The origin of large molecules in primordial autocatalytic reaction networks
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Supporting Information: Appendix S3
Dimensionless rate equations and dependence of $\Lambda$ on dimensionless parameters

Eq. (2) in the main text can be cast in dimensionless form by introducing a concentration scale $\omega$ and a time scale $\tau$. We discuss below the case of a homogeneous spontaneous chemistry.

Define dimensionless quantities $u_n \equiv x_n/\omega$, $t' \equiv t/\tau$, $k_f' \equiv k_f\omega\tau$, $k_r' \equiv k_r\tau$ and $\phi' \equiv \phi\tau$. Then

$$\dot{x}_n = \frac{dx_n}{dt} = \frac{d(u_n\omega)}{dt'(\tau)} = \frac{\omega du_n}{\tau dt'},$$

(S3.1)

and Eq. (2) in the main text becomes

$$\frac{\omega du_n}{\tau dt'} = \sum_{i \leq j, i+j=n} \left( \frac{k_f'}{\omega\tau} (\omega u_i)(\omega u_j) - \frac{k_r'}{\tau} (\omega u_n) \right) - \sum_{i=1, i\neq n}^{\infty} \left( \frac{k_f'}{\omega\tau} (\omega u_i)(\omega u_n) - \frac{k_r'}{\tau} (\omega u_{i+n}) \right) - 2 \left( \frac{k_f'}{\omega\tau} (\omega u_n)^2 - \frac{k_r'}{\tau} (\omega u_{2n}) \right) \frac{\phi'}{\tau} (\omega u_n)$$

(S3.2)

$$\frac{du_n}{dt'} = \sum_{i \leq j, i+j=n} \left( k_f'u_iu_j - k_r'u_n \right) - \sum_{i=1, i\neq n}^{\infty} \left( k_f'u_iu_n - k_r'u_{i+n} \right) - 2 \left( k_f'u_n^2 - k_r'u_{2n} \right) - \phi'u_n$$

(S3.3)

Without loss of generality one can choose $\omega = x_1 = A$ and (whenever $k_r \neq 0$) $\tau = 1/k_r$. Then the dimensionless concentration variables satisfy the same equations as before, but with $A = k_r = 1$. There are now only two independent dimensionless parameters, $k_f'$ and $\phi'$. The dependence on all 4 parameters can be recovered at the end by replacing $u_n$ by $x_n/A$, $t'$ by $tk_r$, $k_f'$ by $k_fA/k_r$ and $\phi'$ by $\phi/k_r$. The behaviour of $\Lambda$ as a function of $k_f$ and $\phi$ (keeping $A = k_r = 1$) is shown in Fig. S3.1.

One may also choose $\tau = 1/\phi$ (whenever $\phi \neq 0$). In that case the two independent dimensionless parameters will be $k_f'$ and $k_r'$. The behaviour of $\Lambda$ as a function of $k_f$ and $k_r$ (keeping $A = \phi = 1$) is shown in Fig. S3.2.

When $k_r = 0$ and $\phi = 0$ both the above choices for scaling fail. In this case the system has no steady state for any finite $N$ as $\dot{x}_N$ is always positive.
FIG. S3.1 Behaviour of $\Lambda$ as a function of $k_f$ and $\phi$. The figure shows the dependence of $\Lambda$ on $k_f$ and $\phi$ for an uncatalyzed chemistry, keeping $A = k_r = 1$, $N = 100$. The curved surface was made with parameter values in the range $0 \leq k_f \leq 2$, $0.01 \leq \phi \leq 2$. $\Lambda$ is found to be a monotonically increasing function of $k_f$ and a monotonically decreasing function of $\phi$. For $\phi = 0$, there is an analytical solution $\Lambda = k_f$ (see Eq. (4) in the main text). This was verified numerically in the range $0 \leq k_f \leq 1$ (see solid line at $\phi = 0$). In the region $k_f > 1$ the numerical integration does not converge at $\phi = 0$ as the steady state solution (Eq. (4) of the main text) $x_n = A\Lambda^{n-1} = Ak_f^{n-1}$ is numerically very large for large $n$. The dotted extension of the line ($1 < k_f \leq 2$) is simply the analytical result. Note that for most of the phase-space $\Lambda < 1$, except for very small values of $\phi$.

FIG. S3.2 Behaviour of $\Lambda$ as a function of $k_f$ and $k_r$. The figure shows the dependence of $\Lambda$ on $k_f$ and $k_r$ for an uncatalyzed chemistry, keeping $A = \phi = 1$, $N = 100$. $\Lambda$ is found to be a monotonically increasing function of $k_f$ and a monotonically decreasing function of $k_r$. 