LIPID FORMATION BY AQUEOUS FISCHER-TROPSCH-TYPE SYNTHESIS OVER A TEMPERATURE RANGE OF 100 TO 400 °C

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Abstract. The formation of lipid compounds during an aqueous Fischer-Tropsch-type reaction was studied with solutions of oxalic acid as the carbon and hydrogen source. The reactions were conducted in stainless steel vessels by heating the oxalic acid solution at discrete temperatures from 100 to 400 °C, at intervals of 50 °C for two days each. The maximum lipid yield, especially for oxygenated compounds, is in the window of 150–250 °C. At a temperature of 100 °C only a trace amount of lipids was detected. At temperatures above 150 °C the lipid components ranged from C_{12} to $>C_{33}$ and included *n*-alkanols, *n*-alkanoic acids, *n*-alkyl formates, *n*-alkanals, *n*-alkanones, *n*-alkanes, and *n*-alkenes, all with essentially no carbon number preference. The *n*-alkanes increased in concentration over the oxygenated compounds at temperatures of 200 °C and above, with a slight reduction in their carbon number ranges due to cracking. It was also noted that the *n*-alkanoic acids increased while *n*-alkanols decreased with increasing temperature above 200 °C. At temperatures above 300 °C synthesis competes with cracking and reforming reactions. At 400 °C significant cracking was observed and polynuclear aromatic hydrocarbons and their alkylated homologs were detected. The results of this work suggest that the formation of lipid compounds by aqueous FTT reactions proceeds by insertion of a CO group at the terminal end of a carboxylic acid functionality to form *n*-oxoalkanoic acids, followed by reduction to *n*-alkanoic acids, to *n*-alkanals, then to *n*-alkanols. The *n*-alkenes are intermediate homologs for *n*-alkan-2-ones and *n*-alkanes. This proposed mechanism for aqueous FTT synthesis differs from the surface-catalyzed stepwise FT process (i.e., gaseous) of polymerization of methylene reported in the literature.

Keywords: aqueous Fischer-Tropsch-type synthesis, lipids, *n*-alkanols, *n*-alkanoic acids, *n*-alkyl formates, oxalic acid

1. Introduction

It has been proposed that hydrothermal systems on Earth provided an appropriate setting for the abiotic formation and accumulation of organic matter on Earth (French, 1964; Corliss *et al.*, 1981; Holm, 1992), thus providing organic compound precursors for the evolution of life (Ferris, 1992; Shock, 1990; Holm, 1992). The formation of these organic compounds may proceed by Fischer-Tropsch-type (FTT) reactions, which is a well known process in industry to produce hydrocarbons and oxy compounds from carbon monoxide and carbon dioxide (Fischer, 1935; Kugler and Steffgen, 1979; Anderson, 1984; Satterfield *et al.*, 1986a, b). The FTT reaction has drawn the attention of geologists as a potential source of abiotic

hydrocarbons and other organic compounds in various geological settings such as volcanoes, meteorites, marine hydrothermal systems, gas seeps from ophiolites, saline groundwaters associated with crystalline rocks, fluid inclusions and crack surfaces in igneous rocks, and even processes on other planetary bodies in the solar system (Abrajano *et al.*, 1988; Charlou and Donval, 1993; Ferris, 1992; Gelpi *et al.*, 1970; Gold and Soter, 1982; Markhinin and Podkletnov, 1977; Markhinin, 1980; Mathez, 1987; McCollom *et al.*, 1999; Nooner and Oró, 1979; Salvi and William-Jones, 1997; Sherwood Lollar *et al.*, 1993; Shock, 1990; Simoneit *et al.*, 1988; Studier *et al.*, 1968; Sugisaki and Mimura, 1994; Szatmari, 1989; Tingle and Hochella, 1993; Welhan and Lupton, 1987; Welhan, 1988).

The FTT reaction under geological conditions is suggested to proceed by the reduction of CO_2 with H_2 in thermal fluids in presence of H_2O and ferrous ion from iron minerals (Berndt *et al.*, 1996), which leads some researchers to believe that the FTT reaction could proceed in an aquatic environment. Thus, further studies are needed to test the FTT reaction in the presence of water, since a contradictory argument against the FTT reaction under hydrous conditions was that it likely could be inhibited by H_2O and H_2S (Miller and Bada, 1988). A recent study showed that the FTT reaction does proceed under aqueous conditions (McCollom *et al.*, 1999).

The purpose of this work is to further study the hydrous FTT reaction over an extended temperature range in order to determine: (1) the formation of abiotic lipids from an aqueous carbon and hydrogen source (e.g., oxalic acid); (2) the optimum temperature for the formation of homologous lipid compounds; (3) the functional group compositions of the lipids (i.e., production of alkanols, alkanoic acids); (4) the production versus alteration (cracking) of lipid products; and (5) the yields obtained at various temperatures.

2. Experimental Methods

In order to avoid the difficulties and hazards of adding gaseous CO, CO_2 and H_2 into reaction vessels operating at high temperature and pressure, we have used both oxalic and formic acids in the Fischer-Tropsch-type aqueous experiments as surrogate sources of these gases (McCollom *et al.*, 1999). At higher temperatures (>150 °C) oxalic acid disproportionates to a mixture of CO_2, CO, H_2, and water (Elliot *et al.*, 1993; Crossey, 1991; Morgan *et al.*, 1992; Palmer *et al.*, 1993). Oxalic acid dihydrate decomposes rapidly (< a couple of hours) in the crystalline state at temperatures of 230–300 °C according to the reaction (Morgan *et al.*, 1992):

$$C_2H_2O_4 \cdot 2H_2O \rightarrow 1.18CO_2 + 0.82CO + 0.18H_2 + 2.82H_2O . \tag{1}$$
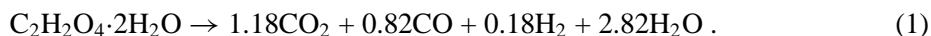
Aqueous oxalic acid ($C_2H_2O_4$) also degrades at 160–230 °C to formic acid (CH_2O_2) and CO_2 and the reaction rate proceeds with first order kinetics (Crossey, 1991):

$$C_2H_2O_4 \rightarrow CH_2O_2 + CO_2 . \tag{2}$$
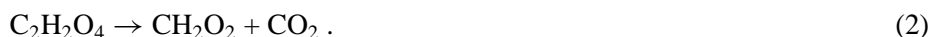
The decomposition of formic acid in the presence of excess water and at high temperatures proceeds according to reactions (Palmer *et al.*, 1993):

$$CH_2O_2 \rightarrow H_2 + CO_2 \tag{3}$$

$$CH_2O_2 \rightarrow CO + H_2O . \tag{4}$$

Formic acid, which has been identified in many geological fluids, may form as an intermediate in the 'water-gas shift reaction' (Martens, 1990; Horvath and Sisken, 1991; Giggenbach, 1997) according to reaction:

$$H_2 + CO_2 \leftrightarrow CH_2O_2 \leftrightarrow H_2O + CO . \tag{5}$$

The experimental conditions of this work were similar to those of French (1964, 1971), Morgan *et al.* (1992), and McCollom *et al.* (1999). The reactions were carried out with preextracted oxalic acid dihydrate (>99.5%, *EM Science*) in stainless steel vessels (13.3 mL internal capacity), where 6.01±0.01 g of oxalic acid dihydrate, and 9.14±0.09 mL water (doubly-distilled H_2O, *Burdick and Jackson*) were mixed. The reaction vessel, which is shown in Figure 1, was equipped with capillary tubes attached to valves at both ends to allow sampling and venting the headspace gas at the end of each experiment. After placing the oxalic acid solution into the vessel, the headspace gas was displaced by heating at about 100 °C for 1 min, then the vessel was tightly sealed and heated in an oven at the selected temperature (100–400 °C) for two days. Following heating, each reaction vessel was cooled with ice to below room temperature. After cooling, the gas was vented and trapped in a graduated cylinder and the volume measured. The organic products were extracted with dichloromethane/methanol (3:1 v/v) and sometimes with only dichloromethane. The extracts were concentrated by nitrogen (99.9% purity, with molecular sieve contaminant trap) blow down at room temperature.

Analyses of the total extracts were performed by gas chromatography-mass spectrometry (GC-MS). Identification of compounds bearing carboxylic acid or alkanol functionalities was facilitated by derivatizing (silylating) aliquots of the extract with *N,O-bis(trimethylsilyl)trifluoroacetamide* (BSTFA). This derivatizing agent replaces the H in hydroxyl groups with a trimethylsilyl [$(CH_3)_3$Si, i.e., TMS] group. The GC-MS analyses were performed on a Hewlett-Packard 6890 GC coupled to a 5973 Mass Selective Detector using a DB-5 (*J and W* Scientific) fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The GC was temperature programmed from 65 °C (2 min initial time) to 300 °C at 6 °C min^{-1} (isothermal for 20 min final time). The MS was operated in the electron impact mode at 70 eV in source energy. Data were acquired and processed with a Hewlett-Packard Chemstation. Identification of selected homologous compounds was facilitated by comparison of GC retention times and mass spectra with authentic standards.
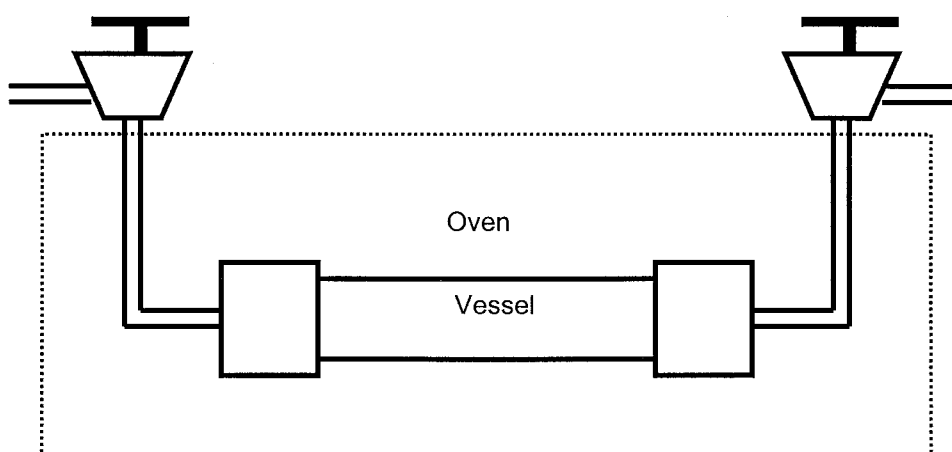
Figure 1. The reaction vessel used in this experiment.

The lipid yield was calculated by use of the following formula:

$$\left[\frac{C_{st} A_{c,s} V_{ex} / V_s A_{st} V_{st}}{C_{ox}} \right] \times 100$$

where C = concentration in g g^{-1}, A = the total integrated signal (area), V = volume in μL, and the subscripts ex = total extract, st = quantitation standard, c = corrected, s = sample, and ox = oxalic acid.

3. Results and Discussion

The percent yield of the total products obtained by the FTT reaction is illustrated in Figure 2, and shows an increase from 0.01% at 100 °C to a maximum value (5.3%) at 200 °C followed by a decrease with increasing temperature above 200 °C. The optimum temperature window for the formation of organic compounds by FTT synthesis is between 150 and 250 °C, and higher temperature reduce the yield due to competing cracking processes (Figure 2). The products from aqueous FTT reactions at temperatures >150 °C are dominated by the formation of homologous series of straight chain (normal) alkanols, alkanoic acids, alkylformates, alkanals, alkan-2-ones, alkanes, alkenes, methylalkanes and phenylalkanes as shown in Figure 3 and Table I.

The mass spectra and elution order of these homologous compound series need brief clarification. Typical examples of mass spectra are shown in Figure 4. The *n*-alkanols and *n*-alkanoic acids are analyzed as the trimethylsilyl (TMS) derivatives and the alkanol derivatives elute after the alkanoic acid derivatives (Figure 3b). The mass spectra of the *n*-alkanoic acid TMS esters exhibit a weak molecular ion (M$^{\cdot+}$), base peak at M-CH$_3$ and key ions at m/z 73, 75, 117, and 129 (e.g., Figure 4a). The

TABLE I

The principal products and their carbon number ranges from aqueous Fischer-Tropsch-type (FTT) reactions at different temperatures for two days

Compound	Temperature (°C)						
	100	150	200	250	300	350	400
n-Alkanols							
Range	T	8–30	8–32	8–31	n.d.	n.d.	n.d.
C_{max}	11	10	8	8	–	–	–
Relative concentration (μg 100 μg^{-1} extract)	–	9	24	20	–	–	–
CPI	–	1.03	0.88	0.92	–	–	–
n-Alkanoic acids							
Range	7–9	7–22	7–13	7–16	7–18	7–13	7–18
C_{max}	7	7	9	7	7	7	8
Relative concentration (μg 100 μg^{-1} extract)	–	7	7	8	20	6	4
CPI	–	0.98	1.14	1.15	1.05	1.07	0.95
Alkyl formates							
Range	T	9–27	9–26	9–10	n.d.	n.d.	T
C_{max}	–	15	15	10	–	–	–
Relative cncentration (μg 100 μg^{-1} extract)	–	4	9	1	–	–	–
CPI	–	1.05	1.14	–	–	–	–
n-Alkanals							
Range	T	10–20	10–19	13–22	n.d.	n.d.	n.d.
C_{max}	–	12	13	12	–	–	–
Relative concentration (μg 100 μg^{-1} extract)	–	3	4	1	–	–	–
CPI	–	1.00	1.00	1.02	–	–	–
n-Alkan-2-ones							
Range	–	10–30	10–11	n.d.	n.d.	n.d.	n.d.
C_{max}	–	18	10	–	–	–	–
Relative concentration (μg 100 μg^{-1} extract)	–	9	1	–	–	–	–
CPI	–	0.98	0.72	–	–	–	–

TABLE I

(continued)

Compound	Temperature (°C)						
	100	150	200	250	300	350	400
n-Alkanes							
Range	T	12–36	12–35	12–35	12–34	12–34	12–35
C_{max}	15	15	12	12	13	14	17
Relative concentration (μg 100 μg^{-1} extract)	–	5	17	58	72	38	24
CPI	–	1.04	1.09	0.99	0.94	0.94	1.02
n-Alkenes							
Range	T	12–24	12–20	12–15	n.d.	n.d.	n.d.
C_{max}	–	15	13	12	–	–	–
Relative concentration (μg 100 μg^{-1} extract)	1	4	11	1	–	–	–
CPI	–	1.2	0.92	–	–	–	–
Methylalkanes							
Range	n.d.	n.d.	n.d.	13–19	13–31	13–33	13–15
C_{max}	–	–	–	14,15	15	14	14
Relative concentration (μg 100 μg^{-1} extract)	–	–	–	8	8	29	21
Phenylalkanes							
Range	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16–18
C_{max}	–	–	–	–	–	–	18
Relative concentration (μg 100 μg^{-1} extract)	–	–	–	–	–	–	18
% Yield	0.007	0.19	5.33	0.96	0.80	0.43	0.24
UCM (μg 100 μg^{-1} extract)	–	73	37	5	0	27	33
U/R	–	2.10	0.53	0.06	0.00	0.35	0.52

n.d. = Not detectable; T = Traces; CPI= Carbon Preference Index = [= $\Sigma(C_{13} + C_{15} + C_{17} + C_{19} + C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31})/\Sigma(C_{12} + C_{14} + C_{16} + C_{18} + C_{20} + C_{22} + C_{24} + C_{26} + C_{28} + C_{30})$ for *n*-alkanes; $\Sigma(C_{13} + C_{15} + C_{17} + C_{19} + C_{21})/\Sigma(C_{12} + C_{14} + C_{16} + C_{18} + C_{20})$ for *n*-alkenes; $\Sigma(C_9 + C_{11} + C_{13} + C_{15} + C_{17} + C_{19})/\Sigma(C_{10} + C_{12} + C_{14} + C_{16} + C_{18} + C_{20})$ for alkyl-formates; $\Sigma(C_9 + C_{11} + C_{13} + C_{15} + C_{17} + C_{19})/\Sigma(C_{10} + C_{12} + C_{12} + C_{14} + C_{16} + C_{18} + C_{20})$ for *n*-alkanals; $\Sigma(C_7 + C_9 + C_{11})/\Sigma(C_8 + C_{10} + C_{12})$ for *n*-alkanoic acids; $\Sigma(C_9 + C_{11} + C_{13} + C_{15} + C_{17} + C_{19} + C_{21} + C_{23})/\Sigma(C_8 + C_{10} + C_{12} + C_{14} + C_{16} + C_{18} + C_{20} + C_{22})$ for *n*-alkanols]; and U/R ratio = Unresolved complex mixture/Resolved compounds.
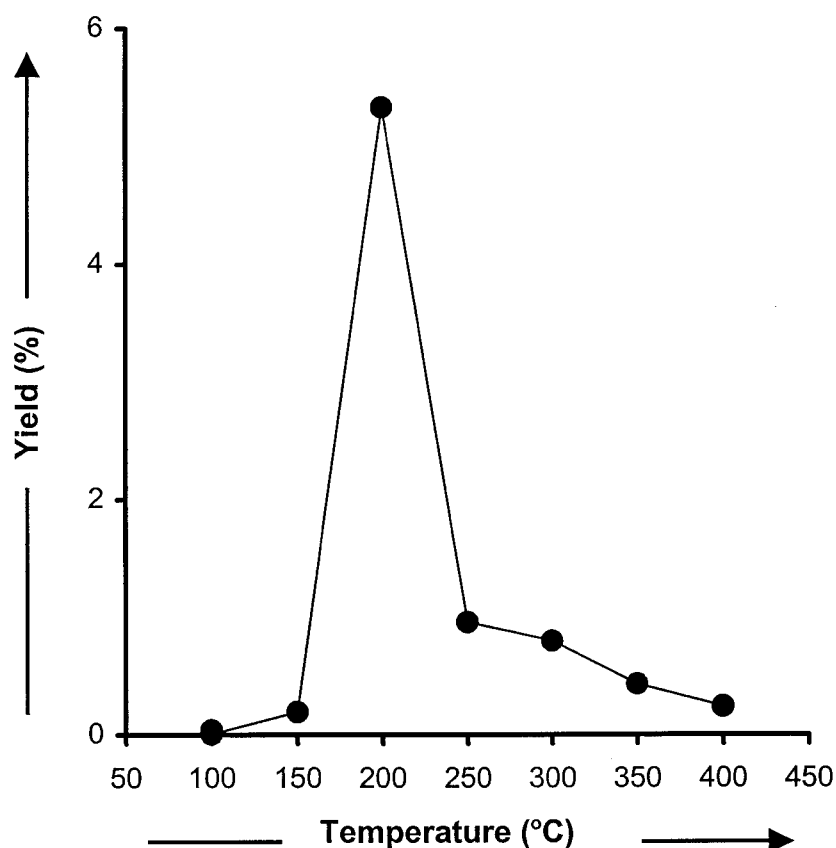
Figure 2. Weight-percent yield of FTT reaction products (based on oxalic acid supplied) versus temperature of the experiments.

series is determined from the m/z 117 fragmentogram. The mass spectra of the *n*-alkanol TMS ethers show no molecular ion, with a base peak at M-CH_3 and key ion at m/z 75 (e.g., Figure 4b). The homologs are determined from the m/z 75 fragmentogram and the M-15 ion series.

The dominant peaks in the underivatized extract are *n*-alk-1-enes and their mass spectra exhibit a weak molecular ion, base peak at m/z 55 and key ion at m/z 83 (e.g., Figure 4c). The dominant fragmentation is the successive elimination of ethylene from $M^{\cdot+}$, yielding a series of even ions (e.g., m/z 238, 210, 182, 154 in the example shown). The *n*-alkanes are determined by the key ion data of m/z 85 or 99 and the corresponding molecular ions. The mass spectra of the *n*-alkan-2-ones are characterized by their molecular ions, with M-H_2O, and base peak (the key ion) of m/z 58 (at m/z 59 for long chain homologs $>C_{25}$) (e.g., Figure 4d). The mass spectra of the *n*-alkanals show a typical ion distribution of intense m/z 68, 82 and 96, a trace molecular ion and M-H_2O (e.g., Figure 4e). The key ion for the series is m/z 82. The mass spectra of the *n*-alkyl formates are similar to those
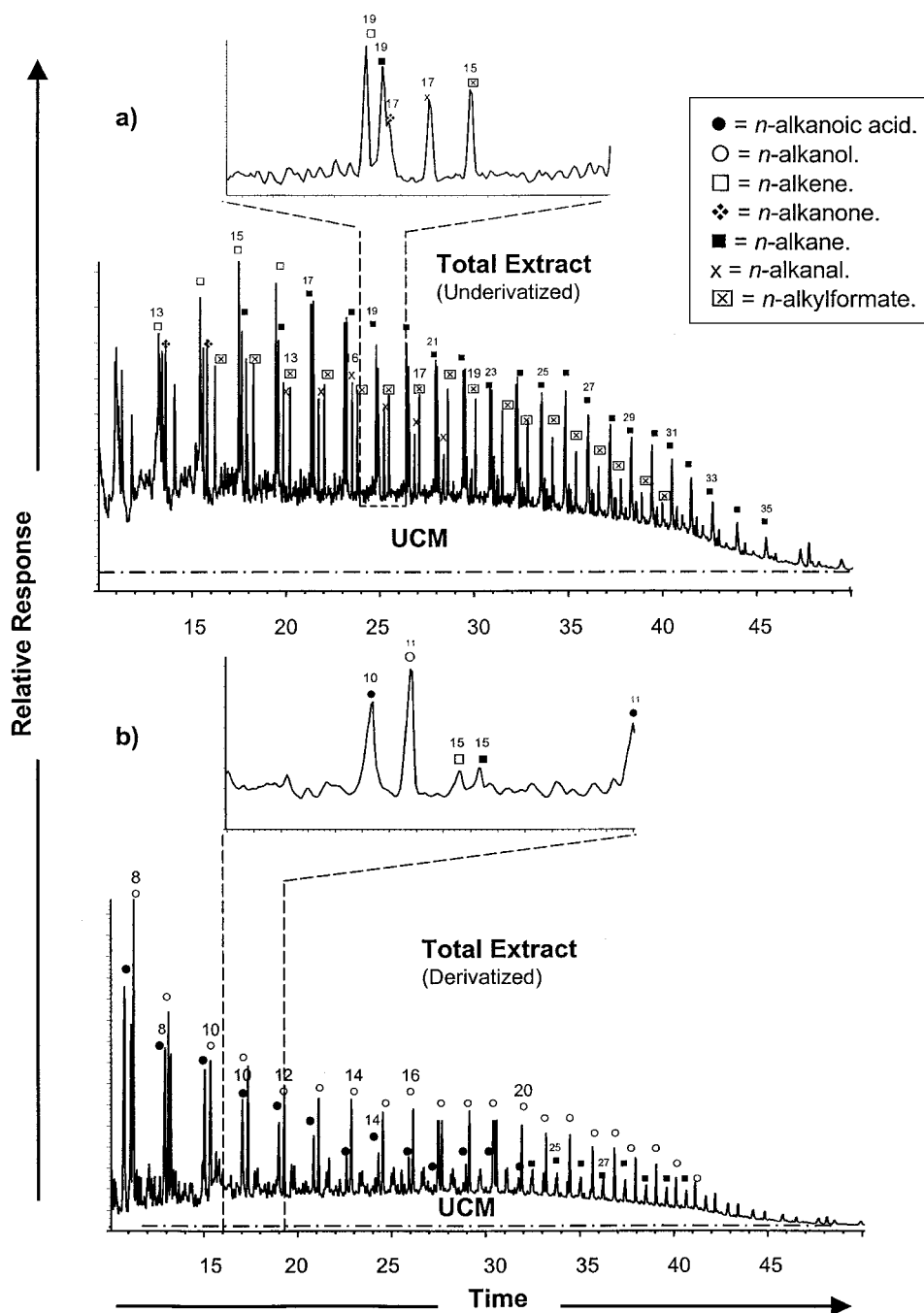
Figure 3. GC-MS total ion chromatograms for the CH_2Cl_2 extract of products from a FTT reaction experiment with an aqueous solution of oxalic acid at 150 °C: (a) total extract, and (b) silylated total extract (numbers refer to carbon chain length of homologs indicated by the key, UCM = unresolved complex mixture).
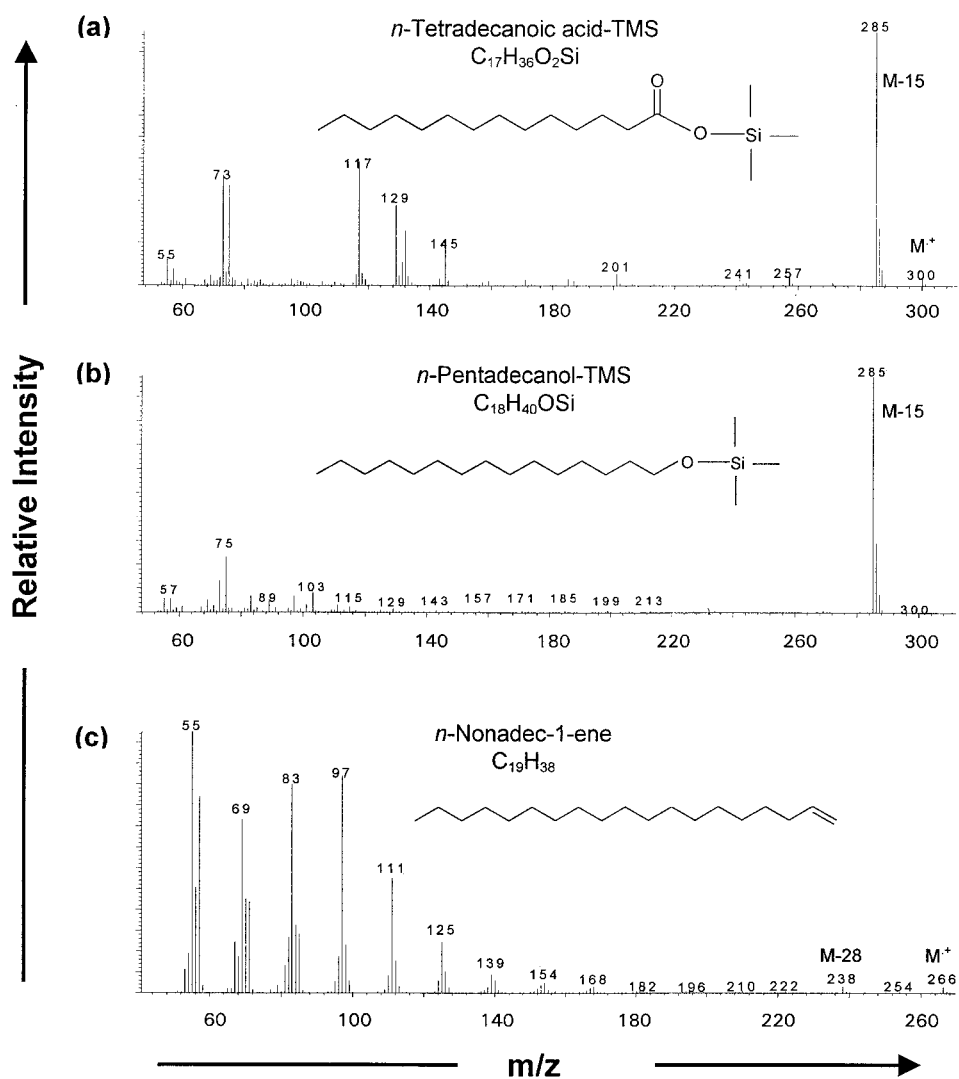
Figure 4. Examples of mass spectra for the dominant homologous compound series (the peaks clustered in the 24–26 min window of Figure 3 are plotted and the Kovats GC retention index is also given for each compound): (a) *n*-tetradecanoic acid-TMS ester (KI = 1852), (b) *n*-pentadecanol-TMS ether (KI = 1866), (c) *n*-nonadec-1-ene (KI = 1892, *n*-nonadecane KI = 1900), (d) *n*-heptadecan-2-one (KI = 1902), (e) *n*-heptadecanal (KI = 1918), and (f) *n*-tetradecyl formate (KI = 1935).
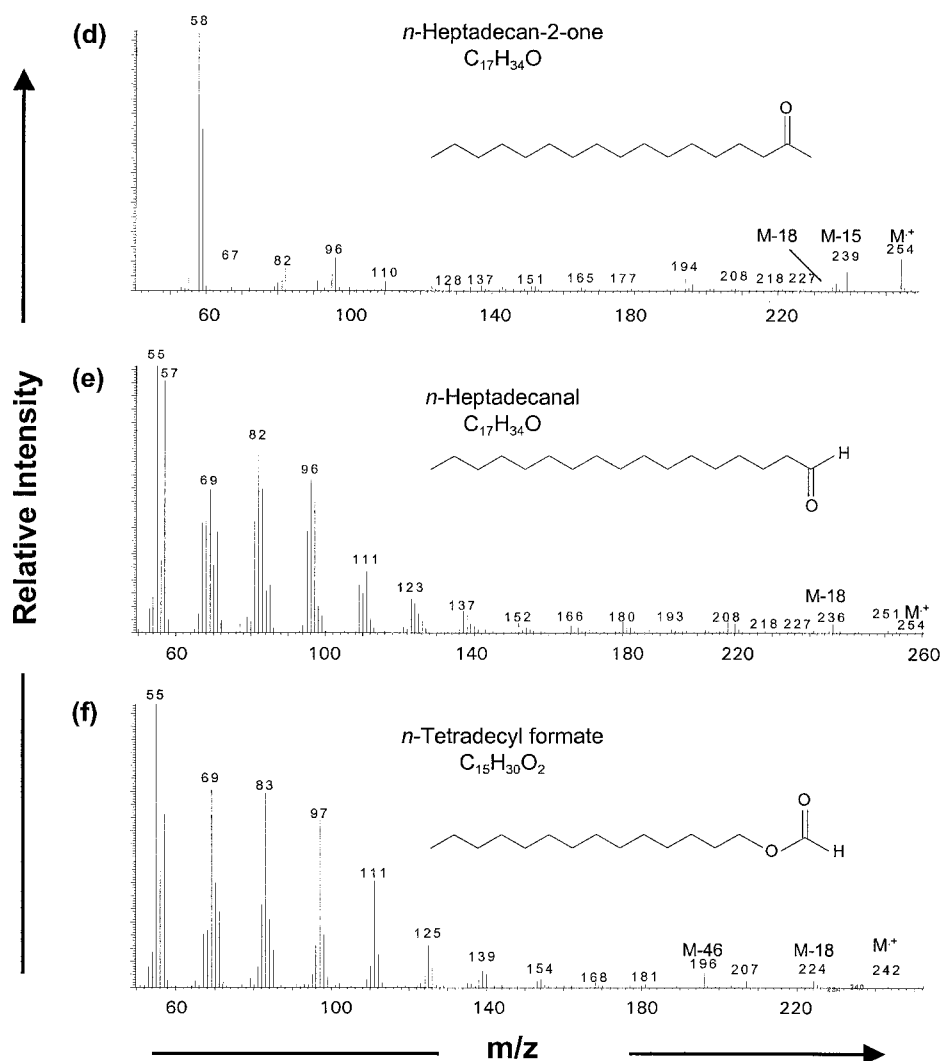
Figure 4. Continued.

of the *n*-alkenes. There is no molecular ion due to the facile elimination of formic acid (CH_2O_2) and H_2O (e.g., Figure 4f). The M-46 peak is equivalent to an olefin which further fragments by elimination of ethylene. The homologs are determined by the m/z 83 key ion, GC retention index, and M-18 and M-46 ion series.

The decrease in the relative response for underivatized polar compounds $<C_{12}$ is related to GC peak broadening at shorter retention times. The response factor for *n*-alkanols and *n*-alkanoic acids was greatly increased by silylation of the total extracts as illustrated in Figure 3. The underivatized *n*-alkanols have identical mass spectra as *n*-alkenes due to the elimination of H_2O from the molecular ion and are
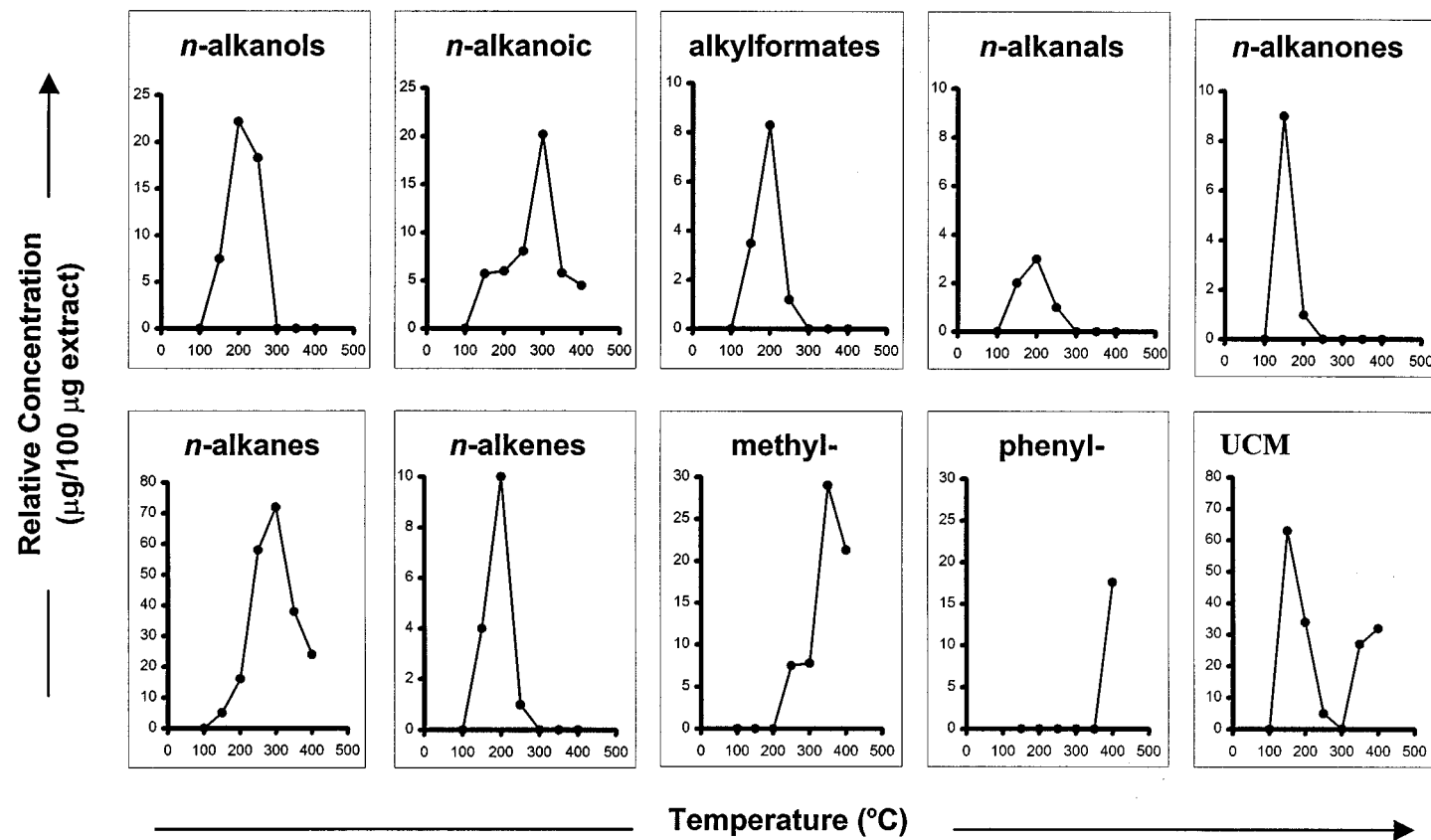
Figure 5. The relative concentrations of the various homologous compound series identified in the FTT synthesis experiments at temperatures from 100 to 400 °C.

thus part of the UCM. The same is the case for the free alkanoic acids. The n-alkanols are detectable to C_{32} in total derivatized extract mixtures, and have high concentrations from 150 to 250 °C but are not detectable at temperatures above 300 °C (Figure 5). Their carbon preference index (CPI) values range between 0.88 and 1.03 (Table I). The concentrations of the n-alkanoic acids reach a maximum for the 300 °C experiment (Figure 5). The n-alkanoic acids, which are detectable in experiments at all temperatures >150 °C, were resolved only to C_{22} and their CPI values range between 0.95 and 1.14 (Table I). Alkyl formates are present at temperatures of 150 to 250 °C with a maximum concentration at 200 °C and homologs ranging to C_{27}. The CPI values vary between 1.05 and 1.14. The n-alkanal series also detected at temperatures of 150 to 250 °C, with maximum concentration in the lower temperature window (150–200 °C, Figure 5), extends from C_{10} to C_{22}, with CPI values between 1.00 and 1.02 (Table I). n-Alkan-2-ones are found in significant amounts only at 150 °C, with traces at 200 °C (Table I and Figure 5). Their homologs range from C_{10} to C_{30}, with a CPI value of 0.98.

Homologous series of n-alkanes ranging to $>C_{37}$ are synthesized at all temperatures, and show no carbon number predominance (i.e., the CPI values range between 0.94 and 1.09). High temperatures of the experiment (>300 °C) dramatically decrease the relative concentration of the n-alkanes from the maximum yield due to competing cracking reactions (Figure 5). The temperature window for n-alkane formation is between 100 to >400 °C. The alkane and alkene homologs $<C_{17}$ are typically lost progressively according to their volatility during the experimental workup (Figure 5). The n-alkenes are detectable in the temperature window of 150 to 250 °C with a maximum concentration at 200 °C (Figure 5). They range to C_{24} and have CPI values between 0.92 and 1.2 (Table I).

Methylalkanes are identifiable at temperatures above 250 °C with a maximum concentration at 350 °C (Figure 5), whereas phenylalkanes (alkylbenzenes) are found only in the highest temperature experiment of 400 °C and range from C_{16} to C_{18} (Figure 5, Table I).

The concentration of the Unresolved Complex Mixture (UCM) of branched and cyclic compounds decreases with increase in temperature, then increases at temperatures above 300 °C (Figure 5 and Table I). The ratio of the Unresolved complex mixture-to-Resolved organic compounds (U/R) generally decreases from 2.10 at 150 °C to 0.00 at 300 °C and then increases slightly to 0.52 at 400 °C (i.e., Table I).

Polycyclic aromatic hydrocarbons (PAH), which were previously reported from gas phase FTT reactions (Nooner and Oró, 1979), are below the detection limit in the products of experiments <350 °C. However, PAH are detectable in the products of one experiment conducted at a temperature of 400 °C.

The carbon preference index of one (i.e., CPI ~ 1) for these lipid products indicates that the build up of these homologous series is by single carbon units. It also supports the interpretation that the oxalic acid is transformed to C_1 species (CH_2O_2, CO_2, CO) as expressed by equations (2) to (4) prior to chain buildup (Crossey,
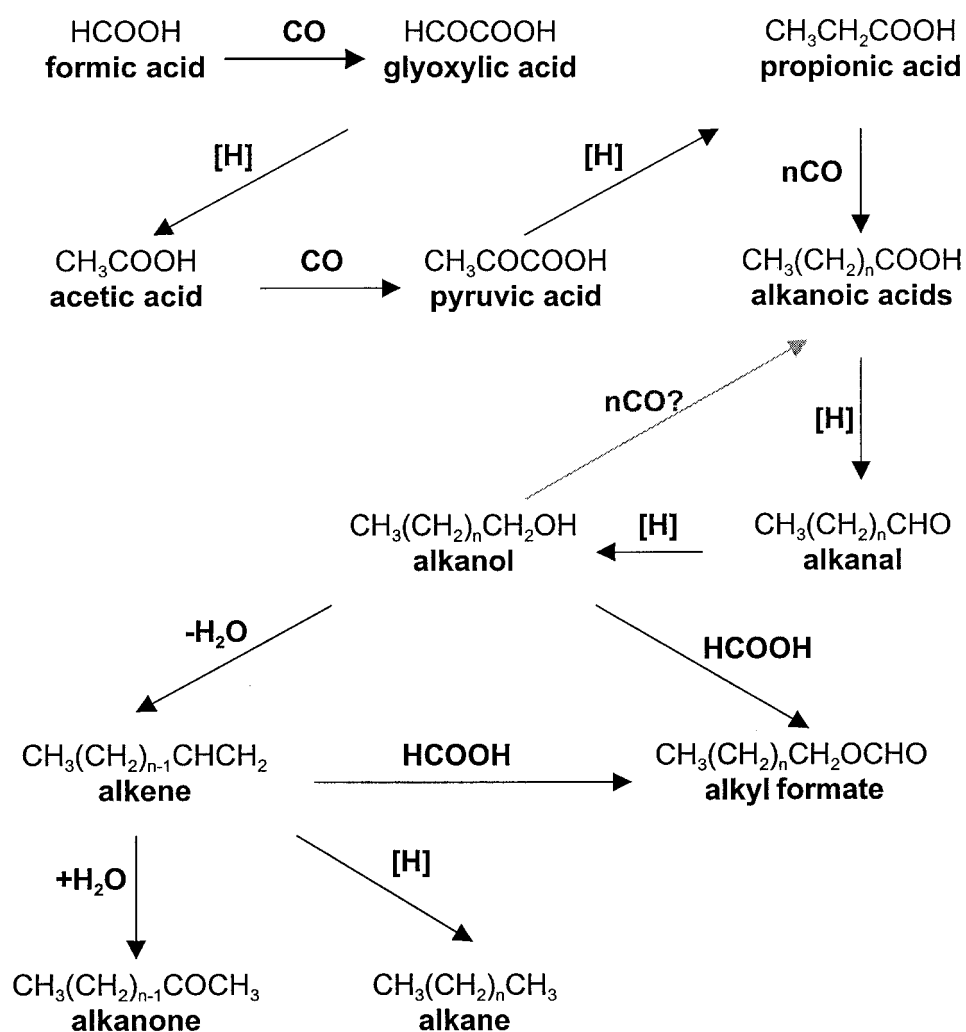
Figure 6. The possible reaction steps that lead to the formation of lipid compounds by aqueous FTT reaction.

1991). The n-alkanoic acids and n-alkanols are present in relatively higher amounts than alkanes below 300 °C. Above that temperature the n-alkanols are not detectable and n-alkanoic acids increase and then decrease. The presence of abundant acids and alcohols in addition to alkyl formates, alkanals, alkanones, alkanes and alkenes at temperatures <250 °C (Figure 3) suggests that chain growth proceeds under these aqueous FTT conditions by insertion of a CO group to the terminal end of an n-alkyl group (C_n) with a carboxylic acid functionality to form the primary acids after reduction, followed by further reduction to alkanals, then alkanols, and the alkenes forming as intermediates to alkanones and alkanes (Figure 6). Dehydration of the alcohols yields alkene isomers (Weres *et al.*, 1988; Leif and Simoneit,

1995), which is supported by their presence at temperatures <250 °C and their absence at >250 °C. At temperatures >300 °C full reduction of the alkenes with H_2 and reaction with CH_3 radicals produces *n*-alkanes and methylalkanes (Table I). This proposed mechanism of FTT lipid formation under aqueous conditions (Figure 6) differs from the gaseous process, which is proposed to proceed by the growth of the hydrocarbon chain as a result of a surface-catalyzed stepwise polymerization of methylene (Bardy and Pettit, 1981; Maitlis *et al.*, 1996; Satterfield and Huff, 1982).

4. Conclusion

Abiotic formation of lipid compounds by FTT reaction is possible under aqueous (e.g., hydrothermal) conditions as suggested by Berndt *et al.* (1996). The maximum lipid yield by FTT reaction is in the 150–250 °C window. The temperature ranges for the abiotic synthesis of various homologous series is: above 100 °C for *n*-alkanes and *n*-alkanoic acids; 125–250 °C for *n*-alkanols, alkenes, *n*-alkanals, *n*-alkan-2-ones, and alkyl formates; and above 250 °C for methylalkanes. Abiotic lipid compounds formed by aqueous FTT reaction do not show a carbon number predominance (i.e., CPI $\sim$ unity) as compared to biosynthetic lipids. It is obvious that cracking processes increase at temperatures above 350 °C.

Acknowledgements

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