Supplementary Information for 'Anomalous thermal fluctuation distribution sustains proto-metabolic cycles and biomolecule synthesis'

Rowena Ball
Mathematical Sciences Institute and Research School of Chemistry, Australian National University, Canberra, ACT 2602 Australia

John Brindley
School of Mathematics, University of Leeds, Leeds LS2 9JT UK

Included in this Supplementary Information are all data necessary to reproduce (and build on) the results presented in the associated article. Choices for numerical integration and data post-processing software are left to individual researchers.

Table S1. Reactions (1)–(4) are the oxidations and acid-base equilibria of the minimal THP oscillator. Reactions (5)–(15) are those of the linked metabolic cycles and aspartate synthesis in Fig. (1) of the paper. X_0 is pyruvate, X_1 is glyoxalate, X_2 is oxaloacetate, X_3 is oxalomalate, X_4 is 4-hydroxy-2-ketoglutarate, X_5 is malate, X_6 is malonate, X_7 is 3-carboxy-malate, X_8 is 3-carboxy-oxaloacetate, X_9 is pyruvate, X_{10} is aspartate.

$$H_2O_2 + HSO_3^- \longrightarrow SO_4^{2-} + H_2O + H^+ \quad (1)$$

$$S_2O_3^{2-} + 2H_2O_2 \longrightarrow \frac{1}{2}S_3O_6^{2-} + \frac{1}{2}SO_4^{2-} + 2H_2O \quad (2)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \quad (3)$$

$$H_2O \rightleftarrows H^+ + OH^- \quad (4)$$

$$X_0^- + X_1^- \rightleftarrows X_4^{2-} \quad (5)$$

$$X_1^- + X_2^{2-} \rightleftarrows X_3^{3-} \quad (6)$$

$$X_3^{3-} + H^+ \longrightarrow X_4^{2-} + CO_2 \quad (7)$$

$$X_4^{2-} + H_2O_2 \longrightarrow X_5^{2-} + CO_2 + H_2O \quad (8)$$

$$X_5^{2-} + H_2O_2 \longrightarrow X_2^{2-} + 2H_2O \quad (9)$$

$$X_2^{2-} + H_2O_2 \longrightarrow X_6^{2-} + CO_2 + H_2O \quad (10)$$

$$X_6^{2-} + X_1^- \rightleftarrows X_7^{3-} \quad (11)$$

$$X_7^{3-} + H_2O_2 \longrightarrow X_8^{3-} + 2H_2O \quad (12)$$

$$X_8^{3-} + H^+ \longrightarrow X_2^{2-} + CO_2 \quad (13)$$

$$X_6^{2-} + X_1^- + NH_4^+ \rightleftarrows X_9^{3-} + H^+ + H_2O \quad (14)$$

$$X_9^{3-} + H^+ \longrightarrow X_{10} + CO_2 \quad (15)$$

Table S2. Thermokinetic parameters for reactions (1)–(15) and reaction enthalpies for reactions (1)–(4). The specific enthalpies of reactions (5)–(15) are negligible.
Due to the scarcity of published thermokinetic data for the organic reactions (5)–15), in the simulations we used rate parameters based on values for reactions involving similar functional groups and substituents or deduced on the basis of textbook chemical kinetics principles [1, 2]. We found that the system behaviour is robust to minor changes in the kinetic parameters for reactions (5)–(15).
*Units as appropriate.

	E (kJ/mol)	z^*	ΔH (kJ/mol)
(1)	35.0	2.08×10^6	-380.0
(2)	68.1	1.63×10^{10}	-572.2
(3)	75.1, 25.8	3.95×10^{16}, 1.61×10^{15}	49.3, -49.3
(4)	55.8, 0	4.55×10^6, 1.32×10^9	55.8, -55.8
(5)	58.0, 59.0	7.7×10^{10}, 2.7×10^8	
(6)	58.0, 59.0	7.7×10^{10}, 2.7×10^8	
(7)	58.0	7.7×10^{10}	
(8)	68.0	7.7×10^{10}	
(9)	58.0	7.7×10^{10}	
(10)	68.0	7.7×10^{10}	
(11)	58.0, 59.0	1.2×10^{10}, 1.4×10^8	
(12)	68.0	7.7×10^{10}	
(13)	63.0	7.7×10^{10}	
(14)	68.0, 70.0	7.7×10^{10}, 2.7×10^8	
(15)	63.0	7.7×10^{10}	

Table S3. Values of the feed concentrations $c_{x,\mathrm{f}}$, flow rate F and cell volume V used in Eqs (1) and (2) of the article.

$F\,(\mathrm{L\,s^{-1}})$		4.8×10^{-7}
$V\,(\mathrm{L})$		1×10^{-5}
$c_{x,\mathrm{f}}\,(\mathrm{M})$	H_2O_2	1.35
	$S_2O_3^{2-}$	0.9
	H^+	2×10^{-7}
	SO_3^{2-}	1.6×10^{-3}
	X_1^-	0.27
	X_0^-	0.14
	NH_4^+	0.1

[1] K. J. Laidler, *Chemical kinetics*, Prentice-Hall, 3rd edn., 1987.
[2] K. A. Connors, *Chemical kinetics: the study of reaction rates in solution*, VCH Publishers Inc., New York, 1990.