Linear stability analysis of the reversible exciplex mechanism

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The reversible exciplex mechanism is

$$\mathrm{A} + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \underset{\mathrm{k}_{-2}}{\overset{\mathrm{k}_2}{\rightleftharpoons}} \mathrm{A} + \mathrm{P}.$$

This mechanism has the conservation relation

$$[\mathrm{A}] + 2[\mathrm{C}] + [\mathrm{P}] = A_0.$$

If we introduce the transformation $a = [\mathrm{A}]/A_0$, $c = [\mathrm{C}]/A_0$, $p = [\mathrm{P}]/A_0$, $\tau = k_2 t$, $\alpha = k_1 A_0/k_2$, $\beta = k_{-1}/k_2$ and $\gamma = k_{-2}A_0/k_2$, the conservation relation becomes

$$a + 2c + p = 1, \tag{1}$$

and we can reduce the dynamics to the following pair of rate equations:

$$\dot{a} = -2\alpha a^2 + c(1 + 2\beta) - \gamma a(1 - a - 2c), \tag{2a}$$
$$\dot{c} = \alpha a^2 - c(1 + \beta) + \gamma a(1 - a - 2c), \tag{2b}$$

where dots represent differentiation with respect to τ.

To find equilibria, we set $\dot{a} = 0$ and $\dot{c} = 0$. Adding the two resulting equations, we find

$$c = \alpha a^2/\beta. \tag{3}$$

Note that $1 - a - 2c = p$ from equation (1). Combining equation (3) with either one of equations (2), we get

$$p = \frac{\alpha}{\beta\gamma} a. \tag{4}$$

(If you convert this back to the original dimensional quantities, you will find that this is just the equilibrium relationship for the overall reaction.)

If we now substitute equation (3) into (2b), we get, after a bit of algebra,

$$a\left[-\alpha a + \beta\gamma(1-a) - 2\alpha\gamma a^2\right] = 0.$$

The first factor gives us $a^\dagger = 0$, and therefore $c^\dagger = 0$ using equation (3).[1] In addition to $(a^\dagger, c^\dagger) = (0, 0)$, there are two more equilibrium points obtained by solving the quadratic factor. We can rearrange this to the standard quadratic form

$$2\alpha\gamma a^2 + a(\alpha + \beta\gamma) - \beta\gamma = 0. \tag{5}$$

This equation has solutions

$$a_\pm = \frac{-(\alpha + \beta\gamma) \pm \sqrt{(\alpha + \beta\gamma)^2 + 8\alpha\beta\gamma^2}}{4\alpha\gamma}.$$

Note that $\alpha_- < 0$, and is therefore an unphysical solution. The only solution of interest is therefore α_+, with corresponding c value c_+ calculated from equation (3).

The Jacobian is

$$\mathbf{J} = \begin{bmatrix} -4\alpha a - \gamma(1 - a - 2c) + \gamma a & 1 + 2\beta + 2\gamma a \\ 2\alpha a + \gamma(1 - a - 2c) - \gamma a & -(1 + \beta + 2\gamma a) \end{bmatrix}.$$

To determine the stability of the trivial equilibrium, substitute $(a^\dagger, c^\dagger) = (0, 0)$ into the Jacobian, then work out the characteristic polynomial:

$$\begin{aligned} |\lambda\mathbf{I} - \mathbf{J}^\dagger| &= \begin{vmatrix} \lambda + \gamma & -(1 + 2\beta) \\ -\gamma & \lambda + 1 + \beta \end{vmatrix} \\ &= \lambda^2 + \lambda(\gamma + 1 + \beta) - \beta\gamma = 0. \end{aligned}$$

[1] We can't use equation (4) to get $p^\dagger$ if $a^\dagger = c^\dagger = 0$. Why not? Instead, we have to use the conservation relation, from which it follows that $p^\dagger = 1$.

Solving the quadratic, we get

$$\lambda_{\pm}^{\dagger} = \frac{1}{2}\left\{-(\gamma+1+\beta) \pm \sqrt{(\gamma+1+\beta)^2 + 4\beta\gamma}\right\}.$$

Since $\lambda_{+}^{\dagger} > 0$, $(a^{\dagger}, c^{\dagger})$ is **unstable**.

If we try to substitute (a_+, c_+) into the Jacobian, we get a mess. Sometimes, the smart thing to do is to see what we can do without a direct substitution. Let us therefore work out the characteristic polynomial for an arbitrary (a, c). We will use the properties of the equilibrium point later.

I'll skip a few steps, which you should be able to verify. After some rearrangement, the characteristic polynomial is found to be

$$\begin{aligned} 0 = |\lambda\mathbf{I} - \mathbf{J}| = \lambda^2 + \lambda\left[4\alpha a + \gamma(1-2c) + 1 + \beta\right] \\ + 2\alpha a(1 + 2\gamma a) - \beta\gamma(1-2c) + 2\beta\gamma a. \end{aligned}$$

To figure out the signs of the two eigenvalues, it's often enough just to know the signs of the coefficients in the characteristic equation. The sign of the coefficient of λ is relatively easy to determine. Note that, from equation (1), $1 - 2c = a + p$. Since $a_+ > 0$, according to equation (4), $p_+ > 0$, and therefore $1 - 2c > 0$. Thus, the coefficient of λ is positive at the positive equilibrium. The sign of the coefficient of λ^0 (i.e. the part of the characteristic polynomial that doesn't depend on λ) is much less clear. Let's first rewrite it a bit:

$$c_0 = 4\alpha\gamma a^2 + 2\alpha a - \beta\gamma(1-2c) + 2\beta\gamma a.$$

Here is where we use the equilibrium property. Since a_+ satisfies equation (5), we can use this equation to specialize our expression for c_0 to the equilibrium case. A simple way to do this is to solve for $2\alpha\gamma a^2$ from equation (5):

$$2\alpha\gamma a^2 = \beta\gamma - a(\alpha + \beta\gamma).$$

Now replace $2\alpha\gamma a^2$ in c_0 by the right-hand side of the latter equation:

$$\begin{aligned} c_0 &= 2\left[\beta\gamma - a(\alpha+\beta\gamma)\right] + 2\alpha a - \beta\gamma(1-2c) + 2\beta\gamma a \\ &= \beta\gamma(1+2c) > 0. \end{aligned}$$

The characteristic polynomial is therefore of the form

$$\lambda + c_1\lambda + c_0 = 0$$

with both c_1 and c_0 positive at (a_+, c_+). From the quadratic equation we have

$$\lambda = \frac{1}{2}\left\{-c_1 \pm \sqrt{c_1^2 - 4c_0}\right\}.$$

If you think through the various possibilities, you should be able to convince yourself that the real parts of both eigenvalues must be negative. Thus, (a_+, c_+) is a **stable** equilibrium point.

A few notes:

- I haven't been able to come up with a simple proof that the discriminant is positive, although I know it has to be (based on other bits of theory I know). A positive discriminant means that the eigenvalues are real and negative (no imaginary part).
- The trick of using the equilibrium condition [in this case, equation (5)] to simplify a coefficient doesn't always work, but it's worth a try if you can see a way to work it in.
- The coefficients of the characteristic polynomial don't always have fixed signs, as in this example, so sometimes you simply won't be able to determine the stability by trying to figure out these signs.
- Other tricks (e.g. rearrangement of the quadratic discriminant, as was done in a similar example in the textbook) can be useful.