

Supporting Information:

Spatially Localized Chemical Patterns Around an $A+B \rightarrow$ oscillator Front

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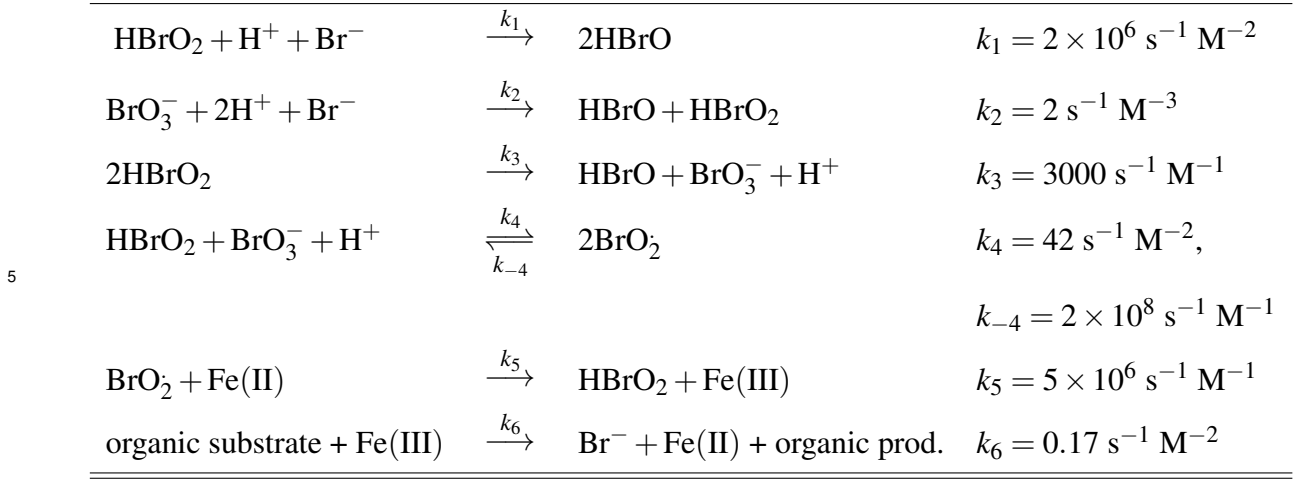
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2 Kinetic Model

3 The Oregonator model can be derived from the FKN mechanism¹ by considering the following set
4 of kinetic steps:²



6
7 The first five steps describe the “oxidation phase” (OP) while the last step simplifies “resetting
8 of the chemical clock”. If, following the traditional notation, we set $H = [\text{H}^+]$, $A = [\text{BrO}_3^-]$,
9 $B =$ organic substrate, $X = [\text{HBrO}_2]$, $Y = [\text{Br}^-]$, $Z = [\text{Fe(III)}]$, $P = [\text{HBrO}]$, $W = [\text{BrO}_2]$ and
10 $C = [\text{Fe(II)}]$, the corresponding kinetic equations read

$$\frac{dX}{dt} = -k_1 HXY + k_2 AH^2Y - 2k_3 X^2 - k_4 AHX + k_{-4} W^2 + k_5 WC \quad (1)$$

$$\frac{dY}{dt} = -k_1 HXY - k_2 AH^2Y + k_6 BZ \quad (2)$$

$$\frac{dZ}{dt} = k_5 WC - k_6 BZ \quad (3)$$

$$\frac{dW}{dt} = 2k_4 AHX - 2k_{-4} W^2 - k_5 WC \quad (4)$$

$$\frac{dC}{dt} = -k_5 WC + k_6 BZ. \quad (5)$$

11 Applying the steady-state approximation, $dW/dt = 0$,³ allows us to eliminate eq. (4) and substi-
12 tute the term $k_5 WC$ with $2k_4 AHX$ (since $k_5 CW = 2k_4 AHX - 2k_{-4} W^2$ and $k_5 C \gg 2k_{-4} W$ at almost

13 all the times during the reaction). The autocatalytic term also needs to be modified in order to en-
 14 sure the conservation of the global amount of the catalyst and to avoid an unlimited depletion of its
 15 reduced form which may cause divergent solutions to the kinetic equations. A typical correction to
 16 this term is $k_4AHXC/(C + c_{min})$ (see³ and references therein), where c_{min} is a small constant. By
 17 replacing $C = C_0 - Z$ (where C_0 is the initial concentration of the catalyst), the previous correction
 18 takes the form $k_4AHX(C_0 - Z)/(C_0 - Z + c_{min})$.

19

20 The final kinetic model is

$$\frac{dX}{dt} = -k_1HXY + k_2AH^2Y - 2k_3X^2 + k_4AHX(C_0 - Z)/(C_0 - Z + c_{min}) \quad (6)$$

$$\frac{dY}{dt} = -k_1HXY - k_2AH^2Y + k_6BZ \quad (7)$$

$$\frac{dZ}{dt} = 2k_4AHX(C_0 - Z)/(C_0 - Z + c_{min}) - k_6BZ. \quad (8)$$

21 Starting from this system, we can reduce the global process to OP by neglecting the term k_6BZ .

22 The dimensionless form of the OP kinetic equations is written by introducing the following time

23 and concentrations scales $\{t_0 = 1/(k_2A_0H_0^2), X_0 = k_4A_0H_0/2k_3, Y_0 = k_4A_0/k_1, Z_0 = k_4^2A_0/(k_2k_3)\}$:

$$\frac{dx}{d\tau} = \frac{1}{\varepsilon_1}(-hxy + qah^2y - x^2 + (1 - z/z_m)/(1 - z/z_m + \varepsilon)ahx) \quad (9)$$

$$\frac{dy}{d\tau} = -\frac{1}{q}hxy - ah^2y \quad (10)$$

$$\frac{dz}{d\tau} = (1 - z/z_m)/(1 - z/z_m + \varepsilon)ahx \quad (11)$$

24 where $q = 2k_2k_3/(k_1k_4)$, $\varepsilon_1 = k_2H_0/k_4$, $\varepsilon = c_{min}/C_0$, $z_m = Z_0/C_0$ and A_0, H_0 are the dimen-

25 sional initial concentration of the bromate and the sulfuric acid, respectively, and define the con-

26 centration scales for A and H .

27

28 The dimensionless model to describe the bulk behavior of the full BZ system including the resetting
 29 step is obtained by using the initial concentration of the organic substrate B_0 to define the time scale
 30 $t_0 = 1/(k_6 B_0)$ and the following concentration scales for the chemical species $\{X_0 = k_4 A_0 H_0 / 2k_3,$
 31 $Y_0 = k_4 A_0 / k_1, Z_0 = (k_4 A_0 H_0)^2 / k_3 k_6 B_0\}$

$$\frac{dx}{d\tau} = \frac{1}{\varepsilon_1} (-hxy + qah^2y - x^2 + (1 - z/z_m)/(1 - z/z_m + \varepsilon)ahx) \quad (12)$$

$$\frac{dy}{d\tau} = \frac{1}{\varepsilon_2} (-hxy - qah^2y + bz) \quad (13)$$

$$\frac{dz}{d\tau} = (1 - z/z_m)/(1 - z/z_m + \varepsilon)ahx - bz. \quad (14)$$

32 Note that the full BZ model presents a different definition of the parameter ε_1 with respect to
 33 the OP kinetics and also includes ε_2 . In both models the parameter q is the same ratio of kinetic
 34 constants independent of chemical concentrations. Varying the value of q allows one to tune the
 35 shape, the amplitude and the frequency of the chemical oscillations by affecting the topology of the
 36 related limit cycle in the phase portrait. The best room-temperature estimate for parameters q from
 37 the rate constants of the FKN model is around 0.00015 (uncertainty of perhaps 50%). However,
 38 in the literature^{4,5} this parameter is typically ranged between 0.0001 and 0.01. Parameter q can
 39 also control the transition from the oscillatory to the excitable regime as can be observed in Fig.1,
 40 where the oscillation period is characterized as a function of B_0 for $q = 0.0001$ and 0.01.
 41 The increment of q , at B_0 fixed, produces a decrease of the oscillation period. A decrease of the
 42 oscillation period is also registered by decreasing B_0 with q fixed. Note that when $q = 0.01$ the
 43 system switches from the oscillatory to the excitable regime if $B_0 \leq 0.3$ M.

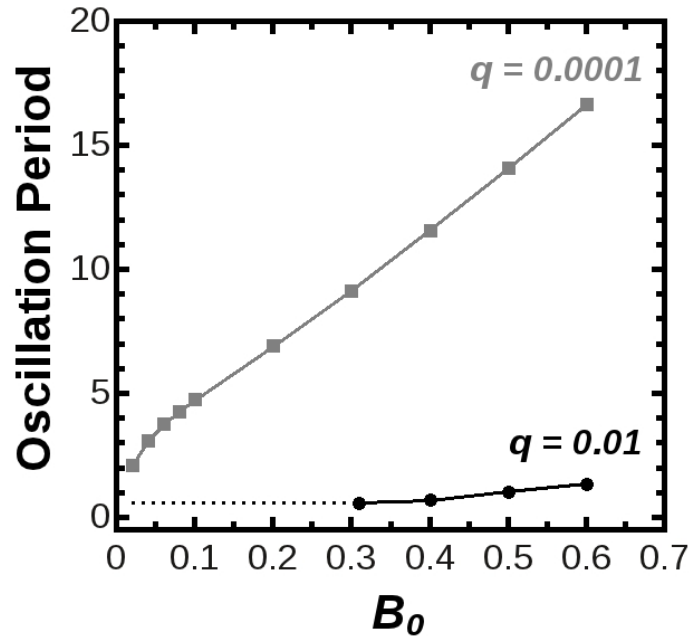


Figure 1: Dependence of the bulk oscillation period upon q and B_0 . The dotted line represents the domain of B_0 where the system is excitable when $q = 0.01$.

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