

Critique of Fischer-Tropsch type reactions in the solar nebula

S. Ramadurai*, F. Hoyle[†] and N. C. Wickramasinghe[†]

*Astrophysics Group, Tata Institute of Fundamental Research, Bombay 400 005

[†]School of Mathematics, University of Wales College, Cardiff CF2 4AG, UK

Abstract. The paucity of kinetic data for the operation of FTT reactions, at the appropriate conditions for the primitive solar nebula, is highlighted. The observed isotopic abundances of D, ¹³C and ¹⁵N in the meteoritic kerogen are summarised. These are shown to be against the operation of FTT reactions in the primitive solar nebula.

Key words : solar system—meteor

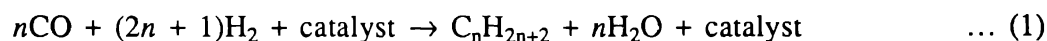
1. Introduction

There are several recent investigations, which have amassed evidences for injection of precursors of biological materials (see Greenberg *et al.* 1992; Oro *et al.* 1992). Further, early analysis of the Murchison Meteorite, a C2 carbonaceous chondrite that fell in Australia in 1969, established with certainty the presence of extra-terrestrial amino acids in the meteorite (Kvenvolden *et al.* 1970, 1971). Since amino acids are important biological constituents, the linking of extraterrestrial life with the origin of these amino acids would have been a natural corollary. But the desire to understand the emergence of biology on the Earth as resulting from physico-chemical processes occurring on simple precursors, using a variety of energy sources under primitive earth or Solar nebula conditions, resulted in several experimental investigations (see for a summary Cronin *et al.* 1988). These include electric discharge systems (Miller *et al.* 1976) and Fischer-Tropsch Type (FTT) reactions (Hayatsu & Anders 1981). While both these sets of experiments and similar experiments by other groups yielded a number of amino acids, it was not possible to reproduce the actual meteoritic distribution ratios of these amino acids. No amount of aqueous alterations can result in the observed (Cronin & Pizzarello 1986) distributions. The mere fact that Fischer-Tropsch type reactions yield amino acids is often quoted as evidence of FTT reactions in the primitive Earth as being responsible for the origin of life on our planet. Here, difficulties associated with this process are discussed in a systematic manner to show the dubious nature of this hypothesis. Further, the observations of isotopic abundances of H, C and N are brought in to support our arguments against FTT reactions initiating the life-process on the Earth.

2. FTT processes and primitive solar nebula

The conditions in the early solar nebula do not seem to be conducive to the operation of FTT processes, with any reasonable efficiency. The basic astronomical problem is that in a cooling solar nebula the thermodynamic balance favours CO at high temperatures, and this strongly bound molecule is inevitably the first to form, effectively mopping up the available C. As the nebula cools below 750K the thermodynamic balance swings from CO to CH₄. However, normally the conversion of CO to CH₄ will not occur to any significant extent, in view of the strong binding of CO. It is at this point that catalytic processes have to be invoked.

The basic experimental data, on which any case can be made, relate to the production of hydrocarbons by reactions of the general type :



The laboratory experiments are usually carried out at high pressures with carefully chosen catalytic surfaces.

The most commonly cited laboratory experiment in an astrophysical context is the one by Lancet & Anders (1970). The experiment described by these authors is said to have been carried out with an equimolar mixture of CO and H₂ at a temperature of 400K and total pressure of 1 atmosphere, using a cobalt catalyst. After the experiment is allowed to run for 320 hr, a significant conversion of CO to CH₄, (87.9%), is claimed together with a formation of waxy material to the extent of 1.5%.

The molecules that are synthesised in any FTT scheme and the yields that are actually obtained must depend sensitively on the effectiveness of the catalytic surfaces that are employed. Lancet & Anders (1970) state that the principal meteoritic mineral phases, stable above 350-400K (e.g., olivine, pyroxene, FeS), are not found to be effective catalysts for this reaction. Furthermore, crushed carbonaceous chondritic material, that has actually been tried out as a potential catalyst, has also been found ineffective. On the other hand, it is claimed that some mineral phases that are stable below 400K, e.g., magnetite, have been found to be suitable catalysts.

Considerable uncertainties are involved in extrapolating the limited kinetic data available for surface catalysed reactions such as (1) to conditions appropriate to the early solar nebula. Firstly it should be noted that no laboratory data has been obtained for a gaseous composition that resembles, even in broad outline, the molecular composition of the solar nebula at 800K. In particular no data is available for a mixture containing H₂, H₂O, and CO with an excess of H₂O over CO as would be expected to occur. The presence of H₂O might be expected to affect the kinetics of reduction reactions in an unfavourable way.

As noted already, the only laboratory data available at the present time relate to experimental systems with equal concentrations of CO and H₂ and with a total pressure of 1 atmosphere. The early solar nebula conditions, on the other hand, give a CO/H₂ ratio of 6.5×10^{-4} and a total pressure of 10^{-15} atm. Extrapolations to obtain a characteristic conversion time from CO to CH₄ have been made using a rate equation given by

$$\text{Rate} \approx (p_{\text{CO}}) \cdot (p_{\text{H}_2})^{-1/2} \exp\left(-\frac{Q}{kT}\right) \quad \dots (2)$$

where p_{CO} , p_{H_2} are respectively the partial pressures of CO and H₂, T is the temperature and Q is the adsorption activation energy for the catalyst. With $Q = 27$ kcal/mol, for a cobalt catalyst, and $T = 360\text{K}$ in the solar nebula, Hayatsu and Anders (1981) extrapolate their laboratory data to derive a characteristic time for CH₄ conversion as

$$t = 3.4 \times 10^5 \text{ yr.} \quad \dots (3)$$

While Hayatsu & Anders (1981) regard the timescale (3) as a generous overestimate for the total conversion, Lewis & Prinn (1980) have argued from the same data for only a small conversion, 1% of CO to CH₄.

However, even if one accepts the timescale (3) for CH₄, the rates for the formation of higher hydrocarbons with index n would be considerably slower, varying with the CO partial pressure as $(p_{\text{CO}})^n$ rather than p_{CO} . Accordingly we find that appropriate conversion times would begin to exceed the age of the solar system for $n > 2$. Thus, even with the most optimistic extrapolations of the available kinetic data, yields of the more complex organic compounds would not be expected in more than a minuscule quantity in the early solar nebula. In this connection we note that recent discussions concerning extraterrestrial synthesis and thermodynamic calculations have put into proper perspective the highly sensitive nature of the amino acid yields to various assumptions about the relevant thermodynamic data that have to be extrapolated from laboratory conditions (Miller & Bada 1991; Shock & Schulte 1991).

Yet another problem for FTT synthesis is the inevitable tendency of catalysts in the solar nebula to become poisoned. Although it is true that a diversity of types of catalytic surfaces might be initially available, the condensation of even a couple of monolayers of non-volatile hydrocarbons and sulphur onto these surfaces would lead to an effective cessation of the catalytic process. Such surface condensation is bound to occur at the low values of $T = 360\text{K}$ postulated by Hayatsu & Anders (1981), if the FTT process gets started at all. Thus the FTT processes invoked here would be instantly self-defeating.

The preceding considerations would appear to fit well with the wartime experience of German chemical engineers, and it fits the difficulties which have been experienced with synthetic oil projects in recent years. It also fits the simple fact of the existence of methane-producing bacteria. If there were any easy way to reduce CO to CH₄ inorganically, even at terrestrial atmospheric pressure, let alone at solar nebular pressures, there would be no niche, in a Darwinian sense, for such bacteria. Such niches would seem to exist widely in the solar system, and in our view the CH₄ that is actually observed in the outer planets and on several satellites of the giant planets must be biogenic rather than products of FTT syntheses.

3. Isotopic evidences

The most decisive evidence against the actual operation of FTT reactions in the solar nebula has come from studies of the distribution of C, N and H isotopes in the kerogen-like material of several carbonaceous chondrites (Yang & Epstein 1982; Kerridge 1983). In most non-isotopic respects this material is said to be closely similar to biogenically derived terrestrial kerogen.

The meteoritic kerogen shows significant depletions of ¹³C relative to ¹²C and large enhancements of D relative to H, compared as usual with inorganic terrestrial standards.

The isotopic release patterns obtained in stepwise pyrolysis and discussed by Kerridge (1983) show evidence for at least three isotopically distinct sets of H, C, N atoms being involved in the composition of meteoritic kerogen. According to Kerridge, this observation

“clearly rules out an origin for the insoluble organics as the residue following operation, on a homogeneous nebular gas, or a synthesis such as Fischer-Tropsch or Miller-Urey, which are known to produce superficially similar waxy material. A mixture of such materials produced in more than one synthesis, involving different starting materials and/or different conditions is not ruled out, but laboratory simulations of the above processes have shown that they are characterised by isotopic fractionations which are significantly smaller for C and very much smaller for N than those reported here.”

It is well known that biological systems are able to produce fractionation of isotopes to varying degrees and in a variety of ways. Biology as a whole is known to concentrate ^{12}C relative to ^{13}C . The average ^{13}C value in terrestrial fossil kerogen is found to be -3.3% . The ^{13}C value of meteoritic kerogens appears to be somewhat variable ranging from -1.7% in Murray and Orguel to -3% in Carraweena and Bondoc (Yang & Epstein 1982; Kerridge 1983). The average meteoritic value of ^{13}C is therefore not significantly different from the corresponding value for the carbon in the terrestrial biosphere. It should be noted however that considerably higher isotopic fractionations than average may be effected by particular types of microorganisms. Thus Rosenfeld & Silverman (1959) have shown an 8% enrichment of ^{12}C in the methane exuded by an anaerobic bacterium during the fermentation of methanol. The organism itself will be expected to concentrate the corresponding excess of ^{13}C within its cellular structure.

The situation for the abundance of D is different, however. In the meteoritic organic matter D is found to be enhanced relative to H with a D/H ratio increased above the normal terrestrial value by a factor in the range 2-10 (Yang & Epstein 1982; Kerridge 1983). The large excesses are strikingly similar to the excess of D that have actually been found in interstellar molecules. Large fractionations of D relative to H are thought to arise in ion-molecule reactions in the interstellar medium. The meteoritic data permit the inference to be drawn that the meteoritic kerogen is derived directly from interstellar grains, in which case interstellar grains must be largely kerogenic in character. Because interstellar grains make up a large fraction of total mass of the galaxy, an efficient non-biologic formation of kerogen or kerogen-like grain material would then present a serious problem. On the other hand, it is entirely possible that comets did acquire an initial excess of D relative to the normal solar D/H ratio by accumulation of small inorganic interstellar molecules containing an excess of deuterium.

Although terrestrial biology as a whole does not produce concentrations of D relative to H, certain abundantly occurring bacterial species are known to do so. For example Cloud *et al.* (1958) and Sisler (1959) discovered that a certain type of commonly occurring marine bacterium produced H_2 gas that was depleted in D by as much as a factor of 20 relative to the D/H ratio in ocean water. In consequence, according to Cloud *et al.* (1958) ‘in as much as the gas is depleted in D, the D is presumably concentrated within the interstitial water, the residual nutrients or the bacteria’. The dominance of these or similar types of deuterium fractionating microorganisms in the cometary precursors of meteorites remains a distinct possibility at the present time.

4. Conclusions

Admitting the possibility that initial isotopic ratios on meteorite parent bodies may in any case have been slightly different from the terrestrial or solar reference values that are usually adopted, there would seem to be little difficulty in accepting a microbial origin of meteoritic organic matter. What seems to be decisively ruled out by the isotope data is that meteoritic organics were synthesised on a large scale in the solar nebula by FTT reactions from a standard solar mix of isotopes, a mix that could not have been significantly different from the usual terrestrial standards of reference. Similar conclusions have been reached by considering the $^{15}\text{N}/^{14}\text{N}$ ratios in the amino acid fraction of the Murchison meteorite (Epstein *et al.* 1987), as also by the analysis of ^{13}C enrichment seen in the L-enantiomer of Alanine, one of the amino acids involved (Engel *et al.* 1990).

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