PREBIOTIC MATTER IN INTERSTELLAR MOLECULES

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With the discovery of the first polyatomic molecules, NH_3, H_2O and H_2CO in 1968/9[1] there was immediate speculation as to how far biological chemical evolution - from atoms to small carbon compounds of biological significance - could have occurred in the Galaxy. There was also potential conflict with the canonical scientific view of the origin of life, traceable to the production of simple bio-molecules from the influence of energetic atmospheric events on the simple gaseous mixture (CH_4, H_2, H_2O and NH_3) presumed to compose the atmosphere of the very young Earth.

Subsequent discoveries have increased the list of identified interstellar molecules in dark nebulae to about 60 (see Table 1) and have also hardened the belief of astronomers that dark nebulae are sites in which formation of new stars and planetary systems occurs. In addition there has been a steady development of the theory of galactochemistry, starting in the early 1970's, explaining the chemical generation of polyatomic interstellar molecules from their atomic precursors[2]. I may illustrate the current state of the art with results of calculations by my own group at Monash[3], showing the predicted time evolution of abundances of species (Fig. 1) and a comparison with best observational estimates of the composition of dark nebulae of age in the vicinity of 10^7 yr (see Table 2). The agreement is surprisingly good in view of the very simple model adopted for molecular clouds.*

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*It is gratifying that a major anomaly, namely that the predicted fractional abundance of CO^+ in Ori A is about 10^{-14}, which appeared to be in conflict with observations[4] indicating an abundance of 10^{-10} to 10^{-12}, has been resolved because it seems that the line attributed to CO^+ is actually a line of methanol. It is also gratifying that our galactochemical model (Fig. 2) predicted a fractional abundance of the new oxide of carbon, C_3O in TMC1 of around 10^{-10}, in excellent agreement with our subsequent observations[5], which imply $X(C_3O) = 9 \pm 3 \times 10^{-11}$.

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Table 1

INTERSTELLAR MOLECULES

H_2	CO	H_2CNH	CC	NaOH?
OH		H_3CNH_2	CS	
CH	OCS	HN_2^+	SiS	
CH^+	NO	NH_3	NS	
H_2O	HNO?	CH_4^*	SO	
H_2S	SiO		SO_2	

CN	HCN	$H_3C{-}CN$	$H_2C{=}CH_2{}^*$
$C{\equiv}CH$	$HC{\equiv}C{-}CN$	$H_3C{-}C{\equiv}C{-}CN$	$H_3C{-}CH_2{-}CN$
$C{\equiv}C{-}CH$?*			
$C{\equiv}C{-}C{\equiv}CH$	$H(C{\equiv}C)_2{-}CN$	$H_3C{-}C{\equiv}CH$	$H_2C{=}CH{-}CN$
$C{\equiv}C{-}CN$	$H(C{\equiv}C)_3{-}CN$	$H_3C{-}(C{\equiv}C)_2{-}H$	$HN{\equiv}C$
$C{\equiv}C{-}CO$			
$HC{\equiv}CH^*$	$H(C{\equiv}C)_4{-}CN$		$HN{=}C{=}O$
			HOCH or $HOCO^+$?
H_2NCN	$H(C{\equiv}C)_5{-}CN^*$		$HN{=}C{=}S$

$H_2C{=}O$	H_3COH	$HO{-}CH{-}O$	$HC{=}O^+$
$H_2C{=}S$	$H_3C{-}CH_2{-}OH$	$H_3C{-}O{-}CH{=}O$	$HC{=}S^+$
$H_3C{-}CH{=}O$	H_3CSH	$H_3C{-}O{-}CH_3$	$HC{=}O$
$HCONH_2$			HOC^+
$H_2C{=}C{=}O$			

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*Detected only in the envelope around the evolved star IRC+10216.

?Claimed but not yet confirmed.

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Figure 1(a)

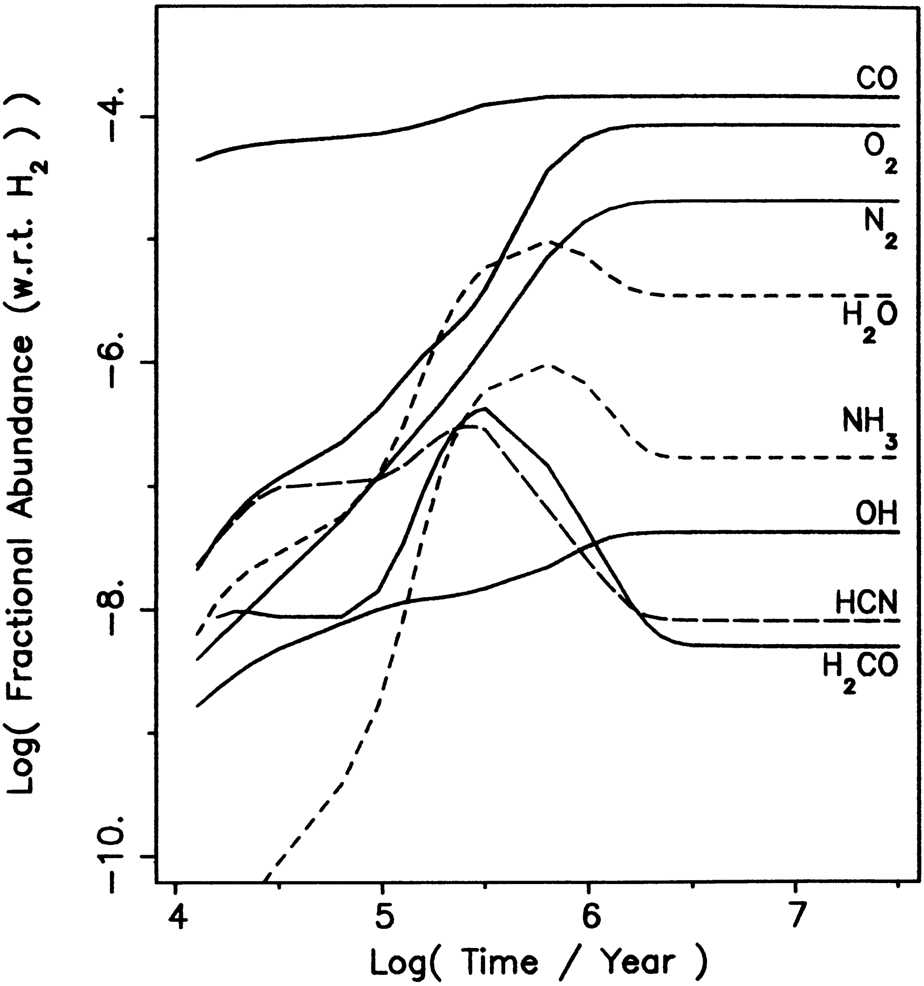

Figure 1 Variation of Predicted Molecular Abundance with Age of Molecular Cloud (Brown & Rice, unpublished). Some curves are dotted for clarity in respect of crossings. (a) small species; (b) C_3O and related species; (c) glycinonitrile and related species, (1) with, (2) without dotted pathways shown in Figure 4.

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Figure 1(b)

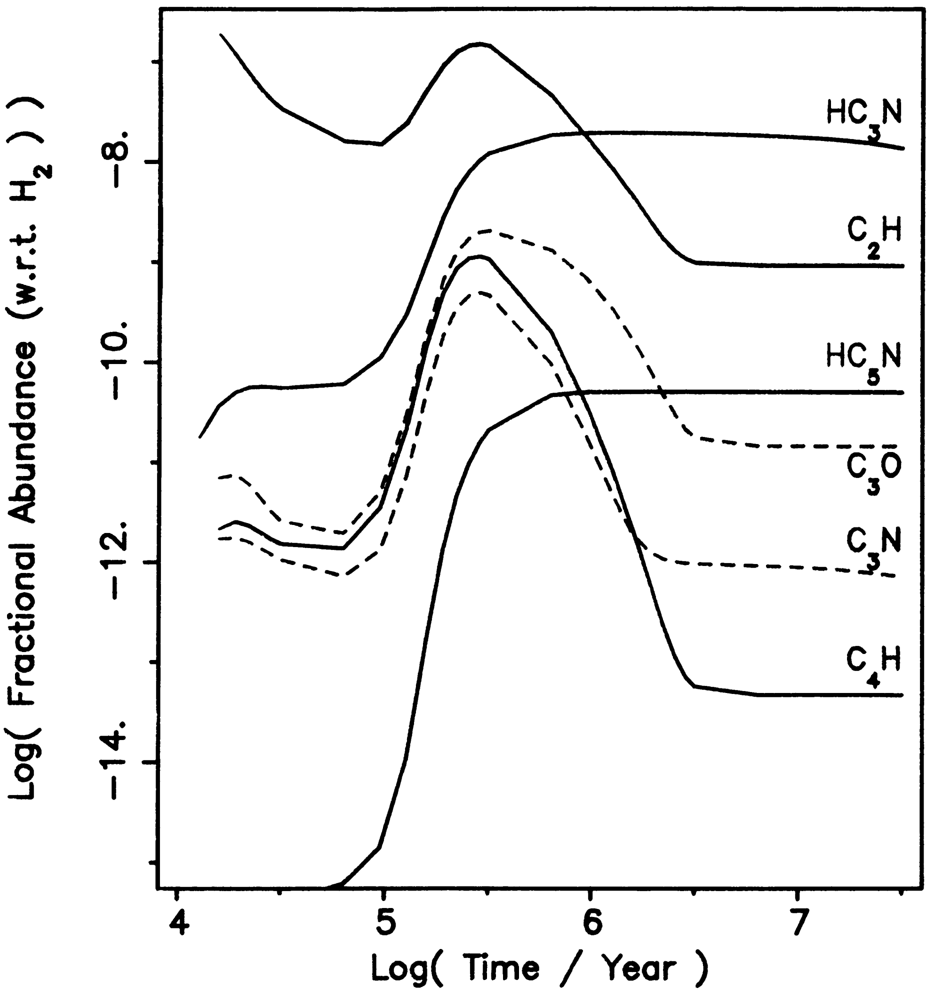

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Figure 1(c)

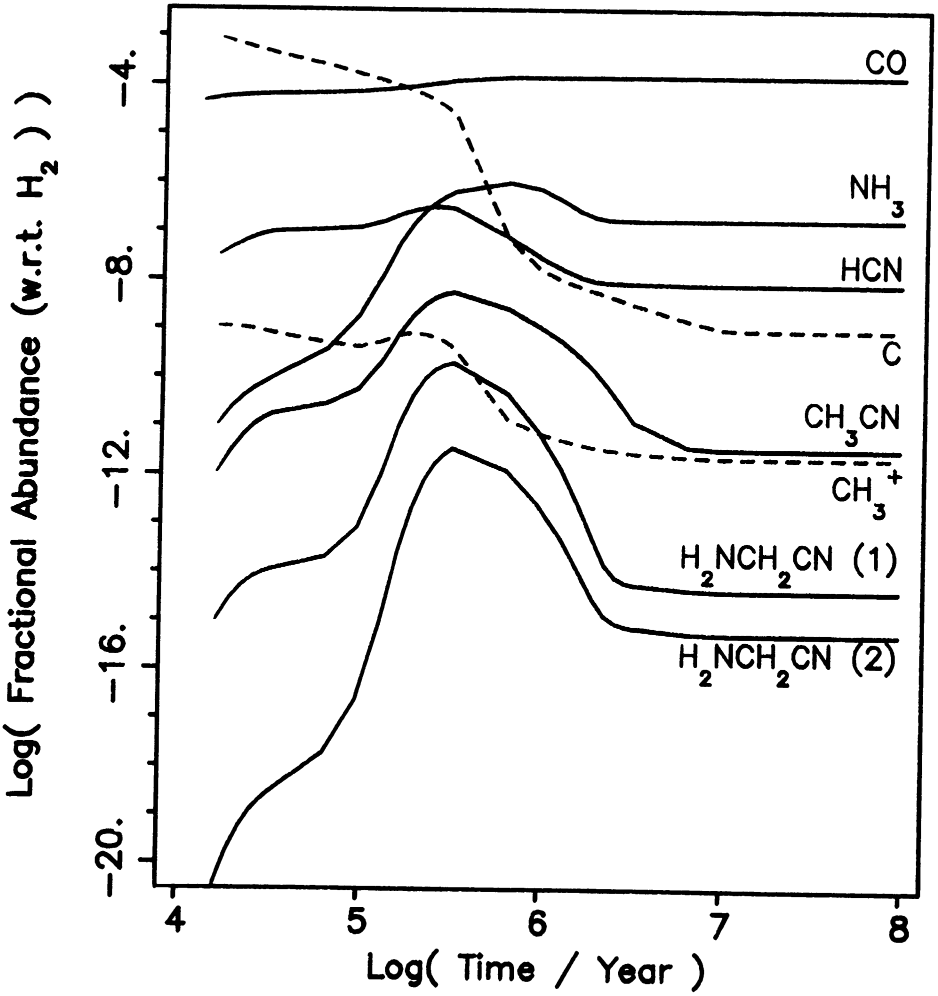

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Table 2

COMPARISON OF BROWN AND RICE MODEL WITH OBSERVED ABUNDANCES IN COOL CLOUDS

T = 10 TO 20 K : $n(H_2) = 10^4$ cm^{-3}
Low Metals

Species	Calc.(10^8yr) -Log(X)	Obs. -Log(X)
CN	8.4 to 8.2	9.0 to 7.5
H_2CO	8.4	8.8 to 8.0
HCN	8.3 to 8.1	7.9 to 7.7
OH	7.4 to 7.2	7.2 to 6.5
N_2H^+	9.2 to 9.1	9.0
HCO^+	7.9 to 7.7	8.1
C_2H	8.7	8.1
NH_3	6.9 to 6.8	7.7 to 7.0
CO	3.8	3.9 to 4.2
CH	9.3 to 9.1	7.7

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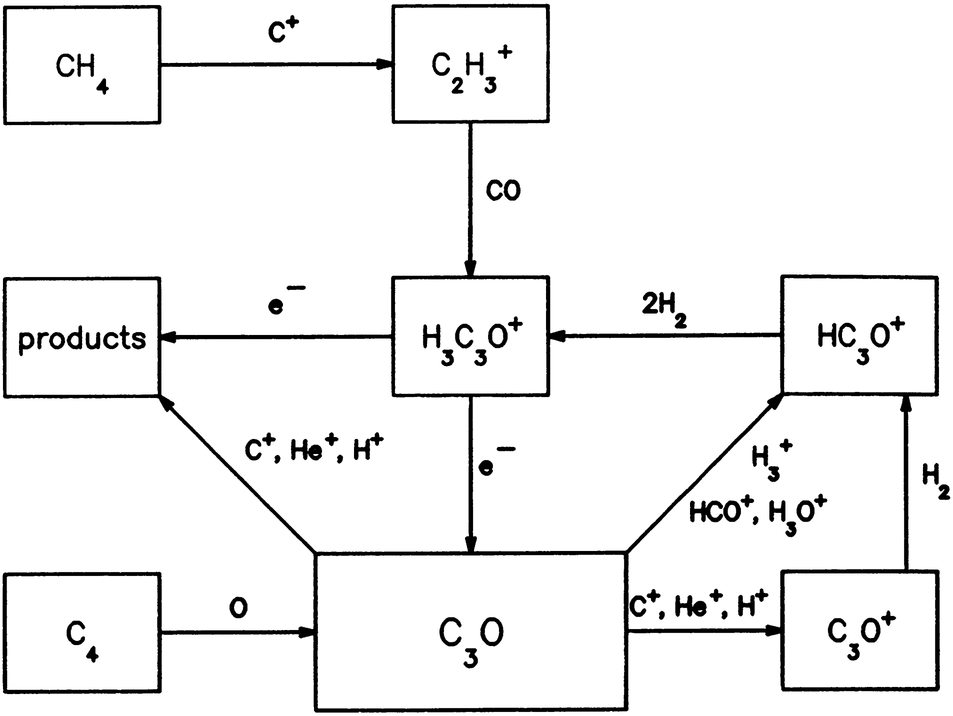

Figure 2 Formation channels for C_3O in Molecular Clouds.

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It is therefore not unreasonable to explore on the basis of our current galactochemical model some questions that would relate to the rate of generation of biologically interesting interstellar molecules and their possible connection with the origin of life. We could discuss at some length the pathways by which biologically significant materials might be constructed from various interstellar molecules - sugars from formaldehyde, pyrimidines and purines (the alphabet of the genetic code) from HCN or isocyanic acid and cyanoacetylene, and so on[6]. However I shall confine myself to two aspects of one particular kind of interstellar molecule of biological importance, namely aminoacids, the building blocks of proteins. The two aspects are:

(a) what progress has occured in trying to detect aminoacids in molecular clouds?

(b) what has galactochemistry to say about gas-phase production of aminoacids in molecular clouds?

Let us deal first with (a). There have been some extensive interstellar searches for the simplest aminoacid - glycine, $H_2N.CH_2.CO_2H$ - all so far unsuccessful. The search is complicated by the fact that there are two distinct conformers of glycine of lower energy than the rest (see Fig. 3). The search by our group[7] was for conformer (4) and included the sources Sgr B2 and Ori A as well as some dark clouds. It yielded estimated upper limits of column densities for Sgr B2 of 10^{14} cm^{-2} and, for the dark clouds, 10^{12} cm^{-2} corresponding to fractional abundances of about 10^{-9} and 10^{-10} respectively (see Table 3). The first search was followed by a search[8] for conformer (3) which gave an upper limit of column density in Sgr B2 of 10^{15} cm^{-2}. Searching goes on at Arecibo[9] for both conformers, but with no positive success so far although the upper limits for column densities in sources such as W49, W51, and in Comet Encke, have been reduced to about $10^{12}cm^{-2}$.

Turning now to (b), let us consider how aminoacids, or their chemically close relatives, might be formed by gas-phase reactions in molecular clouds. We can conveniently restrict consideration to glycine. Among the identified interstellar molecules the most closely related molecules are CH_3CN and CH_3NH_2. Can we envisage further processes that might lead to glycine?

In a formal sense we can write down a reaction between two known interstellar species:

$$CH_3.NH_2 + H.CO_2H \rightarrow H_2N.CH_2.CO_2H + H_2$$

but such a process is chemically exceedingly unlikely and in any case both reactants are of very low abundance in molecular clouds. Reactions involving related ions of these species likewise can be ruled out on grounds of exceedingly low concentrations and that they would very likely yield other products ($H.CO.NH.CH_3 + H_2O$ or protonated alternatives).

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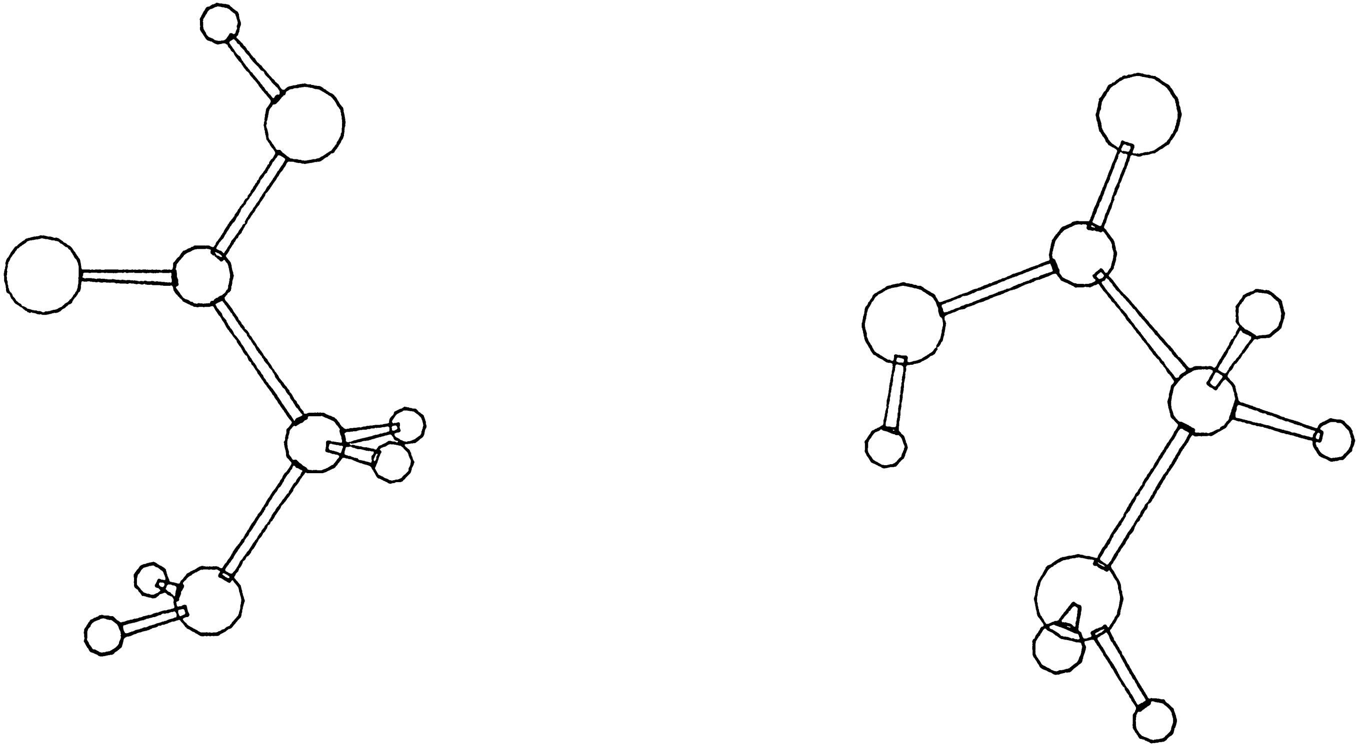

GLYCINE : CONFORMER 3

GLYCINE : CONFORMER 4

Figure 3 The two most stable conformers of glycine.

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Table 3

GLYCINE (4) SEARCH

Source	Upper limits for observed glycine column density and fractional abundance. NL (cm^{-2})	X	Assumed Hydrogen column density. NL (cm^{-2})
Sgr B2(OH)	7×10^{13}	7×10^{-10}	10^{23} - 10^{24} a
Ori A(OH)	3×10^{13}	7×10^{-10}	4×10^{23} - 4×10^{24} b
DR21(OH)	6×10^{13}	1.5×10^{-9}	4×10^{23} - 4×10^{24} b
TMC1	2×10^{12}	2×10^{-10}	$\sim10^{24}$
NGC2264	4×10^{14}	1×10^{-7}	4×10^{21} - 4×10^{22} b
W51	4×10^{14}	5×10^{-9}	8×10^{22} - 8×10^{23} b
NGC7538	4×10^{14}	1×10^{-8}	3×10^{22} - 3×10^{23} b
W3(OH)	2×10^{14}	2×10^{-8}	10^{22} - 10^{23} b
L134N	3×10^{12}	2×10^{-10}	1.3×10^{22} c

[a] Scoville et al., Ap. J., 201, 352-365 (1975).

[b] Wilson et al., Ap. J., 191, 357-374 (1974).

[c] Guélin et al., Astr. and Ap., 107, 107-127 (1982).

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However if we consider CH_3CN and its probable interstellar precursor CH_3CNH^+ [produced via the radiative association $CH_3{}^+ + HCN \rightarrow CH_3CNH^+ + h\nu$] then we might envisage the possible step:

$$CH_3CNH^+ + NH_3 \rightarrow H_3N^+.CH_2CN + H_2$$

which could be followed by

$$H_3N.CH_2.CH^+ + e \rightarrow H_2NCH_2CN + H.$$

This seems a plausible pathway to glycinonitrile ($H_2N.CH_2.CN$).

A competing destruction channel is -

$$CH_3CNH^+ + e \rightarrow CH_3CN + H.$$

An alternative pathway is:

$$CH_3{}^+ + NH_3 \rightarrow CH_2NH_2{}^+ + H_2$$

$$CH_2NH_2{}^+ + HCN \rightarrow H_2NCH_2CNH^+ + h\nu$$

The dissociative electron recombination reaction for $H_3N.CH_2CN^+$ might have branching channels to some other products and so not give a high yield of glycinonitrile. But overall, crude calculations(see Fig. 4) imply that a reasonable rate of glycinonitrile production is feasible and that fractional abundances could at times become as high as 10^{-10}.

A previously unpublished search for the $2_{11} - 2_{12}$ line of glycinonitrile at Parkes (1974, April)[10] gave an upper limit for the column density in Sgr B2 of 1×10^{17}, corresponding to a fractional abundance of about $X < 10^{-7}$.

We can therefore see ways in which a close relative of glycine would be found in molecular clouds. It is not too difficult to discuss pathways to nitriles of other aminoacids, e.g. alaninonitrile, from ethyl cyanide. But the simplest case of glycinonitrile illustrates the possible pathway to proteins and primitive life.

We come now to the question of possible survival of interstellar molecules during the formation of planetary systems by collapse of molecular clouds. Contemporary evidence is provided by studies of meteorites and perhaps soon by studies of comets. This aspect of the story is covered in Professor Ponnamperuma's presentation[11]. I will content myself with the comment that the material in Cl type carbonaceous chondrites was at no stage subjected to temperatures above about 90C[12] and therefore the larger known interstellar molecules, and such species as glycinonitrile, could have survived. The relatively heavy meteoritic falls that occurred in the early history of bodies of the inner Solar System[13] would have brought such material down to the already cooled surface of the young Earth.

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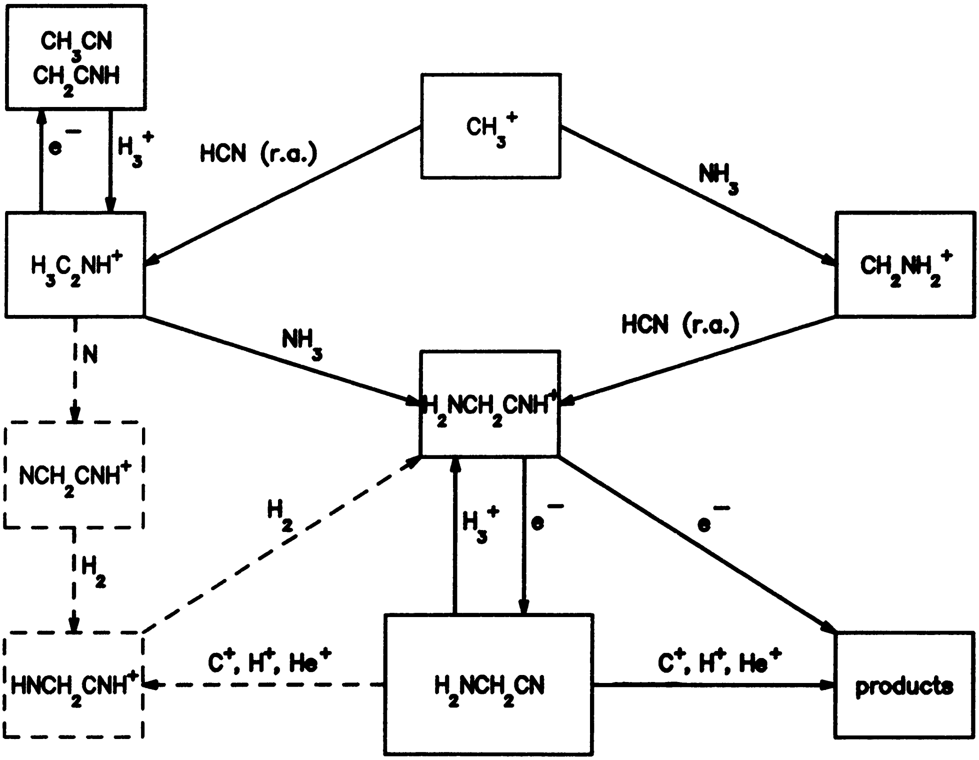

Figure 4 Formation channels for Glycinonitrile. Radiative associations are labelled (r.a.). Predicted relative abundances of glycinonitrile are: (a) peak (3×10^5 yr) 2×10^{-10}, final (10^8 yr) 4×10^{-15}; (b) with dotted pathways omitted, peak 3×10^{-12}, final 5×10^{-16}.

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We therefore have to consider whether some of the prebiotic chemicals on the surface of the early Earth could have come in this way from molecular clouds. Other processes, such as the Fischer-Tropsch syntheses that Anders and the Chicago group particularly have emphasised as accompanyng meteoritic and planetary condensation[12], or the production of prebiotic molecules by energetic processes in the atmosphere of the young Earth[6], perhaps also contributed to the chemical menagerie that is widely presumed to precede the evoluton of the first crude metabolising and reproducing system.

It is inappropriate to pursue here the question of the later stages of prebiotic chemical evolution and the earliest forms of life on Earth. But it is important to remember that the interest in aminoacids relates to their condensation to produce polypeptides - important biopolymers. However it is known[14] that glycinonitrile when heated with kaolin in the presence of acid can produce simple polypeptides. It is therefore feasible to consider possible chemical ancestry of life to pass through interstellar aminoacid nitriles rather than the acids themselves. We should not take for granted that aminoacids are necessarily more important than related types of molecules such as their nitriles in the history of chemical evolution.

We now have a reasonable understanding of interstellar molecules and their relevant galactochemistry even if some aspects, such as the precise role of grain reactions, or the cross-sections for some reaction channels, are not yet settled. This enables us to say that it seems feasible that the chemical ancestry of life on Earth goes back to the parental molecular cloud. If so then similar processes of planetary formation elsewhere in the universe may have led to the evolution of life on other planets. There are many imponderables to be resolved by future work on interstellar molecules as well as other areas of the origin of life. Perhaps one day we shall know all the answers!

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REFERENCES

1. Cheung, A.C., Rank. D.M., Townes, C.H., Thornton, D.D. and Welch, W.J., Phys. Rev. Lett., **21** 1701 (1968).
Cheung, A.C. Rank, D.M., Townes, C.H. Thornton, D.D. and Welch, W.J., Nature (Lond), **221**, 626 (1969).
Synder, L.E. Buhl, D., Zuckerman, B. and Palmer, P., Phys. Rev. Lett., **22**, 679 (1969).

2. Solomon, P.M. and Klemperer, W., Astrophys. J., **178**, 389-421 (1972).
Herbst, E., and Klemperer, W., Astrophys. J., **185**, 505-533 (1973).
Aannestad, P.A., Astrophys. J. Suppl., **25**, 205-222 (1973),
Watson, W.D., Astrophys. J., **188**, 35-42 (1974).
Allen, M. and Robinson, G.W., Astrophys. J., **207**, 745-757 (1976).
Black, J.H. and Dalgarno, A., Astrophys. J. Suppl., **34**, 405-423 (1977).
Mitchell, G.F., Ginszburg, J.L. and Kuntz, P.J. Astrophys. J. Suppl.,
38, 39-68 (1978),
Iglesias, E., Astrophys. J, **218**, 697-715 (1977).
Gerola, H. and Glassgold, A.E., Astrophys. J. Suppl, **37**, 1-25 (1978),
Prasad S.S. and Huntress W.T. Astrophys. J. Suppl., **43**, 1-35 (180); Astrophys. J., **239**, 151-165, (1980).
Brown, R.D. and Rice, E., Phil. Trans. Roy. Soc, **303**, 523-533 (1981).
Graedel, T.E., Langer, W.D. and Frerking, M.A., (1982).

3. Brown, R.D. and Rice, E., unpublished calculations.

4. Erickson, N.R., Snell, R.L., Loren, R.B., Mundy, L. and Plambeck, R.L., Astrophys. J., **245** L83 (1981).

5. Matthews, H.E., Irvine, W.M., Friberg, P., Brown, R.D. and Godfrey, P.D., Nature, **310** 125-126 (1984).

6. See for example: Miller, S.L. and Orgel, L.E. "The Origins of Life on the Earth". (Prentice-Hall, 1974).

7. Brown, R.D. Godfrey,P.D., Storey, J.W.V., Bassez, M.P., Robinson, B.J., Batchelor, R.A., McCulloch, M.G., Rydbeck, O.E.H. and Hjalmasson, A.G., MNRAS, **186**, 5P-8P (1979).

8. Hollis, J.M. Snyder, L.E. Suenram, R.D. and Lovas, F.J. Ap. J, **241**, 1001-1006, (1980).

9. Drake, F.D., Cohen, C., Brown, R.D., et al, unpublished.

https://doi.org/10.1017/S0074180900146431 Published online by Cambridge University Press

10. Godfrey, P.D., Brown, R.D., Storey, J.W.V. & Robinson, B.J., unpublished.

11. This volume, p. 185-197.

12. Anders, E., Hajatsu, R. and Studier, M.J., Science, **182**, 781-790 (1973).

13. Hartman, W.K., Astrophys. & Space Sci., **17**, 48-64 (1972).

14. Akabori, S., Science (Japan), **25**, 54 (1955); Akabori, S., Okama, K and Sato, M., Bull. chem. Soc. Japan, **29**, 608 (1956); **30**, 937 (1957).

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