

Abiotic formation of acylglycerols under simulated hydrothermal conditions and self-assembly properties of such lipid products

Bernd R.T. Simoneit^{a,b,*}, Ahmed I. Rushdi^a, David W. Deamer^c

^a Petroleum and Environmental Research Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA

^b Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA

^c Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

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Abstract

The abiotic formation of aliphatic lipid compounds (i.e., fatty acids, alcohols, and acylglycerols) has been reported to occur at elevated temperatures and pressures under simulated hydrothermal conditions. Although abiotic synthetic chemistry can occur under these conditions, the prebiotic self-assembly of micelles to bilayer to vesicles (protocells) may have occurred elsewhere. Amphiphilic compounds such as fatty acids are important candidates for micelle/bilayer/vesicle formation, because they are abundant products of Fischer–Tropsch-type reactions and are also found in carbonaceous meteorites. Thus, it is of interest to determine whether more complex amphiphilic precursor compounds, capable of assembling into stable membrane structures, can be synthesized under hydrothermal conditions. Hydrothermal experiments were conducted to study condensation reactions of model lipid precursors in aqueous media, i.e., glycerol and alkanolic acids, to form acylglycerols (glyceryl alkanooates) at elevated temperature under confining pressure. Nine different alkanolic acids ranging from C₇ to C₁₆ (except C₈) were used in these experiments. The condensation products were two isomers each of monoacylglycerols and diacylglycerols, as well as the corresponding triacylglycerol. The results indicated that: (1) condensation (dehydration) reactions are possible under aqueous pyrolysis conditions; (2) abiotic synthesis and subsequent condensation reactions of aliphatic lipid compounds are possible under hydrothermal conditions; and (3) such molecules have robust properties of self-assembly into membranous structures that would be suitable boundary structures for primitive forms of cellular life.

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1. Introduction

The abiotic formation and accumulation of organic matter, which may provide organic compound precursors for the origin of life on Earth (Amend and Shock, 1998; Baross and Hoffman, 1985; Ferris, 1992; Hennes et al., 1992; Holm, 1992b; Marshall, 1994; Ozawa et al., 2004;

Shock, 1993; Simoneit, 1992, 1995) have been proposed to occur in hydrothermal systems (Corliss et al., 1981; Holm, 1992a; Shock, 1993; Yanagawa, 1980; Vladimirov et al., 2004). Abiotic synthesis of aliphatic lipid compounds (i.e., fatty acids, fatty alcohols, and acylglycerols) has been reported to occur at elevated temperatures and pressures under simulated hydrothermal conditions (McCollom et al., 1999; Rushdi and Simoneit, 2001, 2004, 2005, 2006). Similarly, the elongation of oligopeptides has also been accomplished (Imai et al., 1999; Ogata et al., 2000). Although synthetic chemistry may occur in these conditions, the prebiotic self-assembly of micelles to bilayers to vesicles (protocells) may have occurred elsewhere at a site

* Corresponding author. Address: Petroleum and Environmental Research Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA. Tel.: +1 541 737 2155; fax: +1 541 737 2026.

E-mail address: simonebe@onid.orst.edu (B.R.T. Simoneit).

where conditions permit the noncovalent forces of self-assembly to come into play. Amphipathic compounds such as fatty acids and acylglycerols are important candidates for self-assembly of micelle/bilayer/vesicle formation. Thus, it is of interest to demonstrate that abiotic lipids (amphiphiles), precursor compounds for abiotic cellular membranes (Deamer, 1997; Apel et al., 2002), synthesized under hydrothermal conditions have self-assembly properties.

Laboratory experiments are needed to investigate the possible reactions of lipid precursors (e.g., fatty acids, fatty alcohols, polyols such as glycerol) at high temperatures in simulated hydrothermal systems. This work examines the formation and stability of the ester bond formed by condensation synthesis reactions with model compounds under aqueous high temperature conditions to form acylglycerides. We simulated hydrothermal systems using distilled water of varying acidities without salts, then evaluated the self-assembly properties of the lipid products in aqueous media.

2. Experimental methods

2.1. Experiment

The experimental procedure used in this work was described by Rushdi and Simoneit (2006). Stainless steel vessels (316SS Sno-Trik high pressure couplings, Leif and Simoneit, 1995) with internal capacities of $286 \pm 2 \mu\text{l}$ were used for the condensation reactions using a mixture of aqueous *n*-alkanoic acids (Aldrich, 99.9%) and glycerol (Sigma–Aldrich, 99.5%) heated at 150 °C. The vessels are capable of handling system pressure to 60,000 psi (413,000 kPa), thus the experiments were conducted by holding fluids at confining pressure (i.e., constant volume).

All the vessels were filled to capacity prior to sealing, with no headspace. Two reaction conditions were used in the first set of experiments: (1) a mixture of doubly distilled water (DDW, Burdick and Jackson) with glycerol plus *n*-alkanoic acids (hydrous pyrolysis), and (2) the same mixtures as above with the addition of pre-extracted oxalic acid (99.5%, EM Science) to provide reducing aqueous pyrolysis conditions. Aqueous oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) disproportionates above 150 °C to formic acid (CH_2O_2) and CO_2 , and formic acid decomposes at elevated temperatures to CO_2 , CO , H_2 , and H_2O (Crossey, 1991; Dinglinger and Schröer, 1937; Palmer et al., 1993). Thus, the net decomposition reaction of oxalic acid provides hydrogen for reduction.

The initial mixture of the first reactions in the experiment set consisted of 0.07–0.14 mM of glycerol and 0.29–0.65 mM of *n*-alkanoic acid in DDW, whereas the second mixtures had the same ingredients plus $0.19 \pm 0.03 \text{ mM}$ oxalic acid in DDW. The vessels were filled to capacity with DDW, sealed and placed immediately into an oven for 72 h at a temperature of 150 °C. The dehydration synthesis reactions proceed easily under these conditions with potential catalysis by the metal of the vessel.

2.2. Extractions

Upon removal from the oven, the vessels were covered with ice in order to quench the reaction, cooled to room temperature and opened carefully in order to release the pressure produced by CO_2 and other gases generated during the experiment. Each sample was transferred immediately by Pasteur pipette to a 5 ml vial. Each vessel was then rinsed three times with dichloromethane/methanol (3:2 v/v) which was combined with the 5 ml vial contents. The solvent extract was then transferred to another

Table 1
Products (relative %) and parameters for aqueous pyrolysis of glycerol and *n*-alkanoic acids

Compound	<i>n</i> -Alkanoic acid											
	C_7		C_9		C_{10}	C_{11}		C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
	–OA	+OA	–OA	+OA	–OA	–OA	+OA	–OA	–OA	–OA	–OA	–OA
Glycerol	33.2	67.9	31.0	5.2	0.6	31.2	14.9	12.9	45.8	28.7	20.1	3.6
<i>n</i> -Alkanoic acid	Nd	2.6	17.3	25.3	50.5	54.7	75.2	37.4	43.3	43.2	44.7	5.1
Methyl alkanoate												
Glyceryl-1-monoalkanoate	27.6	13.3	20.9	33.5	16.4	4.3	5.2	15.2	4.1	9.0	11.7	18.5
Glyceryl-2-monoalkanoate	15.2	6.0	12.0	12.8	11.6	2.3	1.9	9.4	3.1	3.7	9.1	23.6
Glyceryl-1,2-dialkanoate	11.9	4.9	10.1	10.0	12.1	4.1	1.3	12.8	1.6	8.4	6.1	30.9
Glyceryl-1,3-dialkanoate	9.1	4.1	7.6	12.1	6.7	2.8	1.5	8.2	2.0	7.1	8.3	18.4
Glyceryl-1,2,3-trialkanoate	3.0	1.2	1.1	1.0	2.2	0.5	0	4.1	0.1	0	0	0
Alkanoic acid anhydride	T	T	?	?	?	?	?	?	0	0	0	0
1/2(mono) ^a	1.81	2.22	1.75	2.61	1.41	1.87	2.70	1.60	1.30	2.41	1.29	0.78
1,2/1,3(di) ^b	1.30	1.2	1.33	0.82	1.82	1.47	0.89	1.57	0.78	1.19	0.73	1.68
Glyceryl monoalkanoates	42.8	19.3	32.8	46.3	28.0	6.65	7.1	24.6	7.2	12.7	20.8	42.1
Glyceryl dialkanoates	21.0	8.9	17.8	22.2	18.8	6.90	2.8	21.0	3.6	15.5	14.4	49.2
Glyceryl trialkanoates	3.0	1.2	1.12	1.0	2.23	0.53	0.0	4.11	0.13	0	0	0

OA, oxalic acid; Nd, not determined; T, trace.

^a Ratio of glyceryl-1-monoalkanoate/glyceryl-2-monoalkanoate.

^b Ratio of glyceryl-1,2-dialkanoate/glyceryl-1,3-dialkanoate.

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