Supporting Information

Carbon Dioxide Driven Coupling in a Two-Compartment System: Methyl Red Oscillator

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Kinetic model and its parameters (Supporting Tables S1-S5)

no.	Reaction	Rate law	Rate constant
R1	$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^-$	$k_1[SO_3^{2-}][H^+] - k_{1r}[HSO_3^-]$	$k_1 = 2\times10^{10}$ (M s)$^{-1}$ $k_{1r} = 2\times10^3$ s^{-1}
R2	$HSO_3^- + H^+ \rightleftharpoons H_2SO_3$	$k_2[HSO_3^-][H^+] - k_{2r}[H_2SO_3]$	$k_2 = 1.2\times10^{10}$ (M s)$^{-1}$ $k_{2r} = 2\times10^8$ s^{-1}
R3	$3HSO_3^- + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 3H^+$	$k_3[HSO_3^-][BrO_3^-]$	$k_3 = 5.97\times10^{-2}$ (M s)$^{-1}$
R4	$3H_2SO_3 + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 6H^+$	$k_4[H_2SO_3][BrO_3^-]$	$k_4 = 2.2\times10^1$ (M s)$^{-1}$
R5	$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$	$k_5[SO_4^{2-}][H^+] - k_{5r}[HSO_4^-]$	$k_5 = 10^{11}$ (M s)$^{-1}$ $k_{5r} = 1\times10^9$ s^{-1}
R6	$6H_2SO_3 + BrO_3^- \rightarrow 3S_2O_6^{2-} + Br^- + 3H_2O + 6H^+$	$k_6[H_2SO_3][BrO_3^-]$	$k_6 = 2$ (M s)$^{-1}$
R7	$H_2O \rightleftharpoons H^+ + OH^-$	$k_7 - k_{7r}[H^+][OH^-]$	$k_7 = 1\times10^{-3}$ M s^{-1} $k_{7r} = 1\times10^{11}$ (M s)$^{-1}$
R8	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$	$k_8[H^+][CO_3^{2-}] - k_{8r}[HCO_3^-]$	$k_8 = 1\times10^{11}$ (M s)$^{-1}$ $k_{8r} = 4.8$ s^{-1}
R9	$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$	$k_9[H^+][HCO_3^-] - k_{9r}[H_2CO_3]$	$k_9 = 5\times10^{10}$ (M s)$^{-1}$ $k_{9r} = 8.6\times10^6$ s^{-1}
R10	$H_2CO_3 \rightleftharpoons CO_2(aq) + H_2O$	$k_{10}[H_2CO_3] - k_{10r}[CO_2(aq)]$	$k_{10} = 1.65\times10^1$ s^{-1} $k_{10r} = 4.3\times10^{-2}$ s^{-1}
R11	$CO_2(aq) \rightleftharpoons CO_2(gas)$	$k_{11}([CO_2(aq)] - [CO_2(gas)])$	$k_{11} = 10^{-4}$ s^{-1} $[CO_2(gas)] = 1.32\times10^{-5}$ M

Table S1 Chemical reactions, rate laws and rate constants used in the model of the sulfite-bromate pH oscillator (driving system). The rate constants were adopted from Supporting Ref. 1.

Chemical species	Feed concentration, c_{0i}^{CSTR} (M)	Initial concentration, $c_i^{\mathrm{CSTR}}(t=0)$ (M)
SO_3^{2-}	6.4×10^{-2}	6.4×10^{-2}
H^+	3.19×10^{-3}	3.19×10^{-3}
BrO_3^-	10^{-1}	10^{-1}
HSO_4^-	3.19×10^{-3}	3.19×10^{-3}
HCO_3^-	2.1×10^{-3}	2.1×10^{-3}
CO_2(g)	1.32×10^{-5}	1.32×10^{-5}
HSO_3^-	0	0
H_2SO_3	0	0
SO_4^{2-}	0	0
Br^-	0	0
$S_2O_6^{2-}$	0	0
OH^-	0	0
CO_3^{2-}	0	0
H_2CO_3	0	0
CO_2(aq)	0	0

Table S2 Chemical species and theirs initial and feed concentrations in the sulfite-bromate pH oscillator (driving system). For all species $\kappa_i^{\mathrm{CSTR}} = 4.3288 \times 10^{-4}$ s^{-1} was used.

R1	$H_2O \rightleftharpoons H^+ + OH^-$	$k_1 - k_{1r}[H^+][OH^-]$	$k_1 = 1\times10^{-3}$ M s^{-1} $k_{1r} = 1\times10^{11}$ (M s)$^{-1}$
R2	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$	$k_2[H^+][CO_3^{2-}] - k_{2r}[HCO_3^-]$	$k_2 = 1\times10^{11}$ (M s)$^{-1}$ $k_{2r} = 4.8$ s^{-1}
R3	$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$	$k_3[H^+][HCO_3^-] - k_{3r}[H_2CO_3]$	$k_3 = 5\times10^{10}$ (M s)$^{-1}$ $k_{3r} = 8.6\times10^6$ s^{-1}
R4	$H_2CO_3 \rightleftharpoons CO_2(aq) + H_2O$	$k_4[H_2CO_3] - k_{4r}[CO_2(aq)]$	$k_4 = 1.65\times10^1$ s^{-1} $k_{4r} = 4.3\times10^{-2}$ s^{-1}
R5	$HMR \rightleftharpoons H^+ + MR^-$	$k_5[HMR] - k_{5r}[H^+][MR^-]$	$k_5 = 10^{-4.95}\times10^{10}$ s^{-1} $\mathrm{k}_{5r} = 10^{10}$ (M s)$^{-1}$
R6	HMR → HMR (in silicone)	$k_6[HMR]$	$k_6 = 10^{-2}$ s^{-1}

Table S3 Chemical reactions, rate laws and rate constants used in the MR system. Reaction R5 desribes the dissoultion of the protonated form of MR in the silicone tube. k_6 is the fine-tuned parameters in the model.

Chemical species	Feed concentration, c_{0i}^{CSTR} (M)	Initial concentration, $c_i^{\mathrm{CSTR}}(t=0)$ (M)
H^+	10^{-7}	10^{-7}
HCO_3^-	0	0
CO_2(g)	1.32×10^{-5}	1.32×10^{-5}
OH^-	10^{-7}	10^{-7}
CO_3^{2-}	0	0
H_2CO_3	0	0
CO_2(aq)	0	0
HMR	0	0
MR^-	3×10^{-5}	3×10^{-5}

Table S4 Chemical species and theirs initial and feed concentrations in the MR system. For all species $\kappa_i^{\mathrm{tube}} = 8.10784 \times 10^{-3}\ \mathrm{s}^{-1}$ was used.

R1	CO_2 (aq, osc) ⇌ n CO_2 (aq, tube)	k_t([CO_2 (aq, osc)] − [CO_2 (aq, tube)])	$k_t = 10^{-2}\ \mathrm{s}^{-1}$

Table S5 Exchange/coupling of CO_2 between the driving pH oscillator and methyl red solution, where n is the ratio of the volumes of the pH oscillator and MR solution in the silicone tube (22 mL/1.7 mL). k_t is the transfer rate constant (fine-tuned) for carbon dioxide from the pH oscillator to the MR solution.

Supporting Figures (Figure S1-S3)

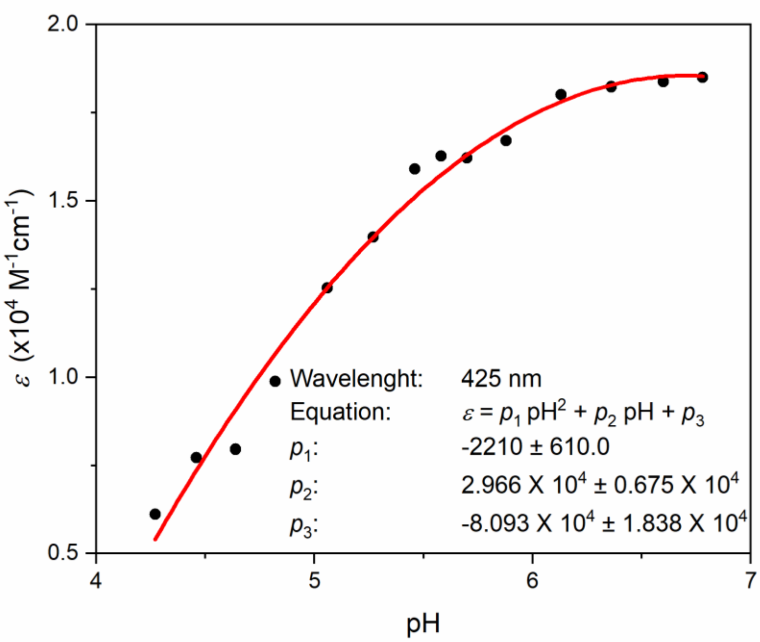

Figure S1 Dependence of the molar absorption coefficient on the pH at λ = 425 nm used in the numerical simulations to calculate the absorbance of the methyl red from its calculated concentration. Solid dots represent data obtained from the experimental measurements.

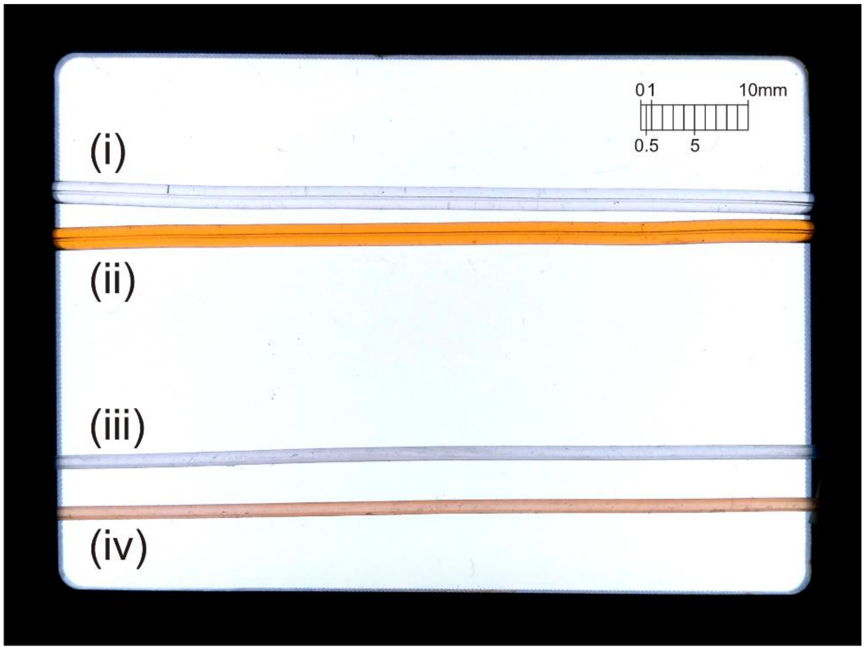

Figure S2 Tygon and silicone tubes used in the experiments: (i), (iii) before and (ii), (iv) after the experiments. The color of the tubes originates from the penetrated methyl red dye.

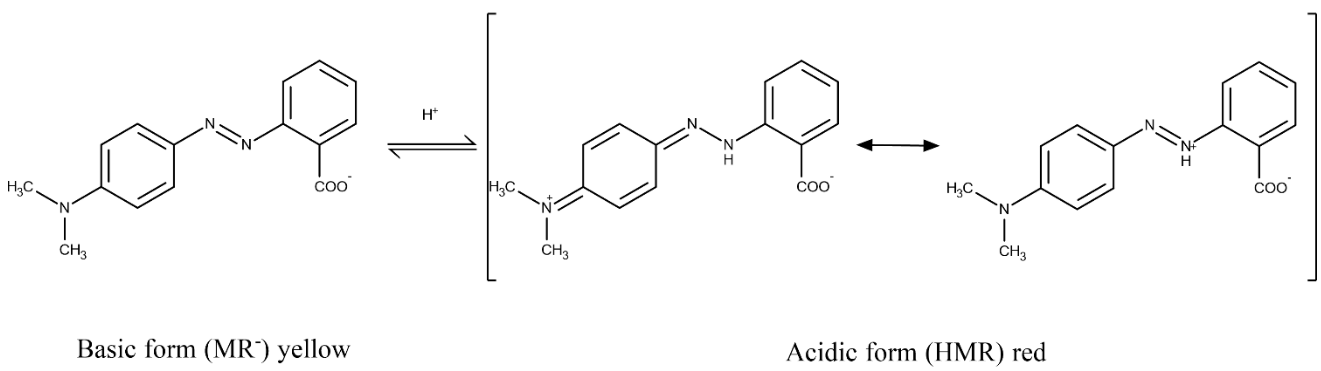

Figure S3 Molecular structures of the protonated and deprotonated forms of the methyl red molecule.

Supporting References

(1) Holló, G.; Lagzi, I. Autonomous Chemical Modulation and Unidirectional Coupling in Two Oscillatory Chemical Systems. *J. Phys. Chem. A* **2019**, *123*, 1498–1504.