

POSSIBLE IMPACT OF A PRIMORDIAL OIL SLICK ON ATMOSPHERIC AND CHEMICAL EVOLUTION

FRANS PEDER R. NILSON

*Department of Biotechnology, Center for Chemistry and Chemical Engineering, Lund University,
221 00 Lund, Sweden*

(e-mail: frans_peder.nilson@biotek.lu.se, fax: +46 46 222 47 13)

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Abstract. Low molecular weight liquid hydrocarbons from various sources, could have formed an oil layer covering the primeval ocean (present already $4.0\text{--}4.4 \times 10^9$ yr ago), preventing water from evaporating into the atmosphere. Water from other sources, precipitated by cold traps at higher altitude in the atmosphere, becomes trapped in the ocean. In a thereby more dry and presumably reducing atmosphere (before 3.9×10^9 yr ago) even more hydrocarbons, as well as reactive molecules will form. An oil layer can possibly act as a dry solvent for reactions, where the reactive molecules can produce monomers and condensing agents. Monomers and eventual polymers formed could become strongly concentrated at the oil-water interface, favouring molecular interactions at high mobility and low dilution, without exposure to the destructive action of UV-light. Increased water leakiness of the oil layer due to accumulation of polar molecules within, would lead to photo-oxidation of liquid hydrocarbons, and subsequent emulsification at the oil-water interface, forming cellular structures. The atmosphere would then have lost its reducing character.

Keywords: dry solvent, hydrocarbons, molecular interactions, oil layer, reducing atmosphere

1. Introduction

According to geological evidence, the upper mantle seems to have had approximately the present oxidation state for $3.6\text{--}3.9 \times 10^9$ yr (Delano, 2001), and the crust and oceans have been present for $4.0\text{--}4.4 \times 10^9$ yr (Peck *et al.*, 2001). Lunar history indicates that great impacts occurred in the Earth-moon system until around 3.8×10^9 yr ago. The existence of reducing conditions in Earth's early secondary atmosphere (before 3.9×10^9 yr ago) can not be excluded, based on present rock samples, or on present volcanic output of gases from (oxidized) recycled, subducted material. Nor is Earth's accretion history, including the formation of core and crust, as well as the mixing of the upper mantle, known in such detail that initially reducing conditions could be excluded.

Liquid hydrocarbons are formed by a number of reactions under reducing conditions. Hydrocarbons have been formed in prebiotic simulation experiments, as films, tars and brown residues called tholins, then often being regarded simply as side products. Reducing conditions would also give higher yields of reactive com-



pounds and useful monomers, compared to more neutral conditions, as prebiotic simulation experiments clearly have shown.

This article will describe how an oil layer covering the primeval ocean, could speed up the formation of living systems (perhaps to within 100×10^6 yr), by providing suitable conditions for the formation of reactive compounds, monomers and polymers as well as for molecular interactions.

2. Hydrocarbon Formation

Geochemical reactions do not seem to rule out the proposed mechanism for the evolution of gases associated with basaltic volcanism, from a rather reduced state during and shortly after accretion, to their present, considerably more oxidized composition (Holland, 1984). The presence of a reducing primitive atmosphere depends on whether the oxidation state of the upper mantle has varied over time, and as igneous rocks are rapidly oxidized after formation, they are not good indicators of mantle evolution (Kasting, 1993). The upper mantle was originally more reduced and has become progressively more oxidized (Kadik, 1997). The composition of volcanic gases prior to 3.9×10^9 yr ago remains unknown, but could have been reducing (Delano, 2001). In the upper mantle, crystallization of initial diamonds occurs under low oxygen fugacity, in equilibrium with the methane-nitrogen rich fluid from metal-silicate melts, of which traces are found in natural diamonds (Simakov, 1998). If the mantle still contains elemental or reduced carbon, an early reducing atmosphere seems rational.

Under reducing conditions, liquid hydrocarbons could be formed through Fischer-Tropsch type reactions, shock wave synthesis, hydrolysis of carbides and through electrical discharge reactions. Aliphatic liquid hydrocarbons of low molecular weight can also be formed by photochemical reactions in a methane rich atmosphere (Toupance *et al.*, 1977; Kasting *et al.*, 1983). A one bar atmosphere of CH_4 could be photo-polymerized into a 1–10 m thick oil layer, within $1\text{--}10 \times 10^6$ yr (Lasaga *et al.*, 1971).

Iron-meteorite impacts into a moist atmosphere could also release hydrogen to create reducing conditions.

Hydrocarbons can also be formed in the absence of a reducing atmosphere, for example in hydrothermal vents (Holm and Charlou, 2001). Large amounts of organic compounds could come from interplanetary dust particles (Maurette *et al.*, 2000) and from carbonaceous asteroids, the main part being hydrocarbons.

3. An Oil Layer Stabilizing a Reducing Atmosphere?

A hexadecanol monolayer can decrease water evaporation from a lake by 40% (Hiemenz, 1977). Wind and wind driven sand particles can rupture a monolayer,

but hardly an oil layer with a thickness of centimetres or decimetres. Therefore an oil layer, from any source, would prevent water evaporation even better.

Liquid hydrocarbons are used as solvents for photochemical reactions, because they are transparent and unreactive towards electronically excited states. Free-radical pairs formed by UV-light, would be trapped in a solvent cage until recombining. It is only in the presence of free radicals and free O_2 that the liquid hydrocarbons will become oxidized, and finally become dispersed.

At some atmospheric altitude there will be a cold trap, because of limited heat convection from below, or because of particles from volcanoes, from asteroid impacts or interplanetary dust, causing water vapour from evaporation, from volcanic activity and from cometary impacts to condense and fall down as rain. Large amounts of NH_3 will follow the rain to become trapped beneath the oil layer. Although most of the water would be trapped under the oil, enough for the synthesis of aldehydes could remain in the atmosphere.

In a reducing atmosphere where water in the ocean is in equilibrium with water vapour in the atmosphere, photochemical reactions would convert the CH_4 to CO and finally to CO_2 , as on Venus and Mars. If a methane-dominated reducing atmosphere becomes more dry because of an oil layer preventing water evaporation, photochemical reactions and electrical discharges will produce higher hydrocarbons, along with the release of H_2 . This means that a reducing atmosphere and an oil layer can become a self-stabilizing system (more oil, more hydrogen and less water vapour), until the free H_2 is lost. The exospheric loss of hydrogen, which is strongly dependent on the exospheric temperature, in turn dependent on the H_2 concentration (McGovern, 1969), would until then, be the major form of oxidation.

4. The Oil Layer Acting as a Dry Solvent

Aliphatic solvents like hexane, heptane, decane, dodecane and petroleum ether contain only 0.01 g of water per 100 g of solution, when at equilibrium with a water phase, while benzene can dissolve 0.06 g of water per 100 g of solution. Therefore an oil layer could be a good solvent for water-sensitive reactions and reagents. The molecules needed for the Strecker synthesis, raining down from the atmosphere – such as aldehydes, HCN and NH_3 – would dissolve in the oil layer. The smallest of these molecules dissolve better in water, but their lower concentration in the oil layer could have been compensated for by their higher reactivity (without solvating water). A low concentration of reactive molecules within the oil layer can be of greater importance than one first would expect. This is because HCN, formaldehyde, carbinolamines or hemiaminals as well as imines, will polymerize into random mixed-type polymers, if available at high concentrations. All steps but the last in Strecker amino acid synthesis are favoured by dry conditions, and there are even indications that HCN-oligomerization might also be favoured, especially if traces of water are present within the layer.

Many possible prebiotic condensing agents have been suggested (Hulshof and Ponnampertuma, 1976; Keefe and Miller, 1995), for example hydrogen cyanide-tetramer, that can work at neutral or alkaline conditions. The main problem with condensing agents, although often used in water solution, is that they can be hydrolysed, which is less of a problem if dissolved in hydrocarbons.

If the oil contained dark compounds, like HCN-polymers, sunlight could increase the surface temperature of the oil enough to drive off water, released by reactions within the oil, creating even more anhydrous conditions.

5. Monomer Accumulation and Polymer Formation

Amino acids, other monomers and many biopolymers can be surface-active, meaning that they can preferentially accumulate to very high concentrations at an oil-water interface, from low concentrations in either bulk phase. In the presence of sea salts the hydrophobic interactions between solutes and the oil-water interface will become even stronger. If amino acids adsorbed to the oil-water interface make contact with condensing agents from inside the oil slick, peptides and proteins could be formed, through dehydration-condensation reactions. Condensing agents and charged groups can interact over large distances, because of the low dielectric constant of hydrocarbons surrounding the condensing agents. A lower total bulk concentration of amino acids could be sufficient, considering the enormous concentrating effect of the oil-water interface.

6. Molecular Interactions and Evolution

Molecules attached to an oil-water interface can interact with each other in two dimensions (diffusion along a plane), instead of in three dimensions (a volume), meaning that dilution into the bulk ocean will be very small. The resulting high interfacial concentration and low dilution would be most important for the molecular interactions, in contrast to other systems where some components are attached to a solid surface (low mobility) and to systems completely in the bulk solution (high dilution).

An oil slick absorbing or scattering UV-light (Cleaves and Miller, 1998), could shield the oil-water interface from the destructive action of UV-light. At the oil-water interface, peptides and proteins could interact with metal-ions, from the sea water, possibly catalysing stereospecific reactions. Day-night cycles could produce strong temperature fluctuations within the oil, leading to melting and reannealing of double-stranded nucleic acids. Peptides and proteins could also act as ion-exchangers for concentrating phosphate ions, which have been considered a problem because of the micromolar levels in marine environments today.

Lateral proton conduction has been found to be 20 times faster at phospholipid-water interfaces compared with that in bulk water (Teissié *et al.*, 1985). Quinol-phosphates formed by photo-activation of quinones, reacting with phosphate ions, could have been powerful phosphorylating agents in the presence of oxidizing agents (Stillwell, 1977).

When a self-replicating reaction system occurs in one spot at the oil-water interface, it could diffuse radially along the interface, leaving a nutrient-depleted interface behind. As new catalytic functions occur, the systems containing these would also spread radially. Systems with different useful functions would quickly meet and combine into even better systems, thus speeding up evolution considerably.

Monomer shortage could favour systems releasing monomers from polymers, as well as systems that can convert precursors to activated building blocks. This would lead to survival of the fastest replicating (metabolically more competent) systems, and to systems containing molecular associations resisting enzymatic degradation because of steric reasons.

Modern bacterial cells contain membrane-bound ribosomes, membrane-bound chromosome attachment proteins, membrane-integrated enzymes and membrane-associated enzymes at the membrane-cytoplasm interface. The cytoplasm has a higher pH (perhaps up to one pH-unit higher) than the outside of the cell. The primeval ocean with NH_3 and the oil with dissolved amines, could offer such a weakly alkaline interfacial environment.

7. Dispersion of the Oil Layer

Non-hydrocarbon molecules accumulating in the oil slick would cause water leakiness, leading to photolysis of water. The released OH-radicals and O-atoms, the latter forming O_2 , would lead to oxidation of liquid hydrocarbons, as well as to transformation of a presumably reducing atmosphere to a non-reducing one. During this period extensive formation of aldehydes could take place in the atmosphere. Ammonia and amines can catalyse the formation of sugars from formaldehyde and glycoaldehyde (Weber, 2001). Some aldehydes would have been oxidized to carboxylic acids, which as amphiphiles could increase the water leakiness.

Cometary impacts and tidal waves which would have been larger at this time because the moon was closer, could force water drops surrounded by amphiphile monolayers and interface-associated molecules to go into the oil. However, because of higher density, the drops would sink through the oil-water interface, becoming covered by a second layer of amphiphiles. This would have produced reaction systems enclosed by double layer membranes.

8. Discussion

Fischer-Tropsch type reactions at high temperature, as well as electrical discharges, can produce aromatic hydrocarbons allowing new solute-solvent interactions because of their polarizability. They could have been of importance in the absorption of light energy. Some unsaturated aliphatic hydrocarbons could also have formed under the earlier described conditions. Thus, the oil layer could have been even more complex than described earlier in the text.

The transition states of some reactions would be less favourable in a hydrocarbon solvent, because of low solvation by the oil. Many reactions run in polar aprotic solvents, but they could probably also proceed in an apolar aprotic solvent like oil, modified by the presence of polar compounds, like long-chain aldehydes (low reactivity due to inductive effect).

An aldehyde molecule within the oil can take up water, released from a reaction within the oil, forming an aldehyde hydrate or gem-diol. The latter compounds can release water, reforming the aldehyde at the hot upper face of the sunlit oil layer where this minor amount of water can evaporate. This process would help to maintain an anhydrous oil layer. In some cases, catalytic amounts of water will help a reaction, while higher water concentrations would lead to hydrolysis of sensitive products or intermediates. Water released at the atmosphere-oil interface, as well as alkenes, alkynes, thiols and hydroquinones, could deactivate the most reactive (and dangerous) molecules, formed by photochemical reactions at the surface of the oil layer.

9. Conclusions

To deny the possible importance of liquid hydrocarbons, especially alkanes, in prebiotic simulation experiments because of their chemical inertness, lack of functional groups or lack of biochemical functions, would be a mistake.

A global oil layer could be a simple common factor for improving and integrating the processes needed for the origin of polymers and the development of auto replicating reaction systems. The main role of an oil layer would be to temporarily stabilize a presumably reducing atmosphere, to provide a dry solvent and to provide an oil-water interface facilitating molecular interactions under kinetically favourable conditions. It could also have protected polymers and some NH_3 from photolysis, while still allowing a constant energy flow. When the oil is photo-oxidized, membrane encapsulated systems could appear.

New exciting prebiotic simulation experiments are suggested, utilising condensing agents dissolved in liquid hydrocarbons, and where low bulk concentrations of reactants could be compensated for by high interfacial concentrations.

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