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The Sonochemical Synthesis of Simple Organic Biomolecules in Aqueous Solutions Containing Dissolved Prebiotic Gases

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Abstract: This review considers the generation of relatively simple biomolecules, e.g., primary amino acids, resulting from the rapid collapse of bubbles in aqueous solutions containing various, low molar mass, gases. Some of the possible primary reactions occurring to produce the biomolecules are introduced and discussed. A brief discussion is included on the possible involvement of hydrodynamic cavitation, at the primordial seashore, as the initiating processes for the formation of the first organic molecules on prebiotic earth and the origins of life on Earth some 4 billion years ago.

Keywords: sonochemistry; cavitation chemistry; biomolecules; prebiotic chemistry

1. Introduction

Under certain imposed experimental conditions, it is possible to have microbubbles in water (and other liquids) collapse (implode) rapidly (in fractions of a microsecond), and near adiabatically, to produce localized "hot spots" with interior bubble core temperatures of several thousand degrees centigrade [1-3]. These events give rise to cavitation chemistry [4]. The most common means of creating "hot spots" in water (or more generally in aqueous solutions) is by exposing the liquid to ultrasound. However, the use of ultrasound to create the conditions for the violent collapse of microbubbles is not unique, and cavitation "hot spots" can be produced by hydrodynamic flow, finely focused light or laser beam impingement on a liquid, or high energy particle capture by a liquid, e.g., background radiation [5]. The latter two means of producing cavitation bubbles is a direct consequence of the deposition of the localized energy leading to a rupture of the forces that hold the molecules of the liquid together (the tensile strength of the liquid), and the creation of a vapor filled bubble. These bubbles grow due to highly localized heating effects, but as the heat transfers into the bulk surrounding fluid the ambient pressure prevails and the expanded bubble collapses. The creation of a cavitation bubble that can implode, using either ultrasound or hydrodynamic flow relies on a transient reduction of the ambient pressure in the region surrounding an already existing bubble. The low-pressure regions in a fluid result in the expansion of bubbles in this region and when this condition passes the expanded bubble inertially collapses. The oscillatory nature of sound waves is perfectly suited for creating the conditions for producing imploding cavitation bubbles. In principle, the negative pressure (rarefaction) that is able to be produced by ultrasound can overcome the tensile strength of a liquid (for water it is more than 1000 atm. negative pressure is needed), however this is never required as adventitious bubbles in a liquid provide for the lower negative pressures needed to produce imploding cavitation bubbles. Most ultrasound reactors operated with sound pressure oscillations of only a few atmospheres. Similar pressure conditions also exist in the case of hydrodynamic reactors.

The vast majority of studies using cavitation chemistry have been carried out using ultrasound reactors and the overwhelming number of investigations undertaken, have been on the decomposition of solutes present in the liquid undergoing sonolysis. One area of study which has been in play since the very early days of sonochemistry has been with respect to the formation of biomolecules from simple solutes and gases dissolved in the fluid being sonicated, e.g. N_2, CO_2, O_2,

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CH_4, etc. The interest in this particular facet of sonochemistry lies with examining the possibility that cavitation chemistry may have been responsible for producing some of the primary organic molecules that were the basis of life on Earth some 4 billion years ago.

This review examines the work that has looked at the sonochemical synthesis of some biomolecules from simple solutes in water in the presence of various dissolved gases. It reveals that cavitation chemistry can produce simple biomolecules under possible prebiotic atmosphere compositions. How these biomolecules may have subsequently reacted to yield complex molecules is briefly described.

2. Synthesis of biomolecules using cavitation chemistry

Some of the very earliest studies on the synthesis of amino acids by sonolysis are summarized in Margulis' book on sonochemistry [6]. It was reported that in the sonication of aqueous solutions containing carboxylic acids, in a nitrogen atmosphere, a number of amino acids were formed. In 1968 Anbar, in a study of sonoluminscence from water jet impact on the surface of salt water, also mentions a separate study where amino acids had been formed, but provides no data, nor details of the conditions used to make the amino acids [7]. Sokolskaya [8] also makes mention of early studies that report on the synthesis of amino acids as well as formaldehyde, HCN, NH_3, on the sonolysis of aqueous solutions containing gases such as N_2, CO, methane, and H_2, in various amounts and combinations.

Henglein and co-workers [9-11] carried out a series of quite detailed studies on the products formed from the sonication of aqueous solutions containing dissolved gases of CH_4, N_2, and CO_2. Depending on the gas type present when sonicating the various aqueous solutions studied, ethane, ethylene, acetylene and higher hydrocarbons were detected (with methane), as well as NH_3, nitrite, and nitrate (with N_2), and CO and formic acid (with CO_2). Henglein and co-workers [9-11] were able to show that the reactions that lead to the products formed, in the various systems examined, was as a result of the thermally induced decomposition (pyrolysis) of water molecules and gases present in collapsing cavitation bubbles, and the subsequent radical reactions ensuing under the very high radical concentration conditions in the bubble core.

Dharmarathne and Grieser [12] recently studied the formation of amino acids on the sonication of aqueous solutions containing various combinations and amounts of methane, under a N_2 atmosphere. They also conducted experiments on aqueous solutions containing only CO_2 and N_2. In both systems they were able to detect several amino acids as products. Table 1 lists some of the amino acids they were able to detect in their study.

Table 1. Amino acids identified in the sonolysis of aqueous solutions containing either CH_4 or CO_2 {carbon sources}, under an N_2 atmosphere.[1]

Amino acid	CH_4/N_2	CO_2/N_2
glycine		
alanine		
ethylglycine		
serine		
proline		
valine		
threonine		
leucine		

[1] Data taken from [12].

Considering that it is well established that the reactions occurring within a collapsing cavitation bubble are essentially those that can be expected for gases under going pyrolysis reactions, some of the key primary reaction steps leading to the formation of amino acids can be suggested. For example, a plausible set of key elementary reactions leading to the formation of glycine in the CO_2/N_2 system

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is (the symbol "))))" in the reactions below represents radical production from cavitation collapse as distinct for subsequent radical reactions):

$$H_2O \xrightarrow{))))} \cdot OH + \cdot H \quad \ldots(1)$$

$$\cdot O\cdot + N_2 \rightarrow \cdot NO + \cdot \dot{N}\cdot \quad \ldots(2)$$

The source of oxygen atoms coming from the reaction (or reactions (6) and (7)),

$$2\cdot OH \rightleftharpoons \cdot O\cdot + H_2O \quad \ldots(3)$$

It seems that reaction (2) is the more likely pathway [11,13] to producing N atoms than the direct thermal homolysis of the N_2 molecule because of the strength of the nitrogen triple bond.

$$\cdot \dot{N}\cdot + \cdot H \rightarrow \cdot \dot{N}H \quad \ldots(4)$$

$$\cdot \dot{N}H + \cdot H \rightarrow \cdot NH_2 \quad \ldots(5)$$

$$CO_2 \xrightarrow{))))} CO + \cdot O\cdot \quad \ldots(6)$$

$$CO \rightarrow C + \cdot O\cdot \quad \ldots(7)$$

$$CO_2 + H\cdot \rightarrow \cdot COOH \quad \ldots(8)$$

$$C + H\cdot \rightarrow \cdot \dot{C}H\cdot \quad \ldots(9)$$

$$\cdot \dot{C}H\cdot + H\cdot \rightarrow \cdot CH_2\cdot \quad \ldots(10)$$

$$\cdot CH_2\cdot + \cdot COOH \rightarrow \cdot CH_2COOH \quad \ldots(11)$$

and finally,

$$\cdot NH_2 + \cdot CH_2COOH \rightarrow H_2NCH_2COOH \text{ (glycine)} \quad \ldots(12)$$

Of course there are many other reactions that can be expected to occur with such a large family of radicals, and model simulation experiments of reactions in a cavitation bubble have considered many others [13,14]. Nonetheless it is possible to produce high molecular weight products with such multiple steps as above and this seems to be borne out in a recent theoretical modeling study [15] showing that amino acids, and other important biomolecules, can be generated with such multiple steps. It should be kept in mind that the very high radical concentrations produced in a collapsing bubble and the confined (many third body collisions will be effective) "hot" environment will allow reactions to occur that under low temperatures and dilute concentrations will not be favorable.

The above information provides very strong evidence that cavitation chemistry can provide the conditions that allow the conversion of simple gases, including prebiotic gases, into basic biomolecules. The connection of this to a possible pathway to the very origins of life is considered in the following section.

3. Linking cavitation chemistry to a possible path for the formation of proto-cells

Although the sonochemical formation of small biomolecules from possible prebiotic gases in the Earth's atmosphere, and waters, is achievable, it is unlikely that ultrasound or even sound was a

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significant driver to produce a significant amount of the early organic molecules on Earth. What the sonochemical studies have shown is that cavitation chemistry is another example of a high-energy initiation process that leads to important life source molecules from simple gases. In the same way that electrical discharge, UV photolysis, etc., studies have shown to be the case {12]. This recognition is however not sufficient to explain how the prebiotic organic molecules lead to life on Earth. A possible pathway, that can be hypothesized, makes use of another generator of cavitation chemistry, as mentioned in the Introduction, namely, hydrodynamic cavitation. Dharmarathne and Grieser [12], have made the suggestion that hydrodynamic cavitation created by waves crashing onto coastal rocks, leads to conditions where the products from the subsequent cavitation chemistry are adsorbed and concentrated onto the seaside rocks from the bathing waters. There have been a number of studies [16-18] conducted showing that certain rock surfaces, particularly clays, can act as catalytic surfaces to produce oligomers of amino acids, oligomers of nucleotides, from their base units. Similarly, reactions of small, unsaturated hydrocarbons on catalytic surfaces can produce hydrocarbons of higher molar mass, possibly even forming amphiphilic molecules. Taking all this together, a hypothetical schematic summary of the steps leading up to the formation of proto-cell like structures can be envisaged, as shown in Figure 1.

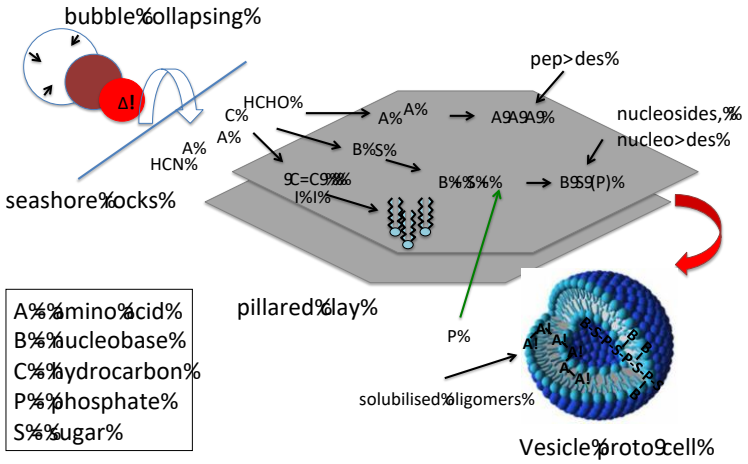

Figure 1. A simplified schematic diagram showing the pathway from the production of simple organic molecules from cavitation bubbles on rocks at the seashore to more complex proto-cell units. The clays provide the surface to concentrate low concentration solutes and to catalytically convert low molar mass solutes (HCN, HCHO, etc.) to molecules that eventually build-up to take the form of the proto-cell.

The model allows for a relatively straightforward connection between the production of important primary biomolecules and structures that are also a possible path to simple cells, albeit a highly complex one [19]. The model also ensures that there is a continuous supply of primary organic molecules in a localized area in order to ensure a growing population of proto-cells and hence the basis to develop further into more complex units. Although the model requires conditions where hydrodynamic cavitation occurs and the right rock composition to be present, these conditions are likely to be wide spread on a vast coastline. Interestingly, the model can be considered to be operative anywhere provided the said conditions prevail, meaning there may be other planets in the universe that have such conditions and therefore possibly life on them.

Conflicts of Interest: "The author declares no conflict of interest of any kind."

References

1. Didenko, Y. T.; McNamara, W. B., III; Suslick, K. S. Hot Spot Conditions during Cavitation in Water. *J. Am. Chem. Soc.* **1999**, 121, 5817-5818.
2. Okitsu, K.; Suzuki, T.; Takenaka, N.; Bandow, H.; Nishimura, R.; Maeda, Y. Acoustic Multibubble Cavitation in Water. *J. Phys. Chem. B* **2006**, 110, 20081-20084.
3. Rae, J.; Ashokkumar, M.; Eulaerts, O.; von Sonntag, C.; Reisse, J.; Grieser, F. Estimation of Ultrasound-Induced Cavitation Bubble Temperatures in Aqueous Solutions. *Ultrason. Sonochem*. **2005**, 325-329.
4. Grieser, F.; Choi, P.-K.; Enomoto, N.; Harada, H.; Okitsu, K.; Yasui, K. (eds) *Sonochemistry and the Acoustic Bubble*: Elsevier: Amsterdam, Netherlands, 2015. ISBN: 978-0-12-801530-8.
5. Shah, Y.T.; Pandit, A.B.; Moholkar, V.S. *Cavitation Reaction Engineering;* Springer: Boston, USA, 1999; pp 1-14, ISBN: 978-1-4613-7168-7.
6. Margulis, M.A.; *Sonochemistry and Cavitation*; Gordon and Breach: SA, Australia, 1995; pp 356-357, ISBN: 2-88124-849-7.
7. Anbar, M. Cavitation during Impact of Liquid Water on Water: Geochemical Implications. *Science* **1968**, 161, 1343-1344.
8. Sokolskaya, A. Glycine and Alanine Synthesis from Formaldehyde and Hydroxylamine in the Field of Ultrasound Waves. *Origins of Life* **1976**, 7, 183-185.
9. Henglein, A. Sonolysis of Carbon Dioxide, Nitrous Oxide and Methane in Aqueous Solution. *Z. Naturforsch., B: J. Chem. Sci.* **1985**, 40b, 100-107.
10. Hart, E.J.; Fischer, Ch.-H.; Henglein, A. Isotopic Exchange in the Sonolysis of Aqueous Solutions Containing D_2 and CH_4. *J. Phys. Chem*. **1987**, 91, 4166-4169.
11. Hart, E.J.; Fischer, Ch.-H.; Henglein, A. Isotopic Exchange in the Sonolysis of Aqueous Solutions Containing $^{14,14}N_2$ and $^{15,15}N_2$. *J. Phys. Chem*. **1986**, 90, 5989-5991.
12. Dhamarathane, L.; Grieser, F. Formation of Amino acids on the Sonolysis of Aqueous Solutions Containing Acetic acid, Methane or Carbon Dioxide, in the Presence of Nitrogen Gas. *J. Phys. Chem. A* **2016**, 120, 191-199.
13. Yasui, K.; Tuziuti, T.; Iida, Y.; Mitome, H. Theoretical Study of the Ambient-Pressure Dependence of Sonochemical Reactions. *J. Chem. Phys*. **2003**, 119, 346-356.
14. Yasui, K.; Tuziuti, T.; Sivakumar, M.; Iida, Y. Theoretical Study of Single-Bubble Sonochemistry. *J. Chem. Phys.* **2005**, 122,224706.
15. Kalson, N.-H.; Furman, D.; Zeiri, Y. Cavitation-Induced Synthesis of Biogenic Molecules on Primordial Earth. *ACS Cent. Sci*. **2017**, 3, 1041-1049.
16. Ferris, J.P.; Hill, A.R., Jr; Liu, R.; Orgel, L.E. Synthesis of Long Prebiotic Oligomers on Mineral Surfaces. *Nature* **1996**, 381, 59-61.
17. Ferris, J.P. Montmorillonite-catalysed Formation of RNA Oligomers: the Possible Role of Catalysis in the Origins of Life. *Philos. Trans. R. Soc., B* **2006,** 361, 1777-1786.
18. Cleaves, H.J., II; Scott, A.M.; Hill, F.C.; Leszczynski, J.; Sahai, N.; Hazen, R. Mineral-organic Interfacial Processes: Potential Roles in the Origins of Life. *Chem. Soc. Rev*. **2012**, 41,5502-5525.
19. Ruiz-Mirazo, K., Briones, C.; de la Escosura, A. Prebiotic Systems Chemistry: New Perspectives for the Origins of Life. *Chem. Rev*. **2014**,114, 285-366.