
Comparison of Mono-Ethylene Glycol Prebiotic Synthesis Efficiency via Formose Reaction in Methanol and Water as Solvents: A Short Communication

Arash Vojood

Young Researchers and Elite Club, Ardabil Branch, Islamic Azad University, Ardabil, Iran

Email address:

voojod.a2012@gmail.com

To cite this article:

Arash Vojood. Comparison of Mono-Ethylene Glycol Prebiotic Synthesis Efficiency via Formose Reaction in Methanol and Water as Solvents: A Short Communication. *American Journal of Physical Chemistry*. Vol. 12, No. 2, 2023, pp. 17-21. doi: 10.11648/j.ajpc.20231202.11

Received: January 26, 2023; **Accepted:** June 12, 2023; **Published:** June 27, 2023

Abstract: Formose reaction (FR) is of particular interest in prebiotic chemistry, as well as origin of life research, since it sets the grounds for non-biological chemical reactions producing sugar. In the formose process, which is based on the aldol condensation mechanism, low-carbon aldehyde molecules are transformed into polyol with higher carbon. Moreover, in an alkaline medium with a heterogeneous catalyst present, this process is sped up. This work assesses the efficiency of prebiotic synthesis of mono-ethylene glycol (MEG) via FR when fumed silica (Aerosil) catalyst was present in methanol polar solvent. Comparisons were then made with the same process in the presence of montmorillonite (MMT) as catalyst in water as solvent. The current study demonstrates that the amount of MGA production starts out low and gradually increases when Aerosil and MMT were used as mineral catalysts while methanol and water, respectively, functioned as solvents at pH values of 7.8 and 7.5. Generally speaking, the results indicated that if the target is to produce MEG, water is a better option as an excellent polar solvent in the FR. Consequently, outputs showed higher MEG production efficiency with FR when methanol and Aerosil rather than water when MMT were used as solvent and catalyst, respectively.

Keywords: Origin of Life, Probiotic Chemistry, Formose Reaction, Mono-Ethylene Glycol, Montmorillonite

1. Introduction

Tasting sweet, mono-ethylene glycol (MEG; 1,2-ethanediol; ethylene glycol) is an organic liquid exhibiting extreme toxicity, colourlessness, and odourless nature. The most popular application of MEG comes in the face for antifreeze liquids for vehicles. Charles-Adolphe Wurtz (1859) first introduced MEG by MEG diacetate saponification with potassium hydroxide (Caustic potash; KOH) [1, 4].

The origin of life (OoL) on the planet has been crucially scrutinized by ontology researchers throughout human history and has been generally debated between experimental scientists and religious scholars [5, 6]. However, the current view of the OoL on Earth is that life emerged from abiotic [7]. But, the history of the Earth lacks clear evidence on the characteristics of the ongoing evolution from a non-living toward a living world [8, 9]. The OoL research has currently changed into a demanding but interesting topic, comprising the interaction of various domains, including biology, chemistry, physics,

astronomy, geology, philosophy, etc. People have become more interested in understanding the chemical OoL [9-12]. Given the highly chemistry associated nature of life, the chemical science has been greatly acknowledged for its vital role in the interdisciplinary efforts to understand the OoL. This implies that the chemists are anticipated to develop methods/procedures for distinguishing between complex and simple organic molecules and describe prebiotic mechanisms [1, 13-15]. A fascinating question related to the origin of carbohydrates as DNA and RNA building blocks. Some believe that the primitive Earth has sourced prebiotic sugars via Formose reaction (FR) [16-19]. Also, according to prebiotic chemists, sugar forms as a result of Formose synthesis, as a Russian chemist named Alexander Mikhaylovich Butlerov proposed in 1861. The OoL is known to be highly associated with the FR due to its possible role as the synthesis route for generating complex monosaccharides and potential process whereby sugar forms abiotically [20-24]. So, one of the probable prebiotic synthesis methods is the FR. Indeed, the synthesis of prebiotic

sugar is referred to as a key determinant of FR [19, 25, 26].

Weiss *et al.* [27] reported that toxic Formose sugars were used for cancer tumor growth suppression activity, but no effect has been observed. Castells *et al.* [28] reported considerable toxicity of Formose combinations due to high content of branched-chain carbohydrates.

One of the potential FR settings possibly came into existence in the Hadean epoch, 4.0–4.5 billion years ago (Ga), when our planet was formed by accretion, had its temperature reduced down to the level of volcanos, and then coated with a high-thickness CO₂-rich atmosphere and oceans of water as a result of volcanic gas release [16, 29, 30]. It has been hypothesized that the so-called simple sugars has been the original products of formaldehyde (HCHO or CH₂O) on the prebiotic Earth [31, 32].

This study evaluated MEG prebiotic synthesis efficiency using FR and Aerosil catalyst in methanol (methyl alcohol; CH₄O or CH₃OH) solvent and compared the results against those of the same process in the presence of montmorillonite (MMT) as catalyst in water as solvent.

2. Material and Methods

2.1. Chemicals and Equipment

Aerosil (with CAS number of 112945-52-5) and MMT (with CAS number of 1318-93-0) from Sigma-Aldrich, and methanol (GC grade), acetone (pure grade), Sodium sulfate (dehydrated) and hydrochloric acid 37% (analytical purity grade) from Merck Company. Moreover, aqueous solution of formaldehyde 37% (pure grade), sodium hydroxide (guaranteed grade), which was used as a strong base, was purchased from Shimi Delta Company.

The applied instruments were gas chromatography/mass spectrometry (Agilent, 5975C), rotary evaporator (Bibby, RE200), pH meter (WTW, inoLab 720), centrifuge (155, Zag chemie), analytical balance (Scaltel, SPB55, ability to read up to an accuracy of 0.0001 g), Heater Stirrer (Bibby, HC502), laboratory oven (Binder, 7200) and FTIR spectrophotometer (Bruker, TENSOR 27).

2.2. Procedure

In this research, first 100 ml of CH₄O with 11 ml of aqueous

formaldehyde solution (formalin) was transferred to a 250-mL three-necked round-bottom flask and Then, NaOH (2M) was added to bring it to the desired pH (7.8), and brought to a temperature of 60°C. Finally 0.08 g of the Aerosil catalyst was added to the flask to start the reaction. So, the FR was started by transferring the Aerosil into the flask containing the mixture.

Additionally, from the beginning of the reaction until the end, N₂ gas was introduced into the flask the reaction, and the temperature was constantly monitored between 55 and 65°C. Then, at the desired times, 5 mL of the mixture was taken from mixture and immediately acidified with a solution of HCl (6N) to stop the reaction. A small amount of H₂O was entered into the system with HCl solution, and no H₂O was added to the system except that. Next, the liquid samples were dried using a rotary evaporator until they became white solids. We dissolved these solid samples in 5 mL of CH₄O, and then used a centrifuge apparatus to separate them so we could analyze them using a gas chromatography/mass spectrometry (GC/MS) device. [1, 22]. Besides, the same operation was exactly repeated by replacing water with 200 ml of deionized H₂O plus 23 ml of formalin and 0.17 g of MMT catalyst to perform the analysis in the GC/MS [24].

3. Results and Discussion

3.1. FTIR Analysis

FTIR analysis of Aerosil and MMT is shown in figure 1 a and b, respectively. According to figure 1a related to Aerosil one broad adsorption band in the region of 3550 cm⁻¹ characterized stretching vibration of the hydroxyl group (O-H) adsorbed water molecules on the surface of Aerosil, one peak in 2361 cm⁻¹ region related to CO₂ gas present in gas phase, one peak in region 2934 cm⁻¹ to stretching C-H [1, 33], one peak in region 1633 cm⁻¹ could be attributed to the bending vibration if the OH group in the water molecules adsorbed on the Aerosil and three peaks in ranges 472, 811 and 1105 cm⁻¹ which are attributed to the stretching and bending Si-O-Si, respectively [1, 34].

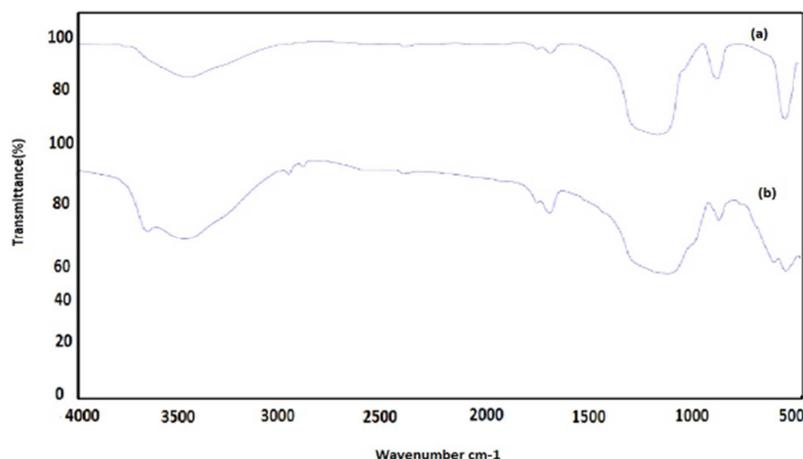


Figure 1. FTIR analysis: (a) Aerosil; (b) MMT.

According to figure 1b related to MMT, the wide absorption peak centered at 3580 cm^{-1} referred to the stretching vibrations of the O-H group [35], the pair of peaks in ranges of 2956 and 2827 cm^{-1} identified the stretching of C-H bond, the peak around 1636 cm^{-1} was related to bending vibration OH which appeared in range of 3580 cm^{-1} in from of one complementary peak, one widepeak in 1105 cm^{-1} region was attributable to stretching vibration of the Si-O bond [36], one peak in region 797 cm^{-1} related to bending vibration AlMgOH, two peaks in ranges 467 and ending 525 cm^{-1} characterized the Si-O-Si and Si-O-Al bonds, respectively, as they exhibit bending vibrations, and one peak in position 617 cm^{-1} which related to out of plane bending vibration Si-O and Al-O [37].

3.2. GC/MS Analysis

Under the conditions established in this study, the FR led to the formation of MEG with the chemical formula $\text{C}_2\text{H}_6\text{O}_2$ (see

Figure 2).



Figure 2. Molecular structure of MEG [38-40].

Figures 2 and 3 demonstrate the outputs of the FR when Aerosil and MMT were used as mineral catalyst and methanol and water served as solvent at pH values of 7.8 and 7.5, respectively. The figures depict an increase in the yield of MGA up to a peak of 0.89 mmol/dL and 2.9 mmol/dL upon 630 min of reaction with (Aerosil – methanol) and (MMT – water), respectively [1, 24].

In general, in Figures 3 and 4, the amount of MGA productions start out at a low amount and slowly increase until it reaches a maximum amount at the 630 minutes.

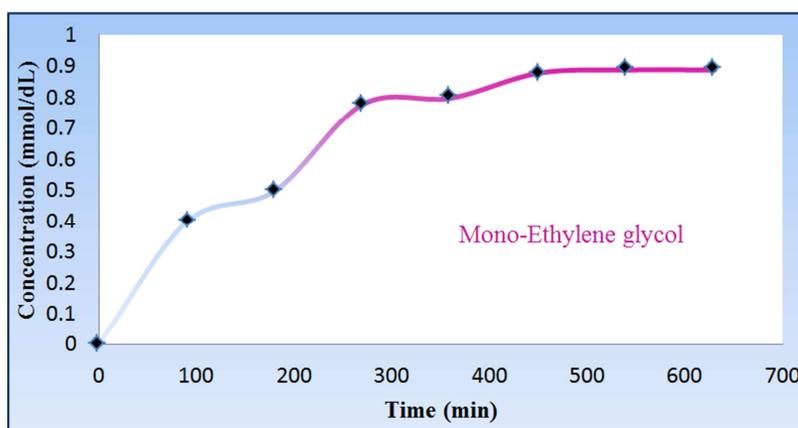


Figure 3. Variations of MEG concentration with FR reaction time when methanol serves as solvent.

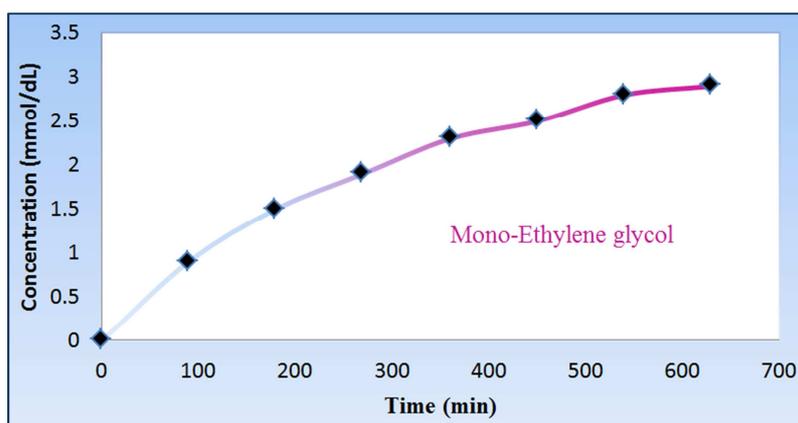


Figure 4. Variations of MEG concentration with FR reaction time when water serves as solvent.

3.3. Dielectric Constant

The dielectric constant (sometimes called the ‘relative permittivity’; symbol: ϵ) is mostly measured for the assessment of the polarity characteristics of liquids [41]. In fact, this constant is a direct measure of polarity of a solvent [42]. The dielectric constant of liquid water (78.4 at 25°C) is

greater than methanol (32.7 at 25°C) [43, 44]. This explains the lower yield of MEG via FR upon catalysis by Aerosil, rather than MMT, when methanol, rather than water, serves as solvent. These findings support the conclusion that lower yields of MEG should be expected in methanol ($\text{pH} = 7.8$) rather water ($\text{pH} = 7.5$).

4. Conclusion

The OoL is probable a series of evolutionary steps, not a single event [8, 45-47]. On other words, it is likely that the process of life came about through many small steps rather than a single big one.

The FR goes through a non-biological chemical process that has roots in sugar synthesis, where a conversion of low-carbon aldehydes to carbon-rich polyols is strived [16, 24, 48-51].

In this paper, the prebiotic synthesis of MEG via FR was investigated using two different catalysts, namely heterogeneous Aerosil (Figure 3) and MMT (Figure 4), with a focus on the synthesis efficiency (*i.e.*, yield of MEG production). Experimental data indicated the higher yield (*i.e.*, by more than 2 folds) of MEG via FR when the reaction was catalyzed by MMT, rather than Aerosil, in methanol, rather than water, as solvent. Our findings further indicated the feasibility of FR both in aqueous and non-aqueous solvents (*e.g.*, ethanol and acetone).

Data Availability Statement

The data presented in this experimental research are available on request.

Conflict of Interest

The author has no conflict of interest, financial or otherwise, in this publication.

Acknowledgements

The author is grateful to Ardabil Branch, Islamic Azad University for scientific and instrumental supports.

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