{-5} G₀, where G₀ is the interstellar flux at the Sun today (Prasad and Tarafdar, 1983). Second, some organic molecules, such as the CHON particles in comets like Halley, may be easily destroyed by shocks during infall, although some debate exists on this point (Visser et al., 2009; Mumma et al., 1993; Zahnle and Grinspoon, 1990). Finally, some of the common meteoritic amino acids, such as α -aminoisobutyric acid (AIB) and isovaline, have not yet been produced by irradiation in the laboratory (Hudson et al., 2008), and it is not known whether this is due to these species only being formed during Strecker synthesis (as hypothesized by Ehrenfreund et al. (2001b)), or simply the ice experiments not using the proper initial mixtures. Nevertheless, overall the ISM formation model paints a plausible picture and may well play a role in the Solar System's organic history.

This paper proposes a third pathway for the formation of these complex organic molecules, which has not been examined previously. In our model, the solar nebula forms within a large molecular cloud similar to those in Orion. The Sun and its disk form completely, and condense and begin to grow. Within the next 1 Myr, nearby O and B stars turn on, bathing the young disk in UV light. These UV photons photo-evaporate gas from the disk (Throop and Bally, 2005; Johnstone et al., 1998), but also irradiate small ice grains exposed in the disk's outer skin layer. The simple ices grains, such as H₂O, CO₂ and NH₃, are exposed to the UV and begin to photolyze into more complex species. Each individual grain is exposed only briefly to UV light; they spend most of their time in the disk's dark, turbulent interior. Grains continue to grow, gas which has not formed planets is lost due to photo-evaporation and viscous loss, and within 5 Myr a gas-free debris disk is left with

its ices enriched in complex organics. These organics can then be incorporated into comets, asteroids, and the planets. Organics produced in this way could complement, and perhaps greatly exceed, those produced by the other two pathways. This method is similar to the exogenic ISM production in that it relies on UV photochemistry, but at far high flux ($10^6 G_0 vs. 10^{-5} G_0$), at warmer temperatures, for a much shorter time. The model allows for subsequent aqueous alteration as seen in the meteoritic record.

Work by Robert (2002) proposed that the organic material was created by X-ray irradiation of the disk by the Sun during its T Tauri phase. They did not present a disk model, but used high-precision D/H measurements of organic and non-organic material to show that D/H fractionation varied with heliocentric distance, as would irradiation. Remusat et al. (2006) compared the meteoritic and interstellar D/H values, along with their C-H bond dissociation energies, and concluded that the Solar System's D/H enrichment was created *in situ*, rather than inherited from the ISM. They proposed that the young Sun might provide the necessary UV source; their model did not study the timescales or fluxes involved.

The source of the Earth's organic inventory (as opposed to the Solar nebula's) is a parallel question which has received some attention. It is believed that although some organics were probably synthesized on the young Earth *in situ* by lightning or spark discharges (Miller and Urey, 1959), shock heating in the terrestrial atmosphere (Chyba and Sagan, 1992), warm ocean vents (Corliss, 1990), or any number of other terrestrial processes, far more were probably delivered from external sources such as comets, asteroids, and interplanetary dust particles (Chyba and Sagan, 1992). This paper does not further address the origin of life or the Earth's inventory, except to acknowledge that increasing global abundance of organics in the solar nebula probably results in increased delivery to the Earth as well.

This paper uses a simple model to describe the production of complex organics in UV-illuminated disks in a variety of cases. The results are necessarily general, and do not explain the abundances or species in one particular sample or disk, but provides an initial assessment of the problem. External UV photolysis has been ignored in almost all previous models, yet it may be one of the most important sources of energy in both the young Solar System and other proto-planetary disks. The problem is set up in Section 2, and the model described in Section 3. Section 4 contains results, which are discussed in Section 5. Conclusions are in Section 6, and Appendix A contains a derivation of the simple grain growth model used here.

2. Background

2.1. Energy sources in the early solar nebula

Various surveys have shown that the majority of stars are born in dense clusters of 300–10⁴ stars, where massive O and/or B stars can form (Adams et al., 2006; Lada and Lada, 2003). Due to the presence of decay products from short-live radionuclides such as ⁶⁰Fe that are only produced in supernovae, our Sun is thought to have formed in such an environment (Hester et al., 2004; Tachibana and Huss, 2003). The effects of such an environment can be enormous, compared with the classical 'closed box' view of Solar System formation where any environmental effects are easily ignored. Photo-evaporation by external stars can remove the disks on Myr timescales or shorter (Throop and Bally, 2005; Matsuyama et al., 2003; Johnstone et al., 1998). Close approaches between stars may be important, especially in the outer disk (Duncan et al., 2008; Adams et al., 2006). The high gas densities in such clusters can cause late infall of molecular cloud material onto disks after planetesimals have begun to form (Throop and Bally, 2008). And,

accretion of ejecta from supernovae and massive stellar winds may contaminate the disk, changing its structure, composition, or both (Throop and Bally, 2010; Cunha et al., 1998).

The effect of the local environment on solid-phase chemistry in the Sun's pre-planetary disk has received scant attention. Passing references can be found in Bergin et al. (2007), Irvine et al. (2000), Throop (2000), Fegley (1999), Prinn (1993), van Dishoeck et al. (1993). Prinn and Fegley (1989) provides a complete review but is now somewhat eclipsed by more newer RT models in the astrophysical literature (discussed below). Their paper does not directly address the formation of organics, but examines the energy budget for chemistry from various sources in the young solar nebula. They find that the largest energy source is the gravitational energy given off by the nebula as it collapses. In addition to the entire bulk disk heating, individual grains are heated and may sublimate ices as they fall into the nebula (Visser et al., 2009; Lunine et al., 1991). While this may cause some fractionation and possible hydrolysis of organic molecules, simply warming ices from 10 K to 200 K for a few hundred seconds during the infall is not itself a pathway to form amino acids. However, their secondlargest source, shocks and lightning, certainly is. They estimate the total usable energy for reactions by these processes to be roughly 4×10^{-6} that of the total gravitational collapse energy of the disk. Radionuclides (e.g. ²⁶Al) were estimated to provide a few orders of magnitude again less energy. They also estimated energy from photochemistry, based on fluxes from both the Sun and interstellar sources. They argued that photochemistry in the solar nebula was unimportant, especially from internal sources. However, more sophisticated recent models show that photochemistry can in fact be the dominant energy source.

2.1.1. Internal UV sources

Several recent models for disk formation consider UV radiative transfer from the central star to the inner disk. The model of Woitke et al. (2009) handles photochemistry using a Monte Carlo method in a 2D disk of mass 1 MMSN, surrounding a T Tauri star. Over 70 chemical species are considered, including five ices, with a total of nearly 1000 different chemical reactions. A broadly similar model with fewer species is described by Jonkheid et al. (2007). The model by Gorti and Hollenbach (2004) describes the UV photochemistry of 73 gas species in a 10 Myr old debris disk, putting it in a much lower optical depth regime than the other models. All three models are computed for a fixed age and do not evolve. The grain size distribution in all is uniform across the disk. All three models present sophisticated pictures of the radiative transfer and photochemistry within the disks, allowing predictions to be made for abundances and line strengths. However, the model does not include ice photolysis, grain growth, differences in grain size across the disk, or external illumination. The UV field reaches $\sim 10^4 G_0$ inward of 10 AU, but this is still much lower flux than the $10^6 G_0$ or more from external illumination.

In calculating the energy budget of the nascent Solar System, Prinn and Fegley (1989) estimated that the line-of-sight UV optical depth through the disk to be "7 million to 110 million orders of magnitude." In their model, this extreme optical depth would prevent solar-driven photochemistry virtually anywhere outside the central 0.35 AU. However, they assumed a direct line-of-sight from the source was required, which Gladstone (1993) points out is not the case because solar Ly α photons can reflect off of interplanetary hydrogen far above the disk plane, thus illuminating the disk by reflected solar light. Considering the higher density and reflectivity of the interplanetary medium (IPM) at the time, and the increase in early solar UV flux at $10^4 \times$ or so over present values, Gladstone (1993) calculate that the young Solar System was exposed to a solar UV flux roughly $10 \times$ the present solar value. Scattering of solar Ly α photons off of winds, jets and infalling material can also be a

large source of UV onto the disk. Similarly, Hollenbach et al. (1994) showed that young stars can create a thin atmosphere above their disk, and this disk provides a source of indirect UV illumination which can drive photo-evaporation (and thus photolysis), at rates $10-100 \times$ lower than external illumination would, or 10^4 - $10^5 G_0$ (Matsuyama et al., 2003). Alexander et al. (2006a,b) also looked at the case of photo-evaporation from the central star in flared disks, which avoids the line-of-sight problem in Prinn and Fegley (1989). Combined with loss to inward viscous evolution, Alexander et al. (2006b) calculated disk loss timescales of several Myr, consistent with observation of disk dispersal in young T Tauri stars. None of the papers by Gladstone, Hollenbach or Alexander considered the photochemistry effects of UV, but between these results and the detailed RT models above, it becomes clear that photochemistry from the central star can be important. Table 3 lists approximate fluxes for the various sources.

2.1.2. External UV sources

While the interstellar UV flux in Taurus-like regions is low (~1 G₀ outside the cloud, and 10⁻⁴ G₀ inside), stars in dense clusters such as the Orion Nebula Cluster (ONC) are subject to fluxes from O and B stars on the order ~10⁶ G₀. Ices in these clusters' disks are exposed to high levels of UV irradiation, enhancing the disks' abundance of organic molecules. In contrast to the internal sources, the external sources are stronger by $10^2 - 10^4 \times$, and illuminate the entire disk evenly rather than dropping off with radial distance.

This paper examines only the effects of the external flux. Existing models provide sophisticated treatments of the internal UV flux and the gas photochemistry; our goal here is to understand the broad global effects of external flux on solid-state chemistry, in preparation for a more detailed model.

2.2. Energy budget

A quick calculation shows the importance of external irradiation relative to other energy sources. First, consider the flux intercepted by a disk from its central star of luminosity *L*. In a disk with a radius:half-height ratio of 10:1, the fraction of flux intercepted by the disk is $\simeq 1/10$, and the total energy deposited at all wavelengths in time Δt is just

$$E_{\odot} \simeq \frac{1}{10} L \Delta t. \tag{1}$$

The total amount of energy available for chemistry through thermal heating, shocks, lightning, and so forth can be no greater than the disk's total collapse energy from the cloud to disk inner radius R_0 , given a disk mass M_d and stellar mass M_s , or

$$E_{\rm c} = \frac{GM_dM_{\rm s}}{R_0}.$$
 (2)

Finally, the total UV energy absorbed by the disk from external stars is roughly

$$E_{\rm UV} = \sqrt{(2)}\pi R_d^2 F_{\rm ext} \Delta t. \tag{3}$$

Typical values for solar-mass stars in dense clusters are $M_s = 1M_{\odot}$, $M_d = 0.01M_{\odot}$, $L = L_{\odot}$, $R_d = 100$ AU, $R_0 = 5$ AU, $F_{ext} = 10^6$ G₀, and $\Delta t = 1$ Myr. Plugging in, we find the ratio E_{sol} : E_c : E_{UV} is approximately 1:100:10⁴. That is, in 1 Myr, the external UV dose received by the disk exceeds by $100 \times$ the entire direct energy input from the central star, and the external UV dose exceeds by $10^4 \times$ the entire collapse energy of the disk.¹ Moreover, although thermal gradients can limit the amount of energy available for chemical reactions

¹ If the opposite were the case, photo-evaporation could not remove the disk.

(Prinn and Fegley, 1989), the UV energy is deposited directly into ice and dust grains, where individual photons cause photolysis. Therefore, the disk's dominant energy source is external flux, and this energy source's effect on chemistry cannot be ignored.

2.3. UV photolysis of Ices

The experiments of Miller (1953, see also Urey, 1952) showed that electric discharges within an atmosphere can rapidly create amino acids. Since this time similar experiments have been repeated with different initial species, temperatures, phases, and energy sources, finding the same general result that amino acids are relatively easy to produce given sufficient energy. In an astrophysical context, amino acids can be produced with energy sources from ion irradiation, to physical shocks, to pyrolysis (heating), to UV irradiation (Bernstein et al., 2002; Chyba and Sagan, 1992; Miller and Bada, 1988; Barak and Bar-Nun, 1975; Miller and Urey, 1959). According to Hudson et al. (2008), "one conclusion is that energetic processing of almost any organic ice that contains C, H, N, and O probably results in the formation of amino acid precursors, which can be hydrolyzed to give the acids themselves."

Most interesting in the regions of cold space are laboratory experiments in the last decade involving UV irradiation of ice mixtures. For instance, experiments by both Bernstein et al. (2002) and Munoz Caro et al. (2002) started with thin ice mixtures including H₂O, CH₃OH, and NH₃, chosen to simulate ISM conditions. The micron-thick ice mixtures were formed at 15 K, and then irradiated for 30 min at 10⁷ G₀. After warming, analysis in a gas chromatograph detected six amino acids, including glycine and alanine. Their laboratory irradiation corresponded to 10⁷ yr in the interior of a dense cloud (10 $^{-4}\,G_0)$, or 12 h in the Orion nebula (10 $^6\,G_0).$ The net photolysis efficiency was around 0.25% (complex organics produced per photon), and by the end of their runs the majority of their C and N had been converted into new compounds (Bernstein et al., 1995). More recent experiments by Nuevo et al. (2008, 2007) measured upwards of a dozen different amino acids formed from irradiation of H₂O, CO₂, and NH₃.

The authors of all three experiments hypothesized that long exposures of cold ices to UV light could explain the multitude of organic molecules found in interstellar regions. If the solar nebula collapsed from such an enriched region of the ISM, subsequent incorporation of these species into preserved primitive bodies such as Murchison would be a natural consequence of their birth environment.

Although UV can lead to the synthesis of organic molecules, excessive UV flux can be damaging to these same molecules, as evidenced by terrestrial sales of skin-protection products. Bernstein et al. (2004) looked into the UV destruction of amino acids, and found that given enough flux they eventually formed nitriles, which are perhaps an order of magnitude more stable against further destruction. Similarly, Ehrenfreund et al. (2001a) found that several hundred years of illumination at 1 G₀ destroyed most of the aminos in ice matrices. Hudson et al. (2008, see also Garrod and Herbst 2006) showed that irradiation and hydrolysis of nitrile-containing ices results in amino acids being created *again*, so long-term irradiation may eventually result in an equilibrium between aminos and nitriles.

In Orion, the flux hitting a disk varies with time as a star orbits through the cluster, changing its distance and tilt angle to the external O/B stars. Typical distances from the Orion core range from about 1 pc to 0.01 pc, causing the impinging flux to be in the range 10^3 – 10^7 G₀ (Fatuzzo and Adams, 2008; Throop and Bally, 2008; Bally et al., 1998). 10^6 G₀ represents the flux hitting the disk skin. However, young disks are very optically thick, so the vast majority of the ice grains are nearer the midplane and thus sheltered from UV. Simple calculations by Throop (2000) based on

the disk mass and small grains gave typical initial optical thicknesses of close to 10⁶ at 10 AU; thus, these individual grains go through a "broil-cool, broil-cool" cycle as they circulate through the disk, only occasionally being exposed to the impinging flux. Disk midplane temperatures can be as warm as 50 K out to 100 AU, so any nitriles produced during the irradiation are likely to go on to form amino acids during when they shaded but still warm (Visser et al., 2009; Watson et al., 2007; D'Alessio et al., 2006).

3. Disk model

The simple model used here is a modified version of that presented in Throop and Bally (2005). The current model is 1D and considers grain growth and external irradiation as a function of orbital distance *R* from a $1M_{\odot}$ star. The disk is azimuthally and vertically homogeneous, with initial parameters specified in Table 1. The initial disk mass is $0.04M_{\odot}$. The disk is made of gas and dust (ice), in an initial mass ratio of 100:1. The disk has 40 logarithmically spaced radial bins, and it is evolved for 3×10^5 yr using a selfadjusting time-stepper coupled with a Crank–Nicolson integrator. At the end of this time, photo-evaporation has largely removed the gas disk. Real disks might continue to be exposed to UV for several Myr, but because of rapid grain growth, most of the irradiation of small grains happens at the beginning of the simulation and the results are not strongly sensitive to the time cutoff.

3.1. UV photolysis

UV photons can create complex organic molecules or their precursors from simple ices. The effect can be roughly parametrized with a 'photolysis efficiency' ϵ_p , where $p \approx 0.25\%$ in molecules per photon for conversion from simple ices into amino acids. This parametrization skips the complex chemical chains involved, but is roughly the correct yield from pure ice (Bernstein et al., 2002).

At each timestep, the model computes the UV exposure onto the disk. The instantaneous UV flux is

$$F(R,t) = \frac{L}{4\pi d^2} (1 - exp(-\tau(R,t)))$$
(4)

where the optical thickness $\tau(R, t)$ is

$$\tau(R,t) = \frac{3}{4\rho_d} \frac{\Sigma_d Q_{\text{sca}}}{r(R,t)},\tag{5}$$

assuming particles of size *r* and density ρ . The surface density Σ_d is that of ice grains alone, and does not change during the simulation. We assume scattering efficiency $Q_{sca} = 1$, which is appropriate for all but the very smallest grains and does not change the results.

At each timestep the flux F(R,t) is computed, and the total number of photons intercepted by each bin is recorded. These are then used to compute the total UV exposure in photons per molecule,

 Table 1

 List of parameters, Nominal case.

Parameter	Value, Nominal
Surface density	$\Sigma \propto R^{-3/2}$
Initial grain size	$r_0 = 0.2 \ \mu m$
Photolysis efficiency	$\epsilon_p = 0.0025$
Sticking efficiency	$\epsilon_s = 1.0$
Stellar mass	$M = 1 M_{\odot}$
Initial disk mass	$M_{\rm 0d}$ = 0.04 M_{\odot}
Disk edges	$R_0 = 0.4 \text{ AU}; R_1 = 30 \text{ AU}$
Ice:gas mass ratio	1:100
UV flux	$F = 10^6 G_0$
UV start time	$t_{\rm UV} = 0 \ {\rm yr}$
Run time	$t_{\rm run}$ = 3 $ imes$ 10 ⁵ yr

(6)

$$\Phi(R,t) = \sum_{t} \frac{F(R,t)}{\Sigma_d} \frac{1}{m_m} \Delta t,$$

where $m_m = 18$ amu is the typical molecular mass.

The model assumes a fixed external flux of $10^6 G_0$. This flux is what the well-studied Orion proplyds at 0.1 pc receive, and is picked for easy comparison with previous results on those disks. Two additional cases look at higher and lower fluxes.

3.2. Grain growth

Grain growth is important to the model, because once surface area is locked up in large grains, it cannot be exposed to UV radiation. Both observational and theoretical arguments shows that grains grow rapidly, reaching centimeter or meter sizes on timescales as short as decades (Dominik et al., 2007; Johansen et al., 2007; Throop et al., 2001). Grain growth (together with gas loss) causes the disks to clear in optical depth from the inside out, typically within 1–5 Myr (*e.g.* Alexander and Armitage, 2007, and references therein).

The physical mechanisms for the early stages of grain growth are not well understood. However, a simple parametrization is useful for the present study. Throop (2000) performed semi-analytic calculations of accretionary grain growth of a size distribution n(r,R,t) of particles. For grains up to a few cm, the grains were coupled to the gas with collision velocities depending on the gas eddy speeds of Mizuno et al. (1988) and Voelk et al. (1980), while for larger sizes they used particle-in-a-box collision probabilities. In both regimes they assumed a constant sticking probability ϵ_s . After integrating their distributions numerically, they combined an analytic expression for grain growth with numerically-determined coefficients from the eddy velocity simulations to describe a the net grain growth. In their model, adopted here and derived in more details in Appendix A, the typical grain size r grows as

$$\frac{dr}{dt}(R,t) = 1.2 \times 10^6 \ e^{42.6p} R^{-2-\frac{3p}{2}} \epsilon_s^2 \ \Sigma_{d1}^2 \ \rho_d^{-5/3} t, \tag{7}$$

for time *t* and orbital distance *R*. Σ_{d1} is the initial dust surface density at 1 AU, and ρ_d is the dust grain solid density. ϵ_s is the sticking efficiency, taken to be a constant in the range 0.001–1. *p* is the radial mass exponent, where $\Sigma \approx R^{-p}$. The constant and exponential are determined semi-analytically, and have units such that the final expression is correct for cgs inputs. For particles above 1 m, processes such as gravitational instability dominate over accretionary growth, and photolysis is unimportant so growth is simply turned off. Although Eq. (7) is a simple expression and considers only a single characteristic size, it broadly agrees with more detailed calculations of grain growth in the micron-to-meter range (*e.g.* Weidenschilling, 1997).

3.3. Photo-evaporation and viscous evolution

The gas disk evolves using the standard prescription of Pringle (1981), with $\alpha = 0.01$. For simplicity only gas is transported, not dust. Photo-evaporation by an external O star of brightness $10^5 L_{\odot}$ is also included; the photo-evaporation model is as laid out in Matsuyama et al. (2003). The photo-evaporation model considers both EUV and FUV flux from the external star as it removes the gas disk in 10^5-10^6 yr. Flux from the disk's own central star is not included. The nominal stellar distance is 0.1 pc (giving a flux $10^6 G_0$); additional cases consider distances of 0.01 pc and 0.5 pc. Photo-evaporation removes gas but not dust, because except at the outer edge, grains grow too quickly to be entrained in the escaping flow of gas (Throop, 2000). In the current model, photo-evaporation sets the timescale for removal of the gas disk, but does not itself affect photolysis.

Dense clusters such as Orion also are rich with outflows, stellar winds, and close stellar encounters. These effects, while easily visible in the nebula, have only minimal effect on individual disks (Throop and Bally, 2008; Allen et al., 2007), so they can be safely ignored.

4. Results

Simulations are presented here for our nominal case as well as six additional test cases, called Massive, High Flux, Low Flux, Slow Grow, Delay, and Debris. The initial conditions for each are listed in Tables 1 and 2.

Results for the Nominal case running for 3×10^5 yr are shown in Figs. 1. Grains grow steadily and reach meter sizes at the inner edge and almost 1 cm at the outer edge. As a result the opacity drops (Fig. 2), reaching unity at the inner edge in about 10,000 yr and dropping below this throughout the entire disk by 10^5 yr. The surface density at the inner edge is highest, but the rapid grain growth more than compensates for this, clearing this region earliest. At first, the production of organics proceeds at a uniform rate across the disk, because all regions of the disk are optically thick and therefore intercepting every single photon (Fig. 3). As the inner-disk opacity drops, photons begin to pass through the disk without interacting. This causes organic production to stop in this region, and this 'production front' slowly moves outward in the disk until organic production has ceased throughout, at about 2×10^5 yr. Further integration beyond this point produces no more changes, because the disk's opacity has dropped below unity and little UV flux is intercepted. Looking at the total UV exposure (Fig. 4), the greatest dose is delivered at the outer edge, which receives ~ 3000 photons molecule⁻¹. The inner region receives a much smaller dose of ≤ 100 photons molecule⁻¹ inward of 5 AU. The outer edge's dose is greater because of both slower grain growth and lower surface density. The dose of 3000 photons molecule⁻¹ is be sufficient to photolyze raw ices into complex organics about seven times over. As seen in Fig 4, the peak organic density is at \sim 20 AU. Outward of this the disk's raw material inventory drops, and inward the grain growth is too fast to allow for much photolysis. By the end of the run, total organic production is 4.5×10^{29} g, or close to half of the original ice mass of $1.1 \times$ 10^{30} g (Fig. 5). Photo-evaporation has removed the entire gas disk

Table 2	2	
List of	parameters	varied.

Trial name	Changed parameter	Organic production
Nominal Massive High Flux Low Flux Slow Grow Delay Debris	$- M_{0d} \rightarrow 0.4M_{\odot}$ $F \rightarrow 10^7 G_0$ $F \rightarrow 2.5 \times 10^4 G_0$ $\epsilon_s \rightarrow 0.001$ $t_{UV} \rightarrow 700,000 \text{ yr}$ $r_0 \rightarrow 1 \text{ m}$	$\begin{array}{c} 4.5\times10^{29}{\rm g}\\ 1.6\times10^{29}{\rm g}\\ 7.0\times10^{29}{\rm g}\\ 3.1\times10^{28}{\rm g}\\ 6.3\times10^{29}{\rm g}\\ 2.9\times10^{28}{\rm g}\\ 4.0\times10^{23}{\rm g} \end{array}$
		-

Table	3	

UV	fluxes	in	different	environments.
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Source	Flux at 10 AU	Reference
UV flux inside dense molecular cloud	10^{-4} 10^{-5} G ₀	Prasad and Tarafdar (1983)
Present day, interstellar	1 G ₀	Habing (1968)
Present day, solar	10 G ₀	Cox (2000)
Young Sun, reflected from IPM	1000 G ₀	Gladstone (1993)
Central T Tauri onto flared disk	3000 G ₀	Alexander and Armitage (2007)
External stars, small cluster External stars, large cluster	$10^{3}-10^{5} G_{0}$ $10^{5}-10^{7} G_{0}$	Adams et al. (2006) Johnstone et al. (1998)



Fig. 1. Grain size, Nominal. Grains grow to almost cm sizes throughout the disk within 3×10^5 yr. Growth is stopped at 5 m (black) as other growth mechanisms begin to take over.



Fig. 2. Opacity, Nominal. By the end, the opacity has dropped to below 1 throughout the disk as grains grow. In the regions of low opacity, photolysis is inhibited because the disk intercepts little flux.



Fig. 3. Organic production, Nominal. The integrated flux and opacity is converted into a maximum organic photolysis yield. The peak density is reached near the outer edge: inward of this grains grow rapidly, and outward the disk density drops off.

in 2.5×10^5 yr. Numerical results from this run and all others are in Table 2.

Next shown (Figs. 6–8) are results from the Delay case. In this, the disk is the same, but the UV source comes on only after a delay of 7×10^5 yr, allowing for some grain growth to happen before photolysis. As can be seen, the resulting organic surface density



Fig. 4. Photons per molecule, Nominal. This shows the net exposure of each original ice molecule in the disk to UV flux. Grains at the outer edge receive the highest flux because of their slow growth and the low surface density.



Fig. 5. Mass evolution, Nominal. As ices are converted into organics, the solid and dashed lines approach each other. The dotted line plots the mass of the gas disk, as it is dispersed by photo-evaporation and viscous evolution.



Fig. 6. Photolysis, Delay. In this case the disk is given a head-start of 700,000 yr to evolve before the UV flux is started. Grains grow, and the total organic production is about 5% of that in the Nominal case.

and UV exposure are about $10\times$ lower than that of the ${\tt Nominal}$ case.

Figs. 9–11 show the Debris case, where the grains have been started at a constant size of r = 1 m. In this case the disk's initial opacity is so low (<0.01 at the outer edge) that very little UV is

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Fig. 9. Photolysis, Debris. Here the grains start as a uniform 1 m size, with the same radial distribution as in the Nominal case. Organic exposure is very low, about 10^{-6} that of the Nominal model.

intercepted, and the organic production is about $10^6 \times$ lower than the Nominal case. Both the Delay and Debris cases simulate different conditions for older disks: that is, disks which have evolved outside the HII region and then enter into it, or ones born before the O/B stars turn on. Low-mass stars are generally believed to form over the course of several Myr, before the first high-mass stars form, so most disks are probably somewhere between these two and the Nominal case.

Fig. 12. Photolysis, Slow Grow. The grain sticking coefficient is reduced from 1.0 to 10^{-3} . Grain growth is slowed, and exposure to UV increases as a result because of long-lasting small grains.

Time [yr]

2.2×10⁵

1.1×10⁵

1.0

0.1

0

0.6

0.4

0.2

0.0

3.3×10⁵

Organic

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Fig. 13. Photons per molecule, Slow Grow.



Fig. 14. Mass evolution, Slow Grow. In this case more than 50% of the original ices can be photolyzed into organic molecules.

run, the disk mass was increased by $10 \times \text{to } 0.4 M_{\odot}$. This decreases the net UV dose per molecule in the inner disk, but in the outer disk where there is already more than sufficient flux in the Nominal case, the result is a net greater production of organics. In the High Flux case, the UV flux is increased by $10 \times \text{to } 10^7 \text{ G}_0$, which is the highest that most disks typically encounter for brief periods. The effect is to increase photolysis, but by less than $10 \times$ because the outer disk is already flux-saturated. Finally, in the Low Flux case, corresponding to a disk which is 0.5 pc distant from the cluster core, the photolysis rate is scaled downward, roughly in proportion to the reduced flux.

Most of the runs share several similarities, including: (a) the total raw exposure is sufficient to photolyze the entire initial ice abundance of much of the disk; (b) the photolysis is greatest at the outer edge; and (c) the dose in a typical cluster is high enough that in 10^5 yr the entire disk outward of 20 AU is photolyzed.

The model here is simplistic in several regards. First, the laboratory yields used here are for photolysis of virgin ice surfaces exposed for short times, and the efficiency ϵ_p will drop with time as the virgin surface becomes irradiated. More processing will also result in the destruction of some amino acids into nitriles and gasphase molecules (Bernstein et al., 2004), so the quantities presented here are upper limits. Heating from inward radial transport and shocks may cause additional destruction. The total UV dose in the Nominal case is high but not extreme: the highest-dose region at the outer edge receives only $7 \times$ the flux required for complete photolysis, and regions inside of the edge receive far less than this (<1 inward of 10 AU). While eventual destruction of many of these

organics must be assumed, the actual amount depends on parameters outside the bounds of this study.

It is assumed that each individual grain is uniform throughout, while in reality flux is deposited only to the outer skin of a grain, where it can build up a crust layer. UV may be able to penetrate up to a few mm in rough or fractured surfaces, but anything beyond this is doubtful. (Orzechowska et al., 2007 claims 1 m penetration of UV into Europa, but this seems highly unlikely in the case of any realistic ice.) However, most of the flux in the simulations is deposited when the grains are less than a few mm, making this a reasonable approximation. For instance, Fig. 3 shows that UV deposition has stopped by about 20,000 yr in the Nominal disk. Fig. 1 shows that by this time, grains in this region remain mmsized. In addition, grains of this size are likely to be fluffy, cracked, collisional aggregates which expose new surface regularly. And in all cases, the rapid grain growth occurs in the inner disk, where the models predict very little photolysis in the first place. The handling of UV deposition here is thus probably accurate enough given the model's other uncertainties.

The model here assumes the disk to be made of ice only, and not silicates. In reality the ice:silicate ratio is approximately 1:1 outward of the snow line, causing the net flux to be roughly halved for homogeneously mixed grains. Even within individual ice grains, the formation process may concentrate some reactants toward the center and others toward the outside, slowing photolysis further (Collings et al., 2003).

In addition to chemically processing grain surfaces, UV photons can erode grains by photo-sputtering molecules into the gas phase, where they are easily removed by the photo-evaporative wind. Sputtering may be as high as 1 meter per Myr (Throop, 2000; Westley et al., 1995) for fresh surfaces at $10^6 G_0$. However, for both photolysis and sputtering, large bodies will probably build up a crust of silicates which will prevent further effects of exposure. It is difficult to estimate this effect without more detailed laboratory modeling of heterogeneous mixtures of thick, collisionally processed ices and silicates. The interaction between sputtering and photolysis should be considered in future models.

Our model handles the radial transport of gas but not dust. Dust transport is a poorly understood yet important process (*e.g.* Brownlee et al., 2006), and should be included in the next generation of models.

The model here finds that the disks become optically thin by 10^{5} – 10^{6} yr, somewhat shorter than the observed disk lifetimes of 1–5 Myr. The difference between these two timescales is that our model considers just monotonic grain growth, while real disks continue to release small secondary dust grains during particle collisions. These continually produced small grains remain visible even as most of the mass of the disk grows into planetesimals. UV photolysis (and photo-evaporation) can therefore continue for much longer periods than the lower-limit timescales predicted here. The assumption of short disk lifetimes here causes our flux numbers to be conservative.

5. Discussion

The model here leads to one robust result: there was sufficient external UV flux in the young Solar System to allow for ice photochemistry to play an important role in the Solar System's chemical makeup. Complex organics can be rapidly produced in flux environments typical of dense star clusters, especially in the outer Solar System. Previous models for photochemistry in our Solar System have not considered ice photochemistry from external UV sources. The current model describes a new pathway for production of complex organics in the young Solar System. This adds to the two existing pathways of aqueous alteration on meteoritic parent bodies and photo-synthesis in the ISM, thus relaxing the conditions required in the early solar nebula. The total external UV energy available can exceed that of all other energy sources combined.

Of the simplifications made here, two are worth discussing. First, photolysis is assumed to be a one-way process, when in reality continued UV can break apart amino acids that it creates. Continued laboratory work and improved modeling will constrain the net production rate, allowing improvements from the upper limit yields presented here. Second, the interaction between photoevaporation and photolysis is simplified. Photo-evaporation is driven by UV absorption into dust or ice grains, and if they are tiny enough the photo-evaporative outflow can entrain these grains, as seen in some large outflows (Balog et al., 2008). Small grains might be continually produced as collisional debris in young disks. So, if the disks are dominated by a continually refreshed population of small dust grains, these grains might act as a shield, protecting the inner disk from UV but themselves providing a large source of irradiated organics delivered back to the ISM in the outflow.

The largest free parameter in these models relates to timing: if disks evolve in a dark environment for more than 10^5-10^6 yr, grains grow to meter sizes and larger where UV has no chance of penetrating to cause any more than trivial amounts of photolysis. In dense star clusters, the formation of low-mass stars is thought to continue steadily up until the moment that massive O/B stars form. Once they have turned on and the molecular cloud is ionized, star formation stops. Low-mass stars that form just prior to the O/B stars will thus end up with the largest amount of organics, while the oldest disks (up to several Myr in the case of Orion) will have much less.

The results here predict that organic molecules will be abundant in young circumstellar disks, but to date only a few of these molecules have been actually detected. However, help is on the way in the form of the Stratospheric Observatory For Infrared Astronomy (SOFIA) and the Atacama Large Millimeter Array (ALMA). SOFIA, operating in the 3–300 μ m range at a spectra resolution of ~100,000, will be able to detect vibrational and bending lines of water ices, methanol, and some CO bands. Organics such as amino acids are too heavy to have easily visible bands, but the structure of the water ice matrix as modified by these heavier molecules will be able to be studied by SOFIA. ALMA will provide brand new 0.1" high-resolution imaging of the disks, allowing insight into the radial distribution of molecules across the disk.

6. Conclusions

- There was sufficient flux from nearby O/B stars in the Sun's birth environment to convert the majority of the ice mass in the young Solar System and other proto-planetary disks into complex organic molecules within a few 10⁵ yr. Even when considering the disks' high optical depth and rapid grain growth, both of which sequester surface area, enough ice remained exposed for photolysis to continue rapidly.
- UV photolysis from external sources is likely to be the source of the meteoritic amino acids, which have D/H ratios difficult to reconcile with the warm, aqueous environments required from Strecker synthesis of these species.
- Organic production is predicted to be substantially less for disks that have evolved for more than 10⁵–10⁶ yr before O/B stars have turned on, because the grain growth in this time locks up surface area against photolysis.
- Externally driven photochemistry is most important in the outer disk, where grain growth is slow. The inner disk is warmer, more massive, and sees more rapid growth, and thus processes such as Fischer–Tropsch reactions may dominate the production of organics here.

- External UV flux in 1 Myr provides roughly 100× as much flux as from the central star, and 10⁴× as much energy as gravitational collapse. This energy is easily usable for chemical reactions because it is directly incident on ice grain surfaces.
- Photo-evaporation can occur at the same time as photolysis of ices, but these two processes operate largely independently. Photo-evaporation removes only the smallest grains, and photolysis can continue long after the gas disk has been removed.

Dense star clusters have historically been thought of as a hazard to planet formation, because the rapid timescales of disk destruction limit the conditions under which planets can form. Our earlier results showed that under some conditions photo-evaporation may in fact *speed* the formation of planetesimals (Throop and Bally, 2005). Our new results here add to this irony, showing that planetary systems that can form in such 'hostile' environments may also be among the richest in organic molecules and the precursors of life.

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Appendix A. Grain growth

Throop (2000) and Throop et al. (2001) developed a simple model for accretionary grain growth. The details of that model were presented only schematically, so a more detailed derivation is given here. In this model, particle grow by pure accretion, which is often considered to be the dominant process for the earliest phase of growth, where particles range from microns to ~ 1 m.

Consider a disk which has collapsed from the ISM, with an initially uniform particle size of r_0 . The disk is arranged such that its full height *H* at radius *R* is given by

$$H = R/10. \tag{A1}$$

Within this disk, dust grains collide and begin to grow by simple accretion. For simplicity, we assume that the particles can be defined by a single grain size r(R) which is a function of orbital distance. A particle-in-a-box collision model gives the grain growth rate as

$$dm/dt = \sigma n \nu m \epsilon_{\rm s} \tag{A2}$$

where the collision cross-section is $\sigma = 2\pi r^2$, *n* is the particle number density, *v* is the collision velocity, the particle mass is $m = \frac{4}{3}\pi r^3 \rho_d$, and $\epsilon_s = [0, 1]$ is the sticking efficiency for a single collision. Assuming vertical homogeneity and no radial transport, the particle volume density *n* can be computed directly from the disk structure as

$$n = \Sigma / (Hm) \tag{A3}$$

and the surface density of the dust component \varSigma_d (normalized to \varSigma_{d1} at 1 AU),

$$\Sigma_d = \Sigma_{d1} \left[\frac{R}{1 \text{ AU}} \right]^{-p}.$$
(A4)

To compute the collision velocity v, Throop (2000) examined the interparticle velocities present in the convecting, turbulent disk. The collision velocity depends on particle size because particles are trapped in eddies of different strengths. Performing semianalytic fits to the work of Voelk et al. (1980) and Mizuno et al. (1988), they approximated the collision velocity for dust grains in a gas disk surrounding a $1M_{\odot}$ star as

$$v = 10^2 r^{1/2} (2.2 \times 10^{-16} R)^{p/4}$$
(A5)

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Fig. 15. Grain size evolution. Plot show accretionary grain growth according to Eq. (A6), for disk of p = 3/2 and $0.1M_{\odot}$; growth is stopped above 1 m radius. Radial bins are spaced logarithmically.

where all units are cgs. Combining these Eqs. (A1)-(A5), integrating, and solving for *r* yields the result

$$dr/dt = 1.2 \times 10^6 e^{42.6p} R^{-2\frac{3p}{2}} \epsilon_s^2 \Sigma_d^2 \rho_d^{-5/3} t$$
(A6)

which can then be easily used to compute r(t) or m(t). The constant and exponential out front are determined semi-empirically and have the proper units such that the result is correct for cgs inputs. The expression shows a strong exponential dependence on the surface density exponent *p*, but this is deceptive: *p* usually has only a small range of values (1-2), and the dependence is reduced by other terms so that *p* only has an appropriately small effect on the grain growth.

Throop (2000) tested this equation (Fig. 15) and found it to agree well with accretionary growth calculations done numerically with full size distributions, using both their own calculations and those of Mizuno et al. (1988) and Weidenschilling (1997). In the case of ϵ_s = 1, it gives an upper limit to the grain size in a young disk growing by coagulation. For a standard $0.05M_{\odot}$ disk with gas:dust ratio of 100:1 and 0.1 µm initial grains, Eq. (A6) predicts growth to 1 cm in 10⁴ yr and 1 m in 10⁵ yr inward of 30 AU. This rapid growth is verified by Weidenschilling (1997), which finds growth of up to several meters within 10⁵ yr at 30 AU. Because the model considers only accretionary growth, it is useful only for particles up to a few meters in size, after which gravity and settling begin to become important. It also ignores radial drift, fragmentation, and possibly faster mechanisms such as gravitational instability (Johansen et al., 2007). Nevertheless, for computing rough particle size estimates and their dependence on disk parameters in the youngest disks, it provides useful limits which are broadly consistent with more complex codes.

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