CATALYTIC REACTIONS IN THE SOLAR NEBULA:

IMPLICATIONS FOR INTERSTELLAR MOLECULES

AND ORGANIC COMPOUNDS IN METEORITES*

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Abstract. Organic compounds in meteorites seem to have formed by Fischer-Tropsch-type, catalytic reactions of CO, H_2, and NH_3 in the solar nebula, at 360–400 K and $(4–10) \times 10^{-6}$ atm. The onset of these reactions was triggered by the formation of catalytically active grains of magnetite and serpentine at these temperatures.

Laboratory experiments show that the Fischer-Tropsch reaction gives a large kinetic *isotope fractionation* of C^{12}/C^{13}, duplicating the hitherto unexplained fractionation in meteorites. All of the principal compound classes in meteorites are produced by this reaction, or a variant involving a brief excursion to higher temperatures. (1) normal, mono-, and dimethyl*alkanes*; (2) *arenes* and *alkylarenes*; (3) dimeric *isoprenoids* from C_9 to C_{14}; (4) *purines* and *pyrimidines*, such as adenine, guanine, uracil, thymine, xanthine, etc.; (5) *amino acids*, including tyrosine and histidine; (6) *porphyrin*-like pigments; (7) aromatic *polymer* with –OH and –COOH groups.

These reactions may also have played a major role in the evolution of life: first, by converting carbon to a sufficiently non-volatile form to permit its accretion by the inner planets; second, by synthesizing organic compounds on the primitive planets whenever CO, H_2, NH_3, and clay or magnetite particles came together at the right temperature. Similar reactions in other solar nebulae may be the source of interstellar molecules, as first suggested by G. H. Herbig. Ten of the twelve polyatomic interstellar molecules have in fact been seen in these syntheses or in meteorites.

1. Introduction

It is generally agreed that type 1 carbonaceous chondrites (C1) are a primitive condensate from the solar nebula, only a step or two away from solar composition (Anders, 1971a; Cameron, 1973). Thus it seems surprising that they contain a rich variety of complex organic compounds. Let us examine the behavior of carbon in the solar nebula, and see what compounds are produced in the primary condensation process. We can then decide what additional processes must be invoked to produce the observed array of compounds in meteorites.

Only a brief summary of the evidence can be given here. The reader is referred to more detailed reviews on the origin of meteorites (Anders, 1971b, 1972), organic compounds in meteorites (Anders *et al.*, 1973; Oró, 1972; Hayes, 1967; Vdovykin, 1967), and to the experimental papers cited in the text.

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2. Formation Conditions of Carbonaceous Chondrites

Three 'cosmothermometers', based on equilibrium or kinetic isotope fractionations of O and C, consistently give formation temperatures near 360 K for Cl chondrites (Anders *et al.*, 1973). This is the temperature at which isotopic fractionations were frozen in, owing to sluggish reaction rates or physical isolation of the meteoritic dust by accretion to larger bodies.

The pressure has been estimated as $\simeq 4 \times 10^{-6}$ atm, from the Ar^{36} content of meteoritic magnetite (Lancet and Anders, 1973). This value is tentative, but happens to be close to Cameron and Pine's (1973) theoretical estimate of 8×10^{-6} atm at 360 K, for their model of the solar nebula.

3. Behavior of Carbon in a Solar Gas

With the physical conditions thus defined, it is instructive to consider what happens to carbon in a cooling solar gas (Figure 1). CO is the stable form at high tempera-
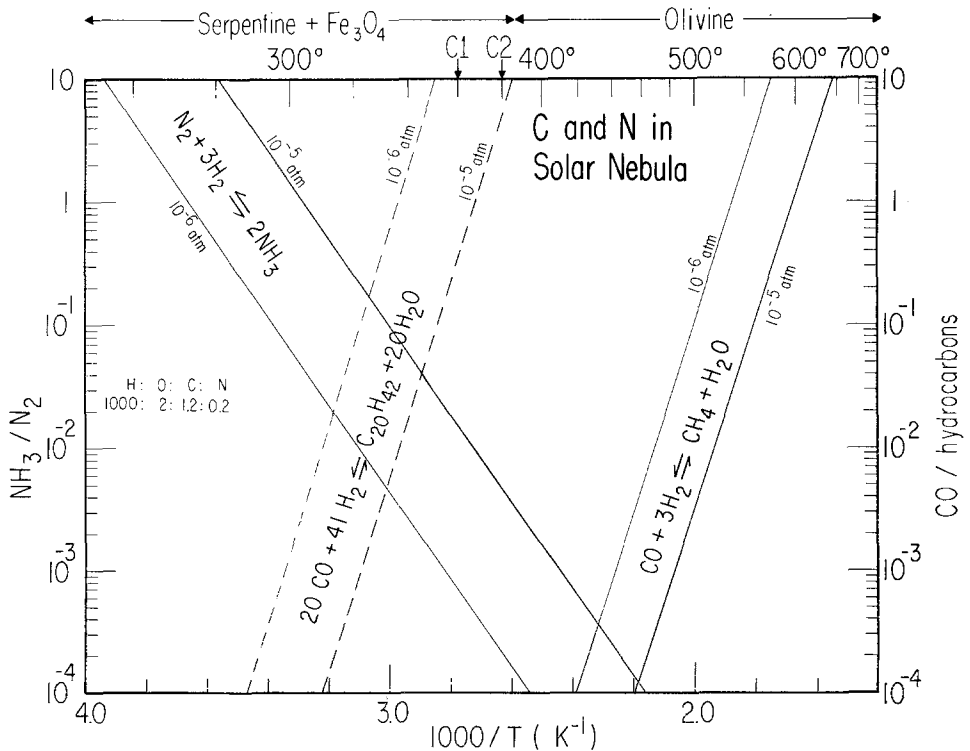

Fig. 1. If equilibrium is maintained on cooling, CO will be converted largely to CH₄ (solid lines) before metastable formation of more complex hydrocarbons by the Fischer-Tropsch reaction becomes possible (dashed lines). However, the reaction is very slow in the absence of catalysts, and may not have begun until ~ 400 K when catalysts such as serpentine and magnetite became available through the hydration of olivine.

tures, but becomes less stable on cooling and should transform to CH_4 below 600 K, as shown by the solid lines in the right-hand portion of Figure 1. However, CH_4 has a condensation temperature of less than 100 K, and if this reaction had gone as written, there should be no carbon and no life anywhere in the inner solar system. Thus events must have taken a different course.

Urey (1953) first noted this paradox in a classic paper. He suggested that the hydrogenation of CO may not have gone smoothly to CH_4 in the absence of man-made catalysts, but stopped at 'complex tarry carbon compounds', representing intermediate stages of hydrogenation. Such compounds, typified by $C_{20}H_{42}$ in Figure 1, are less stable than methane, but could form metastably below $\simeq 400$ K.

4. Model Experiments:

The Fischer-Tropsch Synthesis

Urey's idea soon fell into oblivion, because of the phenomenal success of the Miller-Urey synthesis. We began to investigate this neglected idea in 1964, when it first became apparent that Miller-Urey reactions could not account for certain features of meteorite organic matter. Our approach was to see how CO and H_2 behaved in the presence of some *natural* catalysts expected in the solar nebula: nickel-iron, magnetite, hydrated silicates. We found (Studier *et al.*, 1965a, 1968) that the reaction indeed tends to stop at intermediate stages of hydrogenation, giving metastable products of $H/C \approx 2$ (e.g. $C_{20}H_{42}$) rather than stable methane of $H/C = 4$. In fact, this process (the Fischer-Tropsch synthesis, discovered in 1923) has been used industrially for the production of gasoline.

It is not feasible to conduct such model experiments at the pressure and H_2/CO ratio of the solar nebula – the total amount of carbon in a 1-liter vessel would be only $\simeq 5 \times 10^{-9}$ g. Accordingly, we used higher pressures (0.1–10 atm), and lower H_2/CO ratios (generally 1, sometimes as high as 120). We shall show later on that these results are nonetheless applicable to the solar nebula.

As a safeguard against contamination, we used deuterium rather than light hydrogen in our syntheses, and identified reaction products by mass spectrometry. In general, products were separated by gas chromatography or other techniques prior to mass spectrometry.

The reaction was always carried out under static conditions in a closed vessel, not in a flow system as in the industrial synthesis. We also broadened the range of experimental conditions beyond those of the classical Fischer-Tropsch synthesis. Reaction times ranged from a fraction of an hour to a few months, and the temperature was sometimes raised briefly from 150–250 to 500–700 °C. Such thermal pulses were intended to simulate short-term heating events in the nebula, such as collisions, shock waves, or the chondrule-forming process. In runs where nitrogen compounds were sought we added ND_3 to the reactant gases, and occasionally used other types of catalysts, such as montmorillonite clay, Al_2O_3, or SiO_2. For want of a better term, we shall call this class of reactions 'Fischer-Tropsch' Type (= FTT).

5. Comparison of Meteoritic and Synthetic Organic Compounds

5.1. HEAVY ALKANES

The same few compounds dominate in meteoritic and FT hydrocarbons (Studier et al., 1968, 1972; Nooner and Oró, 1967; Gelpi and Oró, 1970a). Normal alkanes are most prominent, followed by five slightly branched isomers (2Me, 3Me, 2,3DiMe, 3,4DiMe, and 4,5DiMe). This resemblance gains significance if one considers that some 10^5 structural isomers can exist for alkanes with 16C atoms. Terrestrial hydrocarbons show a similar pattern, and so contamination must be considered. However, this seems to be unlikely at least for the meteorites analyzed by Studier et al. (1968, 1972), for reasons given by Anders et al. (1973).

It seems that the meteoritic hydrocarbons were made by FT reactions, or a process of the same extraordinary selectivity. The Miller-Urey reaction, incidentally, shows no such selectivity. Gas chromatograms of spark discharge hydrocarbons show no structure (Calvin, 1969). Apparently all 10^5 possible isomers are made in comparable yield, as expected for random recombination of free radicals.

5.2. CARBON ISOTOPE FRACTIONATIONS

Meteorites show a very large difference in C^{12}/C^{13} ratio between carbonate and organic carbon: 60 to 80 permil (Clayton, 1963; Smith and Kaplan, 1970). This trend remained unexplained for a number of years, because coexisting carbonate and organic matter on Earth shows a much smaller difference, typically 25–30 permil. It probably is a primary feature, unaffected by the later thermal history of the meteorite. Terrestrial calcium carbonate is not known to equilibrate with coexisting organic matter in sediments (Smith and Kaplan, 1970).

It turns out that the Fischer-Tropsch reaction gives an isotopic fractionation of just the right sign and magnitude, owing to a kinetic isotopic effect (Lancet and Anders, 1970). From the temperature dependence of the fractionation between 375 and 550 K, the observed fractionations in C1 and C2 chondrites correspond to about 360 and 400 K (Lancet, 1972). These values agree rather well with the O^{18}-based formation temperatures of carbonates and silicates, 360 K for C1's and 380 K for C2's (Onuma et al., 1972). The Miller-Urey reaction gives a fractionation of only -0.4 ± 0.2 permil (Lancet, 1972).

5.3. AROMATIC HYDROCARBONS; LIGHT ALKANES

Carbonaceous chondrites contain a wide range of aromatic hydrocarbons, from benzene through alkylbenzenes and -naphthalenes to polynuclear hydrocarbons of up to six fused benzene rings (see the reviews cited above). At higher carbon numbers, aromatics tend to be less abundant than normal alkanes, but below about C_{11}, the reverse is true (Studier et al., 1965b, 1968, 1972). In fact, virtually no normal alkanes at all are found between C_2 and C_8, their place having been taken largely by benzene, toluene, xylene, and various alkenes or branched alkanes.

A pattern of this sort does not form directly in the primary Fischer-Tropsch reac-

tion. It does, however, develop when a primary Fischer-Tropsch mixture remains in contact with the catalyst, for a day or so at 350–400 °C, or longer times at lower temperatures (Studier *et al.*, 1968, 1972). Under such conditions, a metastable equilibrium is approached, with methane and aromatic hydrocarbons forming at the expense of ethane and heavier alkanes (Dayhoff *et al.*, 1964). The kinetics and mechanism of such aromatization on the catalyst surface has been discussed by Galwey (1968, 1972). When the heating is prolonged or carried out at higher temperatures, polynuclear aromatics with up to 7 rings are obtained (Studier *et al.*, 1965a, 1968; Oró and Han, 1966). Opportunities for such secondary reactions certainly existed in the history of meteorites, and rates seem to be adequate even at 360 K (Anders *et al.*, 1973).

5.4. ISOPRENOID ALKANES

Tri- and tetrameric isoprenoids from C_{14} to C_{21} were found in carbonaceous chondrites by Gelpi and Oró (1970a) but not by Studier *et al.* (1968, 1972). The latter workers found only some dimeric isoprenoids (C_9–C_{11}, C_{13}), and the current consensus seems to be that the heavier isoprenoids were terrestrial contaminants (Gelpi and Oró, 1970b; Gelpi *et al.*, 1970; Oró, 1972; Studier *et al.*, 1972).

The lighter isoprenoids C_9 to C_{14} can be produced in the FT synthesis. Contamination was precluded by use of deuterium (see Studier *et al.*, 1968, for mass spectra).

5.5. FATTY ACIDS

Nagy and Bitz (1963) reported fatty acids from C_{14} to C_{28} in Orgueil. This work was substantially confirmed by Hayatsu (1965) and Smith and Kaplan (1970). The latter authors found 3 to 91 ppm fatty acids from C_{12} to C_{20} in 7 carbonaceous chondrites. Smith and Kaplan believe that these acids are largely or entirely terrestrial contaminants, because unstable unsaturated acids comprise about 30% of the total, and $C_{16} + C_{18}$ acids are predominant. No attempts have yet been made to look for fatty acids in the model experiments described here, but it is well known that they can be produced in the Fischer-Tropsch and related syntheses (Storch *et al.*, 1951).

5.6. PURINES, PYRIMIDINES, AND OTHER NITROGEN BASES

Several nitrogen heterocyclics (underlined in Figure 2) have been found in the Orgueil meteorite (Hayatsu, 1964; Hayatsu *et al.*, 1968). All these compounds and several others (Figure 2) are made in an FTT reaction in the presence of NH_3 (Hayatsu *et al.*, 1968, 1972). Pyrroles and nitriles were also observed.

A somewhat different set of N-heterocyclic compounds, including 4-hydroxy-pyrimidines but no biological heterocyclics, was reported by Folsome *et al.* (1973) in three carbonaceous chondrites. However, this discrepancy seems to reflect problems of technique. With suitable extraction methods, biological heterocyclics such as adenine and guanine are readily identified (see Figure 6 of Anders *et al.*, 1973).

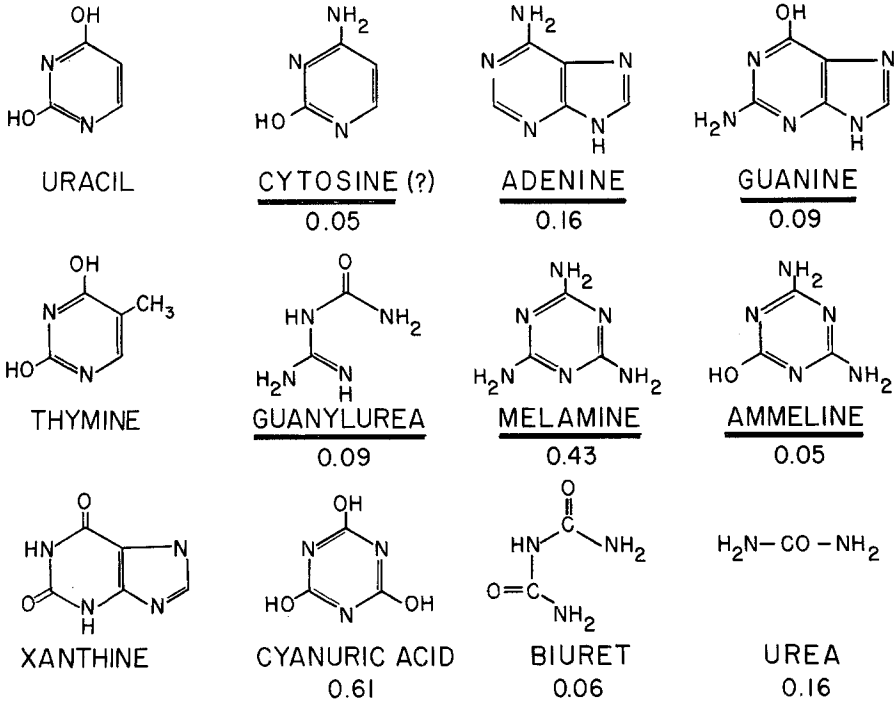## Nucleotide Bases Made by Fischer-Tropsch-Type Synthesis

| URACIL | CYTOSINE (?) 0.05 | ADENINE 0.16 | GUANINE 0.09 |

| THYMINE | GUANYLUREA 0.09 | MELAMINE 0.43 | AMMELINE 0.05 |

| XANTHINE | CYANURIC ACID 0.61 | BIURET 0.06 | UREA 0.16 |

Fig. 2.   Underlined compounds have been identified in meteorites. Numbers indicate yields in percent
(Hayatsu *et al.*, 1968, 1972).

5.7. AMINO ACIDS

Kvenvolden *et al.* (1970, 1971) have shown that the Murchison meteorite contains
at least 17 indigenous amino acids, or compounds hydrolyzable thereto. Ten of these
are not commonly found in terrestrial proteins. These findings were substantially
confirmed by Oró *et al.* (1971) and Cronin and Moore (1971).

Many of the same amino acids, plus several others (Table I) are produced in FTT
syntheses involving a brief initial heating to 500–700 °C (Yoshino *et al.*, 1971; Hayatsu
et al., 1971). Yields are low (0.01–0.1%), but the products include structurally complex
aromatic or heterocyclic amino acids such as tyrosine and histidine that cannot be
made by conventional Miller-Urey syntheses. Regrettably, this work was completed
before the meteorite analyses became available, and so the non-protein amino acids
were not systematically looked for. Some were tentatively identified when seen in
large amounts; others may have comprised the up to 6 unidentified compounds that
were observed in most of these syntheses.

A directed search for these amino acids in the Miller-Urey synthesis has been
largely successful, yielding all those seen in Murchison (Ring *et al.*, 1972; Wolman
et al., 1972). Interestingly, the proportions of amino acids in the synthesis agree to

TABLE I

Amino acids in meteorites and the modified
Fischer-Tropsch synthesis

($\times \times$ = definite; $\times$ = tentative; $\bigcirc$ = not sought)

	Meteorites (Kvenvolden et al., 1970, 1971)	FTT Synthesis (Yoshino et al., 1971; Hayatsu et al., 1971)
Glycine	$\times \times$	$\times \times$
Alanine	$\times \times$	$\times \times$
Valine	$\times \times$	$\times$
Leucine		$\times$
Isoleucine		$\times$
Aspartic Acid	$\times \times$	$\times \times$
Glutamic Acid	$\times \times$	$\times \times$
Tyrosine		$\times \times$
Proline	$\times \times$	$\times$
Ornithine		$\times \times$
Lysine		$\times \times$
Histidine		$\times \times$
Arginine		$\times \times$
N-methylglycine	$\times \times$	$\times \times$
N-ethylglycine	$\times \times$	$\bigcirc$
β-alanine	$\times \times$	$\times \times$
N-methylalanine	$\times \times$	$\bigcirc$
Isovaline	$\times \times$	$\bigcirc$
Norvaline	$\times \times$	$\bigcirc$
α-aminoisobutyric Acid	$\times \times$	$\times$
α-amino-n-butyric Acid	$\times \times$	$\times$
β-aminoisobutyric Acid	$\times \times$	$\times$
β-amino-n-butyric Acid	$\times \times$	$\bigcirc$
γ-aminobutyric Acid	$\times \times$	$\times$
Pipecolic Acid	$\times \times$	$\bigcirc$

within 1–2 orders of magnitude with those in the meteorite. To the extent that such a comparison can be made from the more limited data for the FTT synthesis, the agreement is of the same order.

5.8. PORPHYRINS

Hodgson and Baker (1969) have detected pigments resembling porphyrins in several carbonaceous chondrites. It is not clear whether these were true (= cyclic) porphyrins or linear pyrrole polymers, which mimic porphyrins in many respects. Both kinds have been seen in FTT syntheses (Hayatsu *et al.*, 1972). One pigment whose cyclic nature was confirmed by mass spectrometry had a major peak at mass 580, as expected for an alkyl-substituted porphin $C_{20}D_{14}N_4 + 16CD_2$ (Anders *et al.*, 1973). Though it did not show a doubly-charged ion at mass 290, it displayed other charac-

teristics of porphyrins: strong absorption at 394 nm (in the Soret band range), formation of a red copper complex, and chromatographic and solvent extraction behavior similar to that of porphyrins (Hayatsu *et al.*, 1972).

Porphyrin-like pigments of similar properties have been made by the Miller-Urey synthesis (Hodgson and Ponnamperuma, 1969), but their cyclic nature has not yet been verified by mass spectrometry.

5.9. CHLORO AND THIO COMPOUNDS

Mono- and dichlorobenzenes have been found in several carbonaceous chondrites (Studier *et al.*, 1968, 1972), but in view of the widespread human use of such compounds, it is not at all certain that they are indigenous. Benzothiophenes, first reported by Hayes and Biemann (1968) in pyrolysis experiments, have also been seen in room-temperature solvent extracts (Studier *et al.*, 1972) and hence must be original constituents of the meteorites, not thermal degradation products. It is not known whether these compounds can be made in FTT syntheses, because the necessary experiments have not yet been attempted.

5.10. MACROMOLECULAR MATERIAL

At least 70% of the organic matter in meteorites consists of an ill-defined, insoluble solid, said to resemble humic acids in soils (Briggs and Mamikunian, 1963). It has an aromatic skeleton bearing functional groups such as –COOH and –OH (Bitz and Nagy, 1966; Hayes, 1967). A similar material was obtained in an FTT synthesis extended over 6 months. The mass spectra of the meteoritic and synthetic polymer are similar (Anders *et al.*, 1973), and show mainly benzene, naphthalene, and their alkyl derivatives, as well as alkylindanes, fluorene, anthracene/phenanthrene, alkenes, alkanes, and alkylphenols (Hayatsu *et al.*, manuscript in preparation).

A Miller-Urey reaction in the presence of H_2S (Khare and Sagan, 1973) also gave a polymer, but of aliphatic rather than aromatic structure.
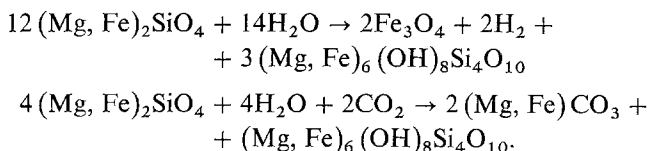
6. Relevance to the Solar Nebula

It appears that FTT reactions can account reasonably well for all features of organic matter in meteorites. The only alternative process, the Miller-Urey synthesis, fails to account for the *n* and *iso*alkanes, arenes, isoprenoids, most *N*-heterocyclics, the polymer, and carbon isotope fractionations, though it remains a possible and perhaps superior source of amino acids.

However, it is not immediately obvious that the FTT model experiments are relevant to the solar nebula. First and foremost, it must be shown that CO was still present at the time the nebula had cooled to 360 K. How did CO traverse the no-man's land between 600 K where it becomes unstable with respect to CH_4, and ~ 400 K where formation of heavy hydrocarbons first becomes thermodynamically feasible (Figure 1)? Second, was the reaction rate fast enough at the extremely low pressures in the nebula?

6.1. Survival of CO

An answer to the first question was suggested by Lancet and Anders (1970), and is shown at the top of Figure 1. The high-temperature meteoritic phases stable above $\simeq 350$–$400\,K$ (olivine, pyroxene, Fe, FeS) are not effective catalysts for the Fischer-Tropsch reaction, while the low-temperature phases forming below $\simeq 400\,K$ (hydrated silicates, magnetite) are. (Though metallic iron is often regarded as a catalyst for this synthesis, the catalytically active phase actually is a thin coating of Fe_3O_4 formed on the surface of the metal; Anderson, 1956). Laboratory data show that catalysis by the high-temperature phases is slower by at least a factor of 10^8. Thus CO may have survived metastably between 600 and $\simeq 400\,K$ until catalysts became available by reactions such as:

$$12\,(Mg, Fe)_2SiO_4 + 14H_2O \rightarrow 2Fe_3O_4 + 2H_2 + \\ + 3\,(Mg, Fe)_6\,(OH)_8Si_4O_{10}$$

$$4\,(Mg, Fe)_2SiO_4 + 4H_2O + 2CO_2 \rightarrow 2\,(Mg, Fe)\,CO_3 + \\ + (Mg, Fe)_6\,(OH)_8Si_4O_{10}.$$

This would also explain why the hydrated silicates, carbonates, and organic compounds all have the same formation temperature of $360\,K$.

6.2. Rate of reaction in the nebula

The second question cannot be answered unequivocally because the kinetics of the Fischer-Tropsch reaction are not well enough understood to permit reliable extrapolations to very low pressures. Still, a tentative analysis of available rate data suggests that the reaction half-time may be no greater than a few centuries, even at 4×10^{-6} atm (Lancet, 1972; see Anders *et al.*, 1973 for a summary).

7. Interstellar Molecules

It seems that FTT reactions in solar nebulae may also be responsible for interstellar molecules, as first suggested by Herbig (1970). Main sequence stars show a marked discontinuity of rotation rates at $1.5\,M_\odot$, suggestive of angular momentum transfer to extrastellar material. Thus solar nebulae may be a common byproduct of star formation. Such nebulae, embedded in interstellar clouds, provide a high-density environment ($\sim 10^{15}$ molecules cm^{-3}) in which matter can be transformed to grains and molecules which are then returned to the interstellar cloud when the nebula is dissipated. The denser parts of such clouds are well-shielded from UV radiation, and may serve as a long-term source of interstellar molecules.

In our own solar system, nearly all volatiles complementary to the inner planets ($3 \times 10^{-3}\,M_\odot$) were so lost. Earth and Venus contain only about 10^{-4} their complement of C, and even lesser amounts of H_2O, N, and noble gases. Because the retained C appears to show the imprint of the Fischer-Tropsch reaction, it seems likely that the lost C, too, had been involved in this process. Of the 12 known interstellar mole-

cules with 3 or more atoms, at least 10 are found in meteorites or in FTT syntheses (Anders, 1973): H_2O, HCHO, CH_3OH, HCOOH, HCN, $HC\equiv CCN$, HNOC, $CH_3C\equiv CH$, CH_3CN, and COS. This is not a compelling argument in favor of the MFT synthesis, because these structurally simple molecules can also be made by the Miller-Urey synthesis (Sagan, 1973). A choice may become possible when more complex molecules are discovered in interstellar space.

Acknowledgements

References

Anders, E.: 1971a, *Geochim. Cosmochim. Acta* **35**, 516.
Anders, E.: 1971b, *Ann. Rev. Astron. Astrophys.* **9**, 1.
Anders, E.: 1972, in H. Reeves (ed.), *L'Origine du Système Solaire*, CNRS, Paris, 179.
Anders, E.: 1973, in M. A. Gordon and L. Snyder (eds.), *Molecules in the Galactic Environment*, John Wiley and Sons, New York, 429.
Anders, E., Hayatsu, R., and Studier, M. H.: 1973, *Science* **182**, 721.
Anderson, R. B.: 1956, in P. H. Emmett (ed.), *Catalysis. IV: Hydrocarbon Synthesis, Hydrogenation and Cyclization*, Reinhold, New York, p. 29.
Bitz, M. C. and Nagy, B.: 1966, *Proc. Nat. Acad. Sci.* **56**, 1383.
Briggs, M. H. and Mamikunian, G.: 1963, *Space Sci. Rev.* **1**, 647.
Calvin, M.: 1969, *Chemical Evolution*, Clarendon, Oxford, Chapters 4–6.
Cameron, A. G. W.: 1973, in D. N. Schramm and W. D. Arnett (eds.), *Explosive Nucleosynthesis*, Univ. of Texas Press, Austin, p. 3.
Cameron, A. G. W. and Pine, M. R.: 1973, *Icarus* **18**, 377.
Clayton, R. N.: 1963, *Science* **140**, 192.
Cronin, J. R. and Moore, C. B.: 1971, *Science* **172**, 1327.
Dayhoff, M. O., Lippincott, E. R., and Eck, R. V.: 1964, *Science* **146**, 1461.
Emmett, P. H. (ed.): 1956, *Catalysis. IV: Hydrocarbon Synthesis, Hydrogenation and Cyclization*, Reinhold, New York.
Folsome, C. E., Lawless, J. G., Romiez, M., and Ponnamperuma, C.: 1973, *Geochim. Cosmochim. Acta* **37**, 455.
Galwey, A.: 1968, *J. Catalysis* **12**, 352.
Galwey, A.: 1972, *Geochim. Cosmochim. Acta* **36**, 1115.
Gelpi, E. and Oró, J.: 1970a, *Geochim. Cosmochim. Acta* **34**, 981.
Gelpi, E. and Oró, J.: 1970b, *Geochim. Cosmochim. Acta* **34**, 995.
Gelpi, E., Nooner, D. W., and Oró, J.; 1970, *Geochim. Cosmochim. Acta* **34**, 421.
Hayatsu, R.: 1964, *Science* **146**, 1291.
Hayatsu, R.: 1965, *Science* **149**, 443.
Hayatsu, R., Studier, M. H., Oda, A., Fuse, K., and Anders, E.: 1968, *Geochim. Cosmochim. Acta* **32**, 175.
Hayatsu, R., Studier, M. H., and Anders, E.: 1971, *Geochim. Cosmochim. Acta* **35**, 939.
Hayatsu, R., Studier, M. H., Matsuoka, S., and Anders, E.: 1972, *Geochim. Cosmochim. Acta* **36**, 555.
Hayes, J. M.: 1967, *Geochim. Cosmochim. Acta* **31**, 1395.
Hayes, J. M. and Biemann, K.: 1968, *Geochim. Cosmochim. Acta* **32**, 239.
Herbig, G. H.: 1970, *Mém. Soc. Roy. Sci. Liège* **XIX**, 13.
Hodgson, G. W. and Ponnamperuma, C.: 1968, *Proc. Nat. Acad. Sci.* **59**, 22.
Hodgson, G. W. and Baker, B. L.: 1969, *Geochim. Cosmochim. Acta* **33**, 943.
Khare, B. N. and Sagan, C.: 1973, *Icarus*, in press.

Kvenvolden, K., Lawless, J., Pering, K., Peterson, E., Flores, J., Ponnamperuma, C., Kaplan, I. R., and Moore, C.: 1970, *Nature* **228**, 923.

Kvenvolden, K., Lawless, J., and Ponnamperuma, C.: 1971, *Proc. Nat. Acad. Sci.* **68**, 486.

Lancet, M. S.: 1972, Ph. D. thesis, University of Chicago.

Lancet, M. S. and Anders, E.: 1970, *Science* **170**, 980.

Lancet, M. S. and Anders, E.: 1973, *Geochim. Cosmochim. Acta* **37**, 1371.

Nagy, B. and Bitz, M. C.: 1963, *Arch. Biochem. Biophys.* **101**, 240.

Nooner, D. W. and Oró, J.: 1967, *Geochim. Cosmochim, Acta* **31**, 1359.

Onuma, N., Clayton, R. N., and Mayeda, T. K.: 1972, *Geochim. Cosmochim. Acta* **36**, 169.

Oró, J.: 1972, *Space Life Sci.* **3**, 507.

Oró, J. and Han, J.: 1966, *Science* **153**, 1393.

Oró, J., Gibert, J., Lichtenstein, H., Wikstrom, S., and Flory, D. A.: 1971, *Nature* **230**, 105.

Ring, D., Wolman, Y., Friedmann, N., and Miller, S. L.: 1972, *Proc. Nat. Acad. Sci.* **69**, 765.

Sagan, C.: 1973, in M. A. Gordon and L. Snyder (eds.), *Molecules in the Galactic Environment*, John Wiley, New York, p. 451.

Smith, J. W. and Kaplan, I. R.: 1970, *Science* **167**, 1367.

Storch, H. H., Golumbic, N., and Anderson, R. B.: 1951, in *The Fischer-Tropsch and Related Syntheses*, John Wiley and Sons, New York, p. 9.

Studier, M. H., Hayatsu, R., and Anders, E.: 1965a, Enrico Fermi Institute preprint No. 65-115.

Studier, M. H., Hayatsu, R., and Anders, E.: 1965b, *Science* **149**, 1455.

Studier, M. H., Hayatsu, R., and Anders, E.: 1968, *Geochim. Cosmochim. Acta* **32**, 151.

Studier, M. H., Hayatsu, R., and Anders, E.: 1972, *Geochim. Cosmochim. Acta* **36**, 189.

Urey, H. C.: 1953, in *XIIIth Intern. Congr. Pure Applied Chem.* (Plenary Lectures), IUPAC, London, 188.

Vdovykin, G. P.: 1967, *Carbonaceous Matter of Meteorites (Organic Compounds, Diamonds, Graphite)*, Nauka Publishing Office, Moscow. English Translation NASA TT F-582.

Wolman, Y., Haverland, W. J., and Miller, S. L.: 1972, *Proc. Nat. Acad. Sci.* **69**, 809.

Yoshino, D., Hayatsu, R. and Anders, E.: 1971, *Geochim. Cosmochim. Acta* **35**, 972.