

BIMOLECULAR KINETIC SCHEME WITH A STABLE AND AN UNSTABLE LIMITING CYCLE OF TWO OSCILLATING COMPONENTS

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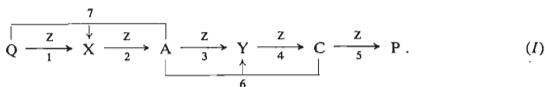
A simple reaction kinetic scheme of two oscillating components was found, whose analog solution shows a stable limit cycle separated from a stable focus by an unstable limit cycle. The scheme leads to trajectories which alternate between the types of limit cycles and stable spirals on changing the rate constants. Modifications of the basic scheme, which consists of five consecutive reactions with two accelerating parallel steps, were studied and its chemical realization was proposed.

In an analysis of the possibilities of oscillating schemes in the case of bimolecular reaction mechanisms, Tyson¹ and Hanusse² arrived at the conclusion that the characteristic equations in neighbourhood of the singular point of the differential kinetic equations must have the real part of one of their roots positive, *i.e.*, the solution must be in the neighbourhood of the singular point unstable if a "realistic" limit cycle is to be obtained. If the real parts of all roots are negative they consider the formation of a limit cycle in chemical systems as unrealistic from the kinetic point of view. The published theoretical studies of various oscillating schemes³⁻⁶ are based on this condition of instability (although it is only sufficient and not necessary). However, this condition a priori restricts the possibilities of the oscillating kinetic schemes.

The object of the present work is to propose a bimolecular chemical system, which is very realistic from the kinetic point of view, involves only two oscillating intermediate products, has in the neighbourhood of the singular point a stable solution, and in spite of this leads to limit cycles.

THEORETICAL

We shall consider a kinetic scheme in which a substance Q is reduced by a reductant Z gradually through a system of consecutive concurrent reactions to products X, A, Y, C, and P. At the same time, the substances Q with A and A with C react in parallel reactions under regeneration of the intermediate products X and Y:



We assume that all steps are bimolecular. The corresponding system of differential kinetic equations is as follows:

$$d[Q]/dt = -k_1[Q][Z] - k_7[Q][A] \quad (1a)$$

$$d[X]/dt = k_1[Q][Z] + 2k_7[Q][A] - k_2[X][Z] \quad (1b)$$

$$d[A]/dt = -k_7[Q][A] + k_2[X][Z] - k_3[A][Z] - k_6[A][C] \quad (1c)$$

$$d[Y]/dt = k_3[A][Z] + 2k_6[A][C] - k_4[Y][Z] \quad (1d)$$

$$d[C]/dt = -k_6[A][C] + k_4[Y][Z] - k_5[C][Z] \quad (1e)$$

$$d[P]/dt = k_5[C][Z] \quad (1f)$$

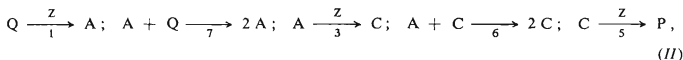
$$d[Z]/dt = -k_1[Q][Z] - k_2[X][Z] - k_3[A][Z] - k_4[Y][Z] - k_5[C][Z]. \quad (1g)$$

As a special case, we shall assume that the steps 2 and 4 are very rapid so that substances X and Y, which are unstable intermediate products, will attain stationary concentrations, $d[X]/dt = d[Y]/dt = 0$. In this way, Eqs (1b,d) are eliminated, (1c,e) much simplified, and the system will involve only two oscillating components A and C:

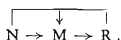
$$d[A]/dt = k_1[Q][Z] + k_7[Q][A] - k_3[A][Z] - k_6[A][C], \quad (2a)$$

$$d[C]/dt = k_3[A][Z] + k_6[A][C] - k_5[C][Z]. \quad (2b)$$

This simplified system of differential equations corresponds to the scheme



i.e., the scheme of Lotka⁷ and Volterra⁸ (steps 7, 6, 5), in which, however, the seemingly autocatalytic steps are realized by a system of two consecutive concurrent reactions with a parallel reaction that synthesizes the intermediate product from two neighbouring components N and R:



Moreover, the scheme is modified by noncatalytic steps (1, 3), which secure the stability of the solution in the region of the singular point in accord with Tyson's

view¹ although, at variance with his statement¹, they do not exclude the limit cycle (see Analog solution). In the original scheme of Lotka and Volterra, the limit cycle does not exist.

TOPOLOGY

The $[A] - [C]$ trajectory has a slope $d[A]/d[C]$ equal to zero on the hyperbola

$$[C] = \{k_1[Q][Z] + [A](k_7[Q] - k_3[Z])\}/k_6[A] \quad (3a)$$

for constant or pseudoconstant $[Z]$ and $[Q]$, the slope $d[C]/d[A]$ equal to zero on the hyperbola

$$[C] = k_3[A][Z]/(k_5[Z] - k_6[A]), \quad (3b)$$

and the slope $d[A]/d[C] = -1$ on the straight line

$$[A] = (k_5[C][Z] - k_1[Q][Z])/k_7[Q], \quad (3c)$$

which for very small values of k_1 and k_3 gives a straight line passing through the origin of coordinates and through the singular point given by the coordinates

$$[A]_0 \approx k_5[Z]/k_6, \quad [C]_0 \approx k_7[Q]/k_6. \quad (3d,e)$$

The singular point is given exactly by the intersection of (3a) and (3b) as follows:

$$k_7k_6[Q][A]_0^2 + [A]_0[Z] \{(k_1k_6 - k_7k_5)[Q] + k_3k_5[Z]\} - k_1k_5[Q][Z]^2 = 0, \quad (3f)$$

$$[C]_0 = (k_1[Q][Z] + k_7[Q][A]_0)/k_5[Z]. \quad (3g)$$

In the neighbourhood of the singular point, we set $[A] = [A]_0 + x$, $[C] = [C]_0 + y$, whereby Eqs (2a,b) are linearized:

$$dx/dt = k_7[Q]x - k_3[Z]x - k_6[A]_0y - k_6[C]_0y, \quad (4a)$$

$$dy/dt = k_3[Z]x + k_6[A]_0y + k_6[C]_0x - k_5[Z]y, \quad (4b)$$

and simplified with the use of (3a,b) as

$$dx/dt = -k_1[Q][Z]x/[A]_0 - k_6[A]_0y, \quad (4c)$$

$$dy/dt = k_5[Z][C]_0x/[A]_0 - k_3[A]_0[Z]y/[C]_0. \quad (4d)$$

The characteristic equation is

$$\begin{vmatrix} -(k_1[Q][Z]/[A]_0 + \lambda) & -k_6[A]_0 \\ k_5[Z][C]_0/[A]_0 & -(k_3[A]_0[Z]/[C]_0 + \lambda) \end{vmatrix} = 0 \quad (5a)$$

and its solution is

$$\lambda_{1,2} = \frac{1}{2} [Z] \left\{ - \left(\frac{k_1[Q]}{[A]_0} + k_3 \frac{[A]_0}{[C]_0} \right) \pm \left[\left(\frac{k_1[Q]}{[A]_0} - \frac{k_3[A]_0}{[C]_0} \right)^2 - 4k_6k_5 \frac{[C]_0}{[Z]} \right]^{1/2} \right\}. \quad (5b)$$

It is seen that the real part of these roots is always negative. If the values of k_1 and k_3 are very small, we obtain with the use of Eqs (3d) and (5b)

$$\lambda_{1,2} \approx \pm i(k_5k_7[Q][Z])^{1/2}. \quad (5c)$$

ANALOGUE SOLUTION

Trajectories

Although the roots of the characteristic equation have their real part negative and the solution in the region of the singular point is hence a stable focus, analog solutions of the mentioned mechanism show for constant $[Q]$ and $[Z]$ (hence for an open sys-

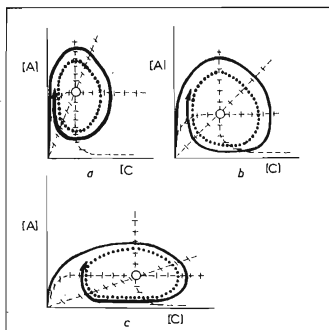


FIG. 1

[A]—[C] Trajectory

The form of the trajectory and the dotted stable limit cycle are determined mainly by the slope of the dashed line (3c) corresponding to the slope $d[A]/d[C] = -1$, whereas the magnitude is determined by the distance of the singular point (open circle) from the origin of coordinates. The slope field is denoted by short abscissae. Dashed curves are hyperbolae corresponding to zero and infinite slopes. The ratio of $k_5[Z]/k_7[Q]$ is larger than one, approximately equal to one, or smaller than one in cases a), b), and c), respectively; $[0, 0]$ is the starting point of the trajectory.

tem) with suitably chosen rate constants the existence of a limit cycle (Fig. 2). The analog solution leads to an alternating sequence of stable foci and limit cycles at relatively small changes of the rate constants (Fig. 2). It follows from the Poincaré-Bendixon's rule that if there is a limit cycle around a stable focus, then in the region within a closed trajectory of the stable limit cycle there must be also an unstable limit cycle⁹. This was proved in our case (Fig. 3) by a choice of different initial conditions within the region delimited by the stable limit cycle, where the curves either proceeded toward the external stable limit cycle or (with a choice in the region delimited by the trajectory of the unstable limit cycle) they approached in spirals to the stable focus.

The results of the analog solution can be hence classified according to whether the trajectories of the stable and unstable limit cycles *a*) are sufficiently separated

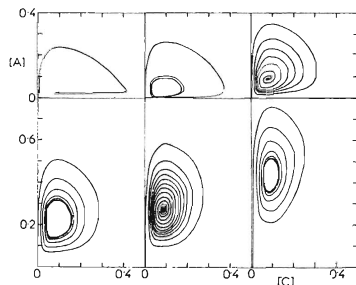


FIG. 2

Two Types of Trajectories in Analog Solution

The rate constants were chosen as $k_1 = 0.01$, $k_3 = 0.1$, $k_6 = 60$, $k_7 = 5$, k_5 (from left to right) = 0.5, 2, 6, 12, 15, 25. Open system, $[Q]/[Q]_{t=0} = 1$, $[Z]/[Z]_{t=0} = 1$.

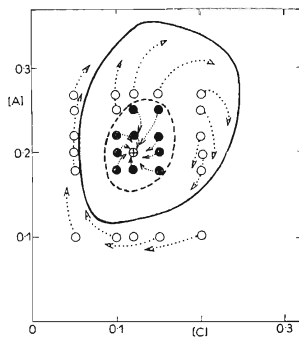


FIG. 3

Existence of Unstable Limit Cycle

The rate constants were chosen as $k_1 = 0.01$, $k_3 = 0.1$, $k_5 = 16$, $k_6 = 80$, $k_7 = 10$; $[Q]/[Q]_{t=0} = 1$, $[Z]/[Z]_{t=0} = 1$. The coordinates of the singular point are $[A]_0 : [Q]_{t=0} = 0.2$, $[C]_0/[Q]_{t=0} = 0.12$. The coordinates of the starting points of the trajectories in the region within the unstable limit cycle are denoted by solid circles, beyond this region by open circles. The coordinates were chosen according to Table I. The unstable limit cycle is denoted by the dashed line, the stable one by the solid line.

(then the trajectories starting from the initial conditions beyond the region delimited by the unstable limit cycle wind always around the stable limit cycle), b) have a common point of contact (then the stable limit cycle, as soon as it commences, degenerates into the focus), c) fuse together (then the solution is a spiral which ends in the stable focus).

Since the trajectories of the limit cycles depend on the individual rate constants, it is possible that the mutual position of both limit cycles can change for several times by the change of the rate constants, thus causing that the type of the solution alternates between stable limit cycles and stable foci, as already found.

Oscillations

The oscillation frequency is in the whole region in good agreement with the value determined for the neighbourhood of the singular point from the root of the characteristic equation (5c):

$$\Delta t_{\max} = 2\pi(k_5 k_7 [Q][Z])^{-1/2}. \quad (5d)$$

The length of the induction period decreases considerably with increasing rate constants k_1 and k_7 , whereas k_6 has an opposite influence and the constants k_5 and k_2 have no effect. If the concentrations of Q and Z are not constant but decrease with time, we obtain naturally damped oscillations of the concentrations of A and C together with a marked gradual exhausting of Q and Z and accumulation of the product P.

Modification of the Scheme

J) If the rate constant k_2 is not so large as to enable the use of the stationary state principle for the substance X, then X is the third oscillating component and we

TABLE I
Coordinates of Starting Points of Trajectories
0 Stable limit cycle; 6 stable spiral; · singular point.

<div style="display: inline-block; border-left: 1px solid black; border-bottom: 1px solid black; padding: 5px;"> $[C]/[Q]_{t=0}$ </div> <div style="display: inline-block; border-right: 1px solid black; border-bottom: 1px solid black; padding: 5px;"> $[A]/[Q]_{t=0}$ </div>	0.05	0.1	0.12	0.15	0.2
0.1	0	0	0	0	0
0.18	0	6	6	6	0
0.2	0	6	·	6	0
0.22	0	6	6	6	0
0.25	0	0	6	6	0
0.27	0	0	0	0	0

have the system of equations (1b), (2a,b) with the singular point (3f,g) and

$$[X]_0 = (k_1[Q][Z] + 2k_7[Q][A]_0)/k_2[Z]. \quad (6a)$$

After linearization in the region of $[A]_0$, $[X]_0$, and $[C]_0$ we obtain a characteristic equation of the third degree which can be written in the form

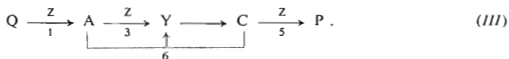
$$\lambda^3 + \lambda^2[Z] \left(k_2 \frac{[X]_0}{[A]_0} + k_3 \frac{[A]_0}{[C]_0} + k_2 \right) + \lambda[Z] \left(k_2 k_3 \frac{[X]_0[Z]}{[C]_0} + k_6 k_5 [C]_0 + k_2 k_1 \frac{[Q][Z]}{[A]_0} + k_2 k_3 \frac{[A]_0[Z]}{[C]_0} \right) + k_2[Z] \left(k_3 \frac{[Z]^2}{[C]_0} k_1[Q] + k_6 k_5 [C]_0 [Z] \right) = 0. \quad (7a)$$

This equation for $k_2 \rightarrow \infty$ takes the form of (5a). Its coefficients are all positive; the necessary and sufficient condition for the stability of the solution in the region of the singular point is given by the Hurwitz' theorem¹⁰ in the form

$$a_1 > 0; \quad a_1 a_2 - a_3 a_0 > 0; \quad a_3(a_1 a_2 - a_3 a_0) > 0, \quad (7b)$$

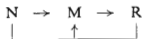
where a_i denotes the coefficient at λ^i . For Eq. (7a), these conditions are always fulfilled, hence the solution is in the region of the singular point stable; nevertheless a limiting cycle exists in the analogue solution for suitable combinations of the rate constants.

2) If we set $k_7 = 0$ (considering k_2 and k_4 very large), then we have to deal with the scheme



Since Eq. (5b) does not involve k_7 , it remains unchanged; the values of $[A]_0$ and $[C]_0$ follow from (3f,g) by setting $k_7 = 0$. The solution is again stable around the singular point, however no limit cycle exists in the analog solution.

It follows that at least two accelerating cycles of the type



are necessary for the existence of a limit cycle of the scheme type considered.

CHEMICAL REALIZATION

The chemical reason for the formation of oscillations is as follows: The "autocatalytic" step 6 + 4 exhausts the substance A, thus breaking both the "autocata-

lytic" steps 7 + 2 and 6 + 4, so that it is necessary to wait until C is removed by step 5. This enables again the "autocatalytic" accumulation of A and this in turn enables the "autocatalytic" accumulation of C, while A is exhausted, steps 6 and 7 are stopped (steps 1 and 3 are slow) and it is necessary to wait until C is exhausted by step 5, and so on. If C is removed too slowly by step 5, then its relatively high concentration keeps the concentration of A low and steady and the oscillations cannot take place. From this point of view, the following conditions are favourable for the formation of oscillations:

$$k_1 \approx k_3 \approx 0; \quad k_2 \approx k_4 \rightarrow \infty; \quad k_6 \gg k_7 \gg 0; \quad k_6 \gg k_5 \gg 0.$$

This type of the oscillation scheme (I) can be expected mainly in the case where the substances Q, X, A, Y, and C correspond to different oxidation states of the mother compound which is reduced (or oxidised) by Z. In this way it is possible to explain the oscillating behaviour of bromate and phenol reported recently^{11,12} (as well as of a number of other organic compounds).

APPENDIX

The differential equations (Ia-g) were solved on a MEDA 42 TA type analog computer. For substance Z, its initial concentration $[Z]_{t=0}$ served as a norm; other substances were normalized with respect to $[Q]_{t=0}$. The initial concentrations of the remaining reaction components were set equal to zero. Further we set $[Q]_{t=0}/[Z]_{t=0} = n$. The system of kinetic equations involves then nk_4 , nk_6 and nk_7 as constants. High values of certain rate constants were realized by increasing the transfer coefficients at the integrator inputs in combination with a potentiometer. For an open system, we set moreover $[Q]/[Q]_{t=0} = [Z]/[Z]_{t=0} = 1$.

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