EXPONENTIAL KINETICS OF FORMATION OF ORGANIC MICROSTRUCTURES

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Abstract. Organic microstructure production in Miller-Urey spark discharge flasks is an energy-dependent, autocatalytic process which follows first order kinetics similar to microbial growth curves. These relationships hold for all three major morphological types of microstructures observed. The three types are assembled from smaller precursor subunits which associate according to a binomial distribution. These structures could have formed bounded systems in which pre-biological processes might have occurred.

When a mixture of CH_4, NH_3 and H_2O receives energy from an electrical discharge a variety of organic compounds are formed (Ponnamperuma *et al.*, 1969). Much effort has gone into trying to identify these monomeric organic molecules and to relate them to the origin-of-life problem (Ponnamperuma and Gabel, 1968; West and Ponnamperuma, 1970). A yellow polymeric material has also been observed Miller, (1955). Folsome *et al.* (1974) have examined this polymeric material microscopically and chemically and find it to be morphologically complex organic microstructures, kerogenous in nature. Three predominant classes of organic microstructures are evident, although all appear to possess a definite surface and a less dense, but clearly structured interior (Figure 1). Type I structures are 20×40 μm spheroids with a rugose textured surface and a multilayered membranous interior. Type II structures are smaller 10×15 μm spheroids with a few marked surface folds and a complex interior composed of 0.028 μm granules imbedded in a membranous matrix. Type III structures are 1×2 μm in size as rods or balls composed mainly of 0.028 μm granules dispersed upon a membranous matrix. The accompanying photomicrograph depicts a typical field of view. The organization of these structures is sufficiently complex to create doubt about the biological origin of microstructures found in carbonaceous chrondrites and in some early Precambrian sedimentary rocks. To learn more about these interesting structures we investigated some aspects of their kinetics of formation.

The experiments were conducted at room temperature in two liter pyrex boiling flasks with a glass side-arm for sampling. Aqueous samples were taken with a syringe through a teflon coated rubber septum. A plastic bag was placed around the sampling port and was flushed with Argon while sampling. Organic microstructure counts were done using a phase-contrast microscope at 900 × and a Petroff-Hausser counting chamber. Counts were obtained from 3 sizes ranges 0.5 μm to 6.0 μm, 6.0 μm to 20 μm and 20 μm or greater. The reaction mixture used was 300 mm CH_4, 100 mm CO, 50 mm N_2 and 50 ml of 2 × distilled water. Flasks were continuously sparked for 48 hours as described by Folsome *et al.* (1974).

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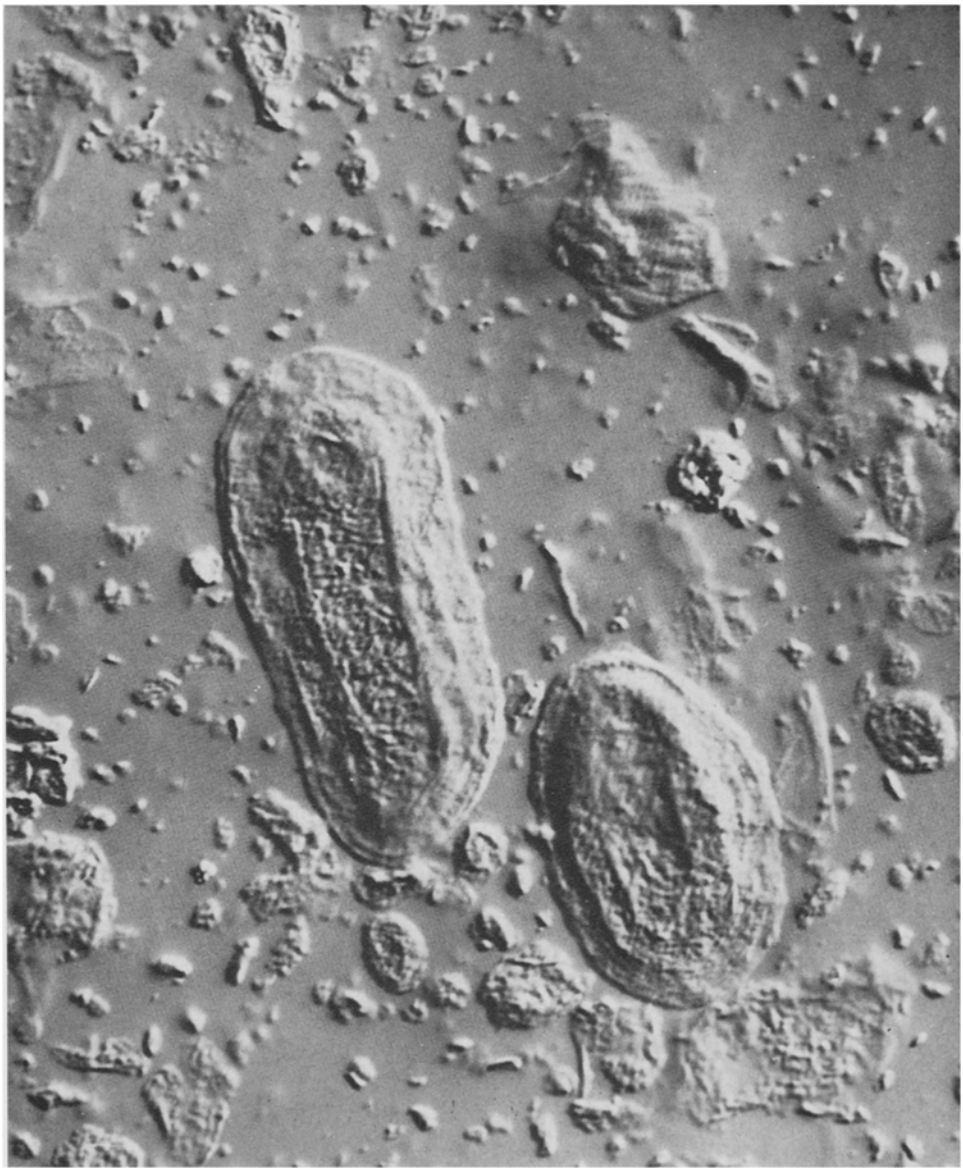

Fig. 1. Organic microspheres photographed by Zeiss-Nomarski differential interference contrast optics at 3200×. These structures, synthesized by electrical discharge upon methane and nitrogen over water, possess striking morphologies and are formed with exponential kinetics in an energy dependent autocatalytic process. Types I, II and III structures are evident in this undiluted sample. Less common are complex aggregates, sheets and tubes. This photomicrograph was taken by Mrs Marion Reed and Prof. Richard Allen of the University of Hawaii Pacific Biomedical Research Center.

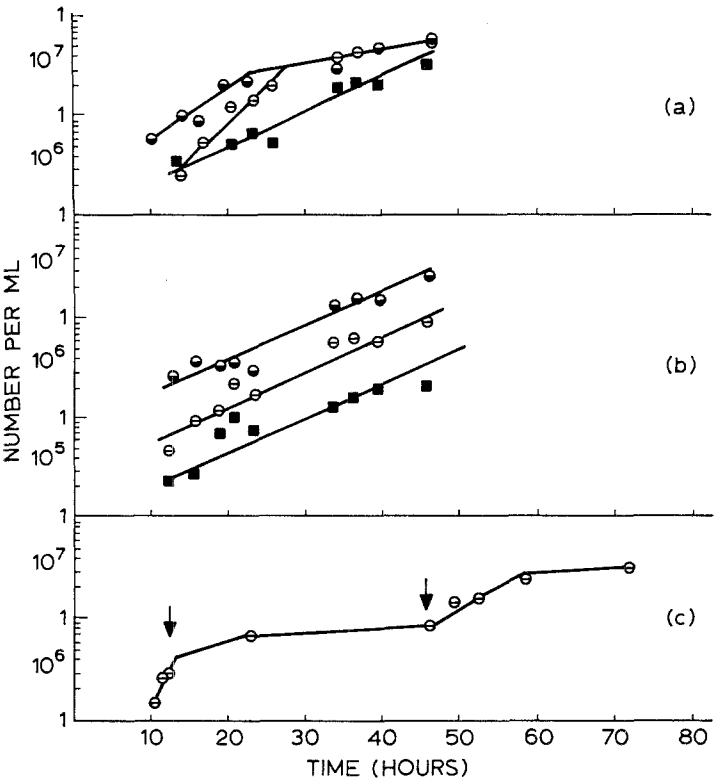

Fig. 2. Kinetics of appearance of organic microstructures. (a) graph of total counts for 3 experiments, (b) graph of the counts for 3 size groups, ◒ small organic microstructures, ⊖ intermediate organic microstructures, ■ large organic microstructures, (c) graph of the total counts from an experiment in which the Tesla coil was turned off for 35 hours. Arrows mark the beginning and end of the period.

Figure 2a shows the kinetics of microstructure appearance. For the first 10 hours the water is clear to the unaided eye. Between 10 and 15 hours the water takes on a yellowish tint and then becomes turbid. When observed under the microscope, organic microstructures are found, which vary in size from 0.5 μm to greater than 80 μm and represent the three major morphological groups (Folsome *et al.*, 1974). During this period there is an exponential increase in numbers until 24 hours, when the rate of production decreases until the count approaches a maximum number of about 5 to 6×10^7 total particles/ml.

The slope of the exponential portion of the curves for 3 separate experiments gives doubling times of 9.5, 6.5 and 4.0 hours. The experiment showing the longest generation time demonstrated exponential growth throughout the 48 hours of the experiment. This was most probably the result of an energy limitation due to a malfunction of the Tesla coil.

In a fourth experiment shown in Figure 2c, sparking (energy input) was stopped for 35 hours and resumed. At 12½ hours, when the rate of production of organic micro-

structures was exponential, the Tesla coil was turned off. The rate of formation increasingly reduced until at 48 hours it had nearly ceased. This demonstrates that organic microstructure production is energy dependent and that there is a pool of precursors from which assembly can occur. Production of the precursors appears to be an energy dependent step and we deduce that production of the organic microstructures is a self-assembly process. When sparking was resumed organic microstructure production again became exponential.

Total particle production was the sum of the microstructures found in each size group. As shown in Figure 2b, the kinetics of each size group reflected the kinetics of the total counts. The 3 size ranges were chosen because they most closely corresponded to the 3 structural types found in electromicrographs made by Folsome *et al.* (1974), while still being easy to classify with the phase-contrast microscope. We hypothesize that the 3 morphological types of organic microstructures are the product of an association between small spherical precursor particles and large membranous precursor

TABLE I

Frequencies observed for small, intermediate and large organic microstructures formed in Miller-Urey spark discharge experiments. The numbers in parenthesis are computed assuming a binomial distribution of 2 kinds of immediate precursors generating; p^2, small spherical subunit components, $2pq$ both components and q^2 large membranous subunit components

Exp. 1				Exp. 2				Exp. 3			
Time (hours)	*S*	*M*	*L*	Time (hours)	*S*	*M*	*L*	Time (hours)	*S*	*M*	*L*
14.0	0.80	0.14 (0.23)	0.06	14.0	0.90	0.10 (0.20)	>0.01	10.5	0.56	0.25 (0.23)	0.18
17.0	0.74	0.20 (0.22)	0.06	17.0	0.77	0.20 (0.21)	0.03	14.5	0.53	0.32 (0.22)	0.15
20.0	0.65	0.22 (0.23)	0.13	20.0	0.73	0.22 (0.22)	0.05	17.0	0.56	0.28 (0.23)	0.16
23.0	0.52	0.33 (0.22)	0.15	23.0	0.79	0.15 (0.23)	0.06	20.5	0.66	0.26 (0.22)	0.07
26.0	0.55	0.31 (0.22)	0.13	26.0	0.78	0.15 (0.23)	0.07	23.5	0.64	0.23 (0.23)	0.12
35.0	0.66	0.28 (0.21)	0.06	35.0	0.69	0.24 (0.22)	0.06	35.0	0.60	0.31 (0.21)	0.09
38.0	0.66	0.27 (0.21)	0.06	38.0	0.65	0.29 (0.21)	0.06	38.0	0.61	0.32 (0.20)	0.06
41.0	0.65	0.26 (0.22)	0.09	48.0	0.69	0.27 (0.21)	0.04	41.0	0.64	0.30 (0.21)	0.06
47.0	0.69	0.22 (0.22)	0.06					48.5	0.71	0.24 (0.21)	0.05

S: Frequency of small organic microstructures; from 0.5–6.0 μm
M: Frequency of intermediate, from 6.0–20 μm
L: Frequency of large; from 20–>80 μm

particles. The simplest rule of association would suggest a binomal distribution of the three size ranges. Table I shows the experimental and predicted distribution. The results agree with this hypothesis. It can also be determined from these data that the ratio of spherical immediate precursor to membranous immediate precursor is about 3.4 to 1. This same ratio was found in all experiments.

In this model system we assume the rate of production of organic microstructures will be dependent on the amount of energy available. However, in a materially bounded, energetically open system continued production of the organic microstructures will become dependent on the concentrations of the original reactants. If pathways are available which lead to cyclical regeneration of the necessary reactants, production of the organic microstructures would achieve a steady state.

Organic microstructures demonstrate autocatalytic, energy dependent assembly in a strikingly biological manner. We suggest that structures of this kind played a necessary and central role in the early origins of life. They provide micro-bounded systems analogous to contemporary cells in that they possess complex internal morphologies and a biological range of high surface to volume ratios. They are synthesized with ease and are the dominant repository of the input materials. Certainly organic microstructures are not living, but they do possess some certain fundamental biological features. The similarity of energy dependent autocatalytic self assembly to biological growth may be more than fortuitous.

Acknowledgements

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